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Luminescent and Redox-Active Polynuclear Transition Metal Complexes†

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1. Scope and Limitations

Great attention is currently paid to the synthesis of polynuclear transition metal complexes and the study of their photochemical, photophysical, and electrochemical properties. This interest is stimulated, in particular, by attempts to design and construct multicomponent systems (often called supramolecular species) capable of performing useful light- and/or redox-induced functions.[1−16]

A great deal of investigations on mononuclear transition metal complexes had previously shown that several families of these compounds are very interesting from the electrochemical, photochemical, and photophysical viewpoints.[17−22] The metal—ligand interaction, in fact, is often (i) weak enough to allow the manifestation of intrinsic properties of metal and ligands (e.g., ligand-centered and metal-centered absorption bands and redox waves) and, at the same time, (ii) strong enough to cause the appearance of new properties, characteristic of the whole compound (e.g., metal-to-ligand or ligand-to-metal charge-transfer bands).

On passing from mononuclear to polynuclear transition metal complexes, the situation becomes even more interesting because in the latter (supramolecular) compounds one can find, besides properties related to each metal-based component, properties related to the structure and composition of the whole array. A suitable choice of the mononuclear building blocks and bridging ligands and an appropriate design of the (supramolecular) structure can in fact allow the occurrence of very interesting and potentially useful processes such as energy transfer along predetermined pathways, photoinduced charge separation, multielectron exchange at a predetermined potential, etc.

The knowledge on the luminescence and redox properties of polynuclear transition metal complexes is rapidly accumulating, but it is disperse in a great number of journals. We have made an attempt to collect the available results, and we present them together with some fundamental introductory concepts and a few comments.

One of the main problems, of course, was to delimit the field of this review. Using personal criteria which are related to our own research interests, *we decided to consider only polynuclear transition metal complexes that can be defined as supramolecular species* (section 2.2) ***and*** *that are reported to exhibit luminescence.* For such compounds *only*, the electrochemical properties have also been reviewed. Furthermore, we decided to include only classical (Werner-type) polynuclear transition metal compounds where the number of metal-based units is exactly known and the connection between the metal centers is provided only by bridging ligands. Thus, a number of interesting systems such as polymer-appended metal

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† In memoriam of Mauro Ciano.

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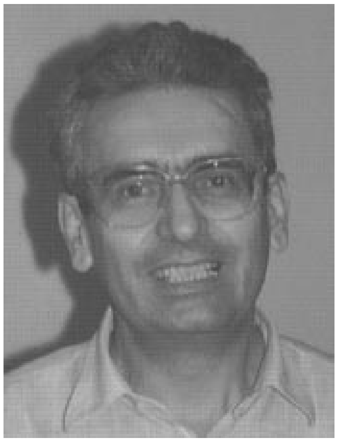

Vincenzo Balzani received his “Laurea” in Chemistry from the University of Bologna in 1960. After a few years as an assistant professor at the University of Ferrara, he joined the Faculty of Science of the University of Bologna in 1969, where he has remained to this day, becoming Professor in 1972. His research interests include photochemistry, photophysics, electrochemistry, electron-transfer reactions, chemiluminescence, supramolecular chemistry, and molecular devices.

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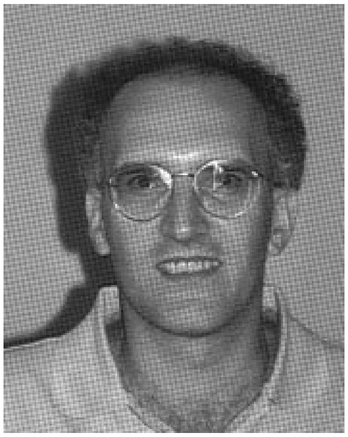
complexes,[23] protein-bound metal complexes,[24] and compounds with direct metal–metal interaction[25] are not dealt with in this review. We have also excluded systems made of covalently bound metal porphyrin units in view of the minor role played in these systems (which can in fact be considered organic chromophores) by the metal ion.



Sebastiano Campagna was born in Mazzarrà S. Andrea in 1959. He received his “Laurea” in Chemistry from the University of Messina in 1983. After a postdoctoral fellowship with Professor V. Balzani at the University of Bologna (1985–1986), he joined the Department of Inorganic Chemistry of the University of Messina in 1987. His research interests include photochemistry and photophysics of supramolecular species and photoinduced energy- and electron-transfer processes.

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We would also like to point out that the main aim of this review is to collect data. The presentation of background concepts is very limited since more detailed treatments can be found elsewhere (for relevant references, see later). Discussion of intercomponent energy- and electron-transfer processes, which constitute the most important outcome of light excitation of polynuclear complexes, is restricted to a few paradigmatic examples.

2. General Background

2.1. Localized Molecular Orbital Approximation

Transition metal complexes are made of metal ions and ligands which can also exist separately from each other. For this reason, as well as for the sake of convenience, the spectroscopic, redox, and kinetic

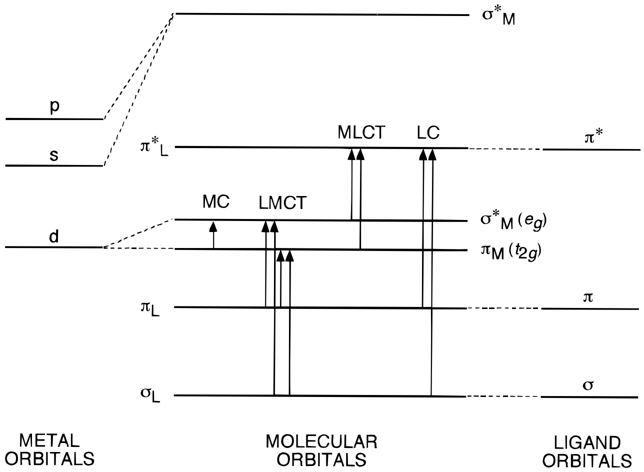


Figure 2.1. Schematic energy-level diagram for an octahedral transition metal complex. The various kind of electronic transitions are also indicated.

properties of transition metal complexes are usually discussed with the assumption that the ground state, the excited states, and the redox species can be described in a sufficiently approximate way by localized molecular orbital configurations.[17−19,22,26−30] To better understand this point, it is convenient to make reference to schematic molecular orbital (MO) diagrams such as that shown in Figure 2.1, which represents the case of an octahedral complex. In such very simplified diagrams, each MO is labeled as metal (M) or ligand (L) according to its predominant localization. Thus, for example, the low-energy σ-bonding MO's, which result from the combination of metal and ligand orbitals of appropriate symmetry, are labeled L since they receive the greatest contribution from the ligand orbitals. In the ground electronic configuration of transition metal complexes in their usual oxidation states, the σ_L and π_L orbitals are completely filled, the π_M orbitals are either partially or completely filled, and the higher orbitals are usually empty. Light absorption and redox processes change the orbital population, and each excited or redox state is assumed to be described by a single MO configuration.

2.1.1. Classification of Excited States in Mononuclear Complexes

The assignment of the various bands which appear in the absorption spectra of transition metal complexes is often a very difficult problem because the absorption spectra reflect, of course, the complexity of the electronic structure of these molecules. By using a diagram like that shown in Figure 2.1, it is possible to make a classification of the various electronic transitions according to the localization of the MO's involved. Specifically, we may identify three fundamental types of electronic transitions:[22,26−30]

(i) transitions between MO's predominantly localized on the central metal, usually called *metal-centered* (MC), ligand-field, or d-d transitions; (ii) transitions between MO's predominantly localized on the ligands, usually called *ligand-centered* (LC) or intraligand transitions; and (iii) transitions between MO's of different localization, which cause the displacement of the electronic charge from the ligands to the metal or *vice versa*. These transitions are called *charge-transfer* (CT) transitions and, more specifically, can be distinguished into *ligand-to-metal charge-transfer* (LMCT) and *metal-to-ligand charge-transfer* (MLCT) transitions.

Less frequently encountered types of transitions (not shown in Figure 2.1) are those from a metal-centered orbital to a solvent orbital (*charge-transfer to solvent*, CTTS), or between two orbitals predominantly localized on different ligands of the same metal center (*ligand-to-ligand charge-transfer*, LLCT).

The chemical and physical properties of these orbitally different excited states have been discussed in several reviews and books[17−22,26−30] and will not be dealt with here.

It must be pointed out that the above classification of electronic transitions and electronically excited states is somewhat arbitrary and loses its meaning whenever the involved states cannot be described by localized MO configurations. It should also be noticed that the energy ordering of the various orbitals may be different from that shown in Figure 2.1. For example, in the case of $[Ru(bpy)_3]^{2+}$ the π^*_L orbital is thought to be lower in energy than the σ^*_M orbital. More generally, the excited-state energy ordering is extremely sensitive to the type of the ligands and the nature and oxidation state of the metal. For example, the lowest excited state in $[Ir(phen)Cl_4]^-$, $[Ir(phen)_2Cl_2]^+$, and $[Ir(phen)_3]^{3+}$ is MC, MLCT, and LC, respectively;[17,30,31] the lowest excited state of $[Rh(bpy)_2Cl_2]^+$ is MC, whereas that of $[Ir(bpy)_2Cl_2]^+$ is MLCT;[32] the lowest excited state of $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ is MLCT, whereas that of $[Ru(bpy)_3]^{3+}$ and $[Os(bpy)_3]^{3+}$ is LMCT.[22] Further complications arise from the fact that the energy splitting between the spin states (e.g., singlet and triplet) belonging to the same orbital configuration is very large for the MC and LC excited states because in these cases the two interacting electrons occupy the same region of space, whereas it is smaller for the CT states. It follows that the excited-state energy ordering may be different in the spin-allowed and spin-forbidden manifolds. Finally, it should be recalled that in transition metal complexes there may be a considerable degree of spin−orbit coupling. This effect, being related to the central heavy (metal) atom, is different for different types of excited states. Almost pure LC states are scarcely affected, whereas for MC and CT states of metals belonging to the third transition row it may become almost meaningless to talk about discrete spin states.[33,34] In the current literature, however, the spin label is generally used even when its meaning is not strict. Finally, it should be recalled that for compounds having open-shell ground-state configuration (e.g., Cr(III) compounds), intraconfiguration MC excited states can be found at low energies.[26]

2.1.2. Redox Behavior of Mononuclear Complexes

In the localized MO approximation, oxidation and reduction processes are viewed as metal or ligand centered.[19,21,35] The highest energy occupied molecular orbital (HOMO) is most usually metal centered, whereas the lowest unoccupied molecular orbital (LUMO) is either metal or ligand centered, depending on the relative energy ordering. When the ligand field is sufficiently strong and/or the ligands can be easily reduced, reduction takes place on the ligand. When the ligand field is weak and/or the ligands cannot be easily reduced, the lowest empty orbital can be metal centered.

In several cases oxidation and/or reduction lead to a decomposition of the complex, whereas in other cases the oxidized and/or reduced forms are stable, which is of course a fundamental requirement for most device-type applications.

Typical examples of well-behaved compounds are the Ru^{II}–polypyridine complexes. Their oxidation is metal centered and leads to Ru(III) compounds (low-spin $\pi_M(t_{2g})^5$ configuration) which are inert to ligand substitution:

$$[Ru^{II}(L)_3]^{2+} \rightarrow [Ru^{III}(L)_3]^{3+} + e^- \qquad (2.1)$$

Only this first metal-centered oxidation process can be observed in the potential window available in the usual solvents (e.g., acetonitrile), but in SO_2 solution at −70 °C other processes involving ligand oxidation can be observed.[36] Exact comparison between the potentials reported in the literature[21] is not an easy task because of the different experimental conditions used. It can be stated, however, that the Ru(III)/Ru(II) reduction potential in most complexes which contain only polypyridine-type ligands falls in a rather narrow range around +1.25 V (vs SCE, acetonitrile solution).[21,37] Substitution of one bpy ligand by two Cl^- ions to give $[Ru(bpy)_2Cl_2]$ lowers the potential to +0.32 V, whereas the strong π-acceptor CO causes an increase of the reduction potential above +1.9 V.[21]

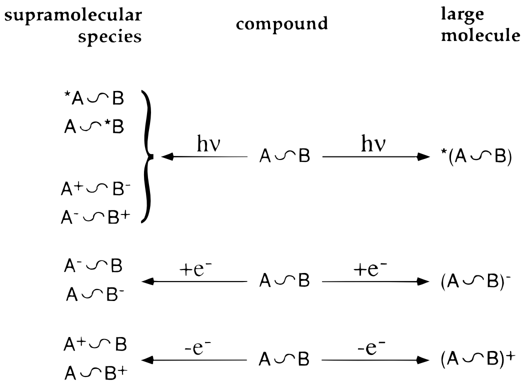
Reduction of the Ru^{II}–polypyridine complexes takes place on a π^* orbital of the polypyridine ligands. Therefore the reduced form, keeping the low-spin $\pi_M(t_{2g})^6$ configuration, is usually inert and the reduction process is reversible:

$$[Ru^{II}(L)_3]^{2+} + e^- \rightarrow [Ru^{II}(L)_2(L^-)]^+ \qquad (2.2)$$

The added electron is localized on a single ligand.[19,37] Several reduction steps can often be observed in the accessible potential range. In DMF at −54 °C, up to six CV waves can be observed for $[Ru(bpy)_3]^{2+}$ in the potential range between −1.33 and −2.85 V (vs SCE), which are assigned to successive first and second reduction of the three bpy ligands yielding a complex that can be formulated as $[Ru^{2+}(bpy^{2-})_3]^{4-}$.[38] The localization of the acceptor orbitals in the reduction process is often particularly clear in mixed-ligand complexes involving polypyridine-type ligands with different energies of their π^* orbitals.[21]

If Koopman's theorem is valid for the starting complex and for its one-electron reduced form, the π^*_L and σ^*_M orbitals involved in the reduction processes (redox orbitals) are the same orbitals which are involved in the MLCT and MC transitions, respectively (spectroscopic orbitals).[19] Thus, reversibility of the first reduction step, indicating a ligand centered LUMO, also implies (to a first approximation) that the lowest excited state is MLCT.

Scheme 2.1. Illustration of Photochemical and Electrochemical Criteria Used To Classify a Complex Chemical Species as a Supramolecular Species or as a Large Molecule[a]



[a] The symbol "∼" indicates any type of "bond" that keeps together the A and B moieties.

2.2. Polynuclear Complexes as Supramolecular Species

2.2.1. Characteristics of Supramolecular Species

From a photochemical and electrochemical viewpoint, a supramolecular species may be defined as a complex system made of molecular components with definite individual properties.[7,10] This happens when the interaction energy between components is small compared with other relevant energy parameters. As shown in Scheme 2.1,[10] light excitation of a supramolecular species A∼B (∼ indicates any type of bond or connection that keeps together the A and B components) leads to excited states that are substantially localized either on the A or on the B component (or causes directly an electron transfer from A to B or *vice versa*, see later). When the excited states are substantially delocalized on both A and B, the species is better considered as a large molecule. Similarly, oxidation and reduction of a supramolecular species can substantially be described as oxidation and reduction of specific components (Scheme 2.1), whereas oxidation and reduction of a large molecule leads to species where the hole or the electron are delocalized on the entire species.

The above concepts can easily be applied to polynuclear metal complexes. Consider, for example, a dinuclear compound $[(L)_nM_aL\text{-}S\text{-}LM_b(L)_n]^{(x+y)+}$, where L-S-L is a bridging ligand in which the two coordination sites L are connected by a spacer S (see section 3). Although the presence of the bridging ligand can create some ambiguities, in most cases $[(L)_nM_aL\text{-}S\text{-}L]^{x+}$ and $[L\text{-}S\text{-}LM_b(L)_n]^{y+}$ may be considered molecular components with well-defined individual properties: for example, integral oxidation states can be assigned to M_a and M_b, and independent excitation of the $[(L)_nM_aL\text{-}S\text{-}L]^{x+}$ and $[L\text{-}S\text{-}LM_b(L)_n]^{y+}$ components is feasible. Such complexes can be considered supramolecular species. When localized redox and excitation processes cannot be performed, a complex has to be considered a large molecule. As mentioned in section 1, in this article we will consider only polynuclear metal complexes that can be classified as supramolecular species.

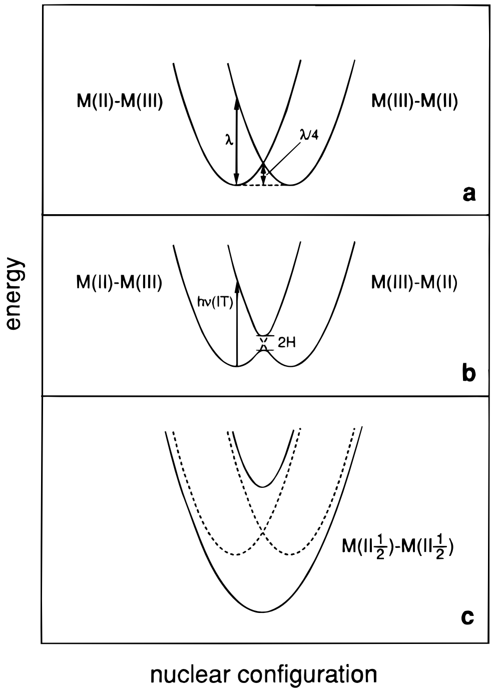


Figure 2.2. Potential energy curves for mixed-valence compounds with negligible (a), weak (b), and strong (c) electronic coupling. In b and c, the dashed curves represent the zero-order states.

2.2.2. Electronic Interaction in Polynuclear Complexes

A very important role in determining whether a polynuclear complex can be considered a supramolecular species or it should be better dealt with as a large molecule is played, of course, by the bridging ligands. The problem of metal−metal interaction through a bridging ligand has been discussed in considerable detail in the case of the so-called mixed-valence complexes.[39−41] Let us consider a homodinuclear complex of the type $[(L)_nML\text{-}S\text{-}LM(L)_n]^{5+}$, hereafter abbreviated as M-M, where all the ligands are uncharged. In a fully localized description, the overall 5+ charge corresponds to a $M^{II}-M^{III}$ complex. On the other hand, in a fully delocalized description a $M^{II1/2}-M^{II1/2}$ complex would result. The factors determining the localized or delocalized nature of the complex can easily be appreciated following the approach originally developed by Hush.[40]

Consider the valence-localized "electronic isomers" $M^{II}-M^{III}$ and $M^{III}-M^{II}$. A specific equilibrium geometry corresponds to each of these species, in terms of both *inner* (e.g., metal−ligand distances at both centers) and *outer* (e.g., orientation of solvent molecules around both centers) nuclear degrees of freedom. This is depicted in Figure 2.2a using parabolic potential energy curves for the two electronic isomers and a generalized nuclear coordinate involving both inner and outer nuclear displacements. Figure 2.2a emphasizes the fact that at the equilibrium geometry of each electronic isomer the other isomer can be considered an electronically excited state. The energy separation between these two states at the equilibrium geometry is usually called reorganizational energy and is indicated by λ (this quantity is related to the intrinsic barrier $\Delta G^{\ddagger}(0)$ of the Marcus electron-transfer theory, $\Delta G^{\ddagger}(0) = \lambda/4$, *vide infra*). At the crossing point, both electronic isomers have the same energy and geometry. This is the nuclear configuration where there are no Franck−Condon restrictions to electron exchange between the two centers. Its energy is, in this model, one quarter of the reorganizational energy. If for some reason (e.g., very long metal−metal distance, or insulating character of the bridging ligand) the electronic interaction between the M(II) and M(III) centers, H, is absolutely negligible, the curves of Figure 2.2a adequately represent the system at any geometry along the nuclear coordinate. The system is expected to exhibit properties which are an exact superposition of the properties of the isolated $[(L)_nML\text{-}S\text{-}L]^{2+}$ and $[L\text{-}S\text{-}LM(L)_n]^{3+}$ components. Furthermore, even if the system acquires sufficient activation energy to reach the intersection region, the probability of electron exchange is negligible. In the field of mixed-valence chemistry, this is usually called class I behavior.[39]

In most dinuclear complexes, however, some electronic interaction is likely to occur between the M(II) and M(III) centers, either as a consequence of direct orbital overlap or via a superexchange mechanism (*vide infra*). In such cases, the curves of Figure 2.2a are only zero-order representations. The electronic interaction has almost no effect on the zero-order curves in the vicinity of the equilibrium geometries, where the difference in energy between the electronic isomers is much larger than H, but causes mixing of the zero-order states (avoided crossing) in the vicinity of the crossing point (Figure 2.2b). Systems of this type can still be considered as valence localized, and will still exhibit the properties of the isolated $[(L)_nML\text{-}S\text{-}L]^{2+}$ and $[L\text{-}S\text{-}LM(L)_n]^{3+}$ components. However, new properties promoted by the $M^{II}-M^{III}$ interaction can be observed, such as the so called optical *intervalence-transfer* (IT) transition (with $h\nu = \lambda$) interconverting the two electronic isomers:

$$[(L)_nM^{II}L\text{-}S\text{-}LM^{III}(L)_n]^{5+} \xrightarrow{h\nu} [(L)_nM^{III}L\text{-}S\text{-}LM^{II}(L)_n]^{5+} \quad (2.3)$$

The barrier to thermal electron transfer is only negligibly smaller than that calculated on the basis of the zero-order curves ($\lambda/4$). This behavior is usually called class II.[39]

If electronic coupling is provided by the bridging ligand, the zero-order levels can be substantially perturbed even in the vicinity of their equilibrium geometries. In the limit of a very large electronic coupling, when $H \approx \lambda$, the true first-order curves will show a single minimum at an intermediate geometry (Figure 2.2c). In this case the dinuclear complex is better considered as a fully delocalized $M^{II1/2}-M^{II1/2}$ species, with properties that are almost unrelated to those of the $[(L)_nML\text{-}S\text{-}L]^{2+}$ and $[L\text{-}S\text{-}LM(L)_n]^{3+}$ components. This case is commonly indicated as class III.[39]

The above classification of mixed-valence compounds has been illustrated using symmetric redox systems, that is, systems made of identical units in which there is no driving force for intramolecular electron transfer. The arguments concerning the degree of electron delocalization are, however, general and can be easily extended to systems which exhibit redox asymmetry because of the presence of different metals (e.g., $[(L)_nM_a^{II}L\text{-}S\text{-}LM_b^{III}(L)_n]^{5+}$) or different ligands (e.g., $[(L_a)_nM^{II}L\text{-}S\text{-}LM^{III}(L_b)_n]^{5+}$). More details about asymmetric systems will be given in section 2.2.3.3. Clearly, mixed-valence class I and II compounds belong to our operational definition of supramolecular species, while class III systems fall in the "large molecule" limit.

So far we have discussed the problem of localization and delocalization with respect to the oxidation states. For example, upon oxidation of $[(L)_nM^{II}L\text{-}S\text{-}LM^{II}(L)_n]^{4+}$ one can obtain either the $[(L)_nM^{II}L\text{-}S\text{-}LM^{III}(L)_n]^{5+}$ species (localized, supramolecular case) or the $[(L)_nM^{II1/2}L\text{-}S\text{-}LM^{II1/2}(L)_n]^{5+}$ species (delocalized, large-molecule case). In the former case, two electronic configurations that differ in the population of two orbitals can be interconverted by means of an intercomponent electron-transfer process (eq 2.3).

An important situation that can be discussed along the same lines is that of localization or delocalization of electronic photoexcitation. Upon irradiation of a $(L)_nM_aL\text{-}S\text{-}LM_b(L)_n$ compound one can obtain either a $^*[(L)_nM_aL]\text{-}S\text{-}LM_b(L)_n$ species (localized excitation, supramolecular case), or a $^*[(L)_nM_aL\text{-}S\text{-}LM_b(L)_n]$ species (delocalized excitation, large-molecule case). In the former case, two electronic configurations that differ in the populations of four orbitals can be interconverted by an energy-transfer process (eq 2.4):

$$^*[(L)_nM_aL]\text{-}S\text{-}LM_b(L)_n \rightarrow (L)_nM_aL\text{-}S\text{-}^*[LM_b(L)_n] \tag{2.4}$$

The above discussion (Figure 2.2) emphasizes that the degree of electronic interaction (H) in a supramolecular species must be small. It must be recognized, however, that "small" is not intended in an absolute sense, but with respect to the energy of vibrational trapping (λ). In the polynuclear complexes dealt with in this review, the relative magnitudes of λ and H are such that a localized description (and therefore a supramolecular-type approach) is appropriate.

2.2.3. Electron- and Energy-Transfer Processes

Important and distinctive photochemical processes of supramolecular species are those taking place between components. Particularly important for the topics discussed in this review are two processes that can follow light excitation of a component (photoinduced electron and energy transfer), and an electron-transfer process that takes place directly upon light excitation (optical electron transfer). To discuss these processes, we will refer to a generic supramolecular system A∼B (Scheme 2.1). In the case of a $[(L)_nM_aL\text{-}S\text{-}LM_b(L)_n]$ dinuclear complex (section 2.2.2) A, ∼, and B represent the $(L)_nM_aL$, -S-, and $LM_b(L)_n$ moieties, respectively.

2.2.3.1. Photoinduced Electron Transfer. It is well known that light excitation increases both the oxidizing and the reducing power of a molecule.[18] In a multicomponent supramolecular system, therefore, light excitation can often be followed by an electron-transfer process, e.g.:

photoexcitation

$$A{\sim}B + h\nu \rightarrow {}^*A{\sim}B \tag{2.5}$$

photoinduced oxidative electron transfer

$$^*A{\sim}B \rightarrow A^+{\sim}B^- \tag{2.6a}$$

photoinduced reductive electron transfer

$$^*A{\sim}B \rightarrow A^-{\sim}B^+ \tag{2.6b}$$

The relevant thermodynamic parameters are the reduction potentials of the $A^+/{}^*A$, B/B^-, and $^*A/A^-$, B^+/B couples. To a first approximation, the reduction potentials for the excited state couples may be calculated from the reduction potentials of the ground-state couples and the one-electron potential corresponding to the zero–zero excitation energy:

$$E(A^+/{}^*A) \approx E(A^+/A) - E^{0-0} \tag{2.7}$$

$$E({}^*A/A^-) \approx E(A/A^-) + E^{0-0} \tag{2.8}$$

As a consequence, feasibility of an excited state electron-transfer process can be assessed by means of the well-known Weller equation.[42] For the process of eq 2.6a, it is given by

$$\Delta G^\circ \approx -E^{0-0} - E(B/B^-)' + E(A^+/A)' - E_{IP} \tag{2.9}$$

where ΔG° is the free energy change of the process, E^{0-0} is the spectroscopic energy of the excited state, $E(B/B^-)'$ and $E(A^+/A)'$ are the one-electron energies corresponding to the reduction of the two species (i.e., the components of the supermolecule) involved in the process, and E_{IP} is the Coulombic stabilization energy of the products.

Detailed discussion of the current theoretical models used to interpret the rates of electron- and energy-transfer processes in supramolecular species are given in several review articles and books.[7,43−49] We will only recall a few fundamental concepts.

In an absolute rate formalism (Marcus model),[43] the rate constant for an electron-transfer process

$$A{\sim}B \rightarrow A^+{\sim}B^- \tag{2.10}$$

can be expressed as:[43,44]

$$k = \nu_N\kappa \exp(-\Delta G^\ddagger/RT) \qquad \Delta G^\ddagger = \left(\frac{\lambda}{4}\right)\left(1 + \frac{\Delta G^\circ}{\lambda}\right)^2 \tag{2.11}$$

where ν_N is the average nuclear frequency factor, κ is the electronic transmission coefficient, $\Delta G^\ddagger$ (expressed by the Marcus quadratic relationship) is the free activation energy, ΔG° is the standard free energy change of the reaction, and λ is the reorganizational energy (Figure 2.3). This equation predicts that for a homogeneous series of reactions (i.e., for reactions having the same λ and κ values) a log k vs ΔG° plot is a bell-shaped curve involving (i) a "normal" region for endoergonic and slightly exoergonic reactions in which log k increases with increasing driving force, (ii) an activationless maximum for $\lambda = -\Delta G^\circ$, and (iii) an "inverted" region, for strongly

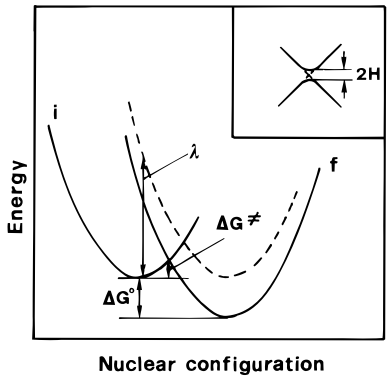


Figure 2.3. Profile of the potential energy curves of an electron-transfer reaction: **i** and **f** indicate the initial (A∼B) and final (A^+∼B^-) states of the system (eq 2.10). The inset shows a detail of the crossing of the two curves. The dashed curve indicates the final state for a self-exchange (isoergonic) process.

exoergonic reactions, in which log k *decreases* with increasing driving force.

The reorganizational energy λ can be expressed as the sum of two independent contributions corresponding to the reorganization of the "inner" (bond lengths and angles within the two reaction partners) and "outer" (solvent reorientation around the reacting pair) nuclear modes:

$$\lambda = \lambda_i + \lambda_o \qquad (2.12)$$

The outer reorganizational energy, which is by far the predominant term in electron-transfer processes, can be calculated by the expression:[44]

$$\lambda_o = e^2\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right)\left(\frac{1}{2r_A} + \frac{1}{2r_B} - \frac{1}{2r_{AB}}\right) \qquad (2.13)$$

where e is the electronic charge, ϵ_{op} and ϵ_s are the optical and static dielectric constants of the solvent, r_A and r_B are the radii of the reactants, and r_{AB} is the interreactant center-to-center distance.

The transmission coefficient κ in eq 2.11 is related to the detailed shape of the potential energy curves in the intersection region. Strictly speaking, the reactant and product potential energy curves of Figure 2.3 correspond to zero-order wave functions of the system. If there were no electronic interaction between these zero-order states, no mechanism for transition from reactants to products would be available. Actually, in most practical systems a small but finite electronic interaction occurs between A and B in the reactant pair, and a perturbation Hamiltonian H coupling the initial (A∼B) and final (A^+∼B^-) states of the system should be considered. This electronic coupling mixes the zero-order states in the intersection region, leading to the first-order avoided-crossing surfaces shown in the inset of Figure 2.3. A quantitative expression for the transmission coefficient can be obtained[44] within the framework of the Landau−Zener treatment of avoided crossings. The relevant result is shown by eqs 2.14 and 2.15:

$$\kappa = 2[1 - \exp(-\nu/2\nu_N)]/[2 - \exp(\nu/2\nu_N)] \qquad (2.14)$$

$$\nu = (2H^2/h)(\pi^3/\lambda RT)^{1/2} \qquad (2.15)$$

Two limiting cases can be identified on the basis of the eqs 2.11, 2.14, and 2.15:

(i) If the electronic interaction H is very small, $\nu \ll \nu_N$, $\kappa = (\nu/\nu_N) \ll 1$, and k is given by eq 2.16:

$$k = \nu \exp(-\Delta G^{\ddagger}/RT) \qquad (2.16)$$

This is called the *nonadiabatic* limit of electron-transfer reactions, in which the rate-determining step is the electron transfer at the transition-state geometry. The unimolecular rate constant is much smaller than the nuclear frequency and is very sensitive to factors that may influence the degree of electronic interaction between the reactants (for example, center-to-center distance, steric hindrance of substituents, orientational factors, nature of interposed groups or medium, etc.).

(ii) If H is sufficiently high that $\nu \gg \nu_N$, $\kappa = 1$, and k is given by eq 2.17:

$$k = \nu_N \exp(-\Delta G^{\ddagger}/RT) \qquad (2.17)$$

This is called the *adiabatic* limit of electron-transfer reactions, in which the rate-determining step is the nuclear motion that leads to the transition-state geometry. The unimolecular reaction rate constant may approach (for small $\Delta G^{\ddagger}$) the nuclear frequency factor, and the reaction is insensitive to factors that may influence the degree of electronic interaction between the reactants.

The value of H depends on the overlap between the electronic wave functions of the donor and acceptor groups, which should decrease exponentially with increasing donor−acceptor distance. The calculation of H in real systems is generally a difficult theoretical problem. In favorable cases, on the other hand, it is possible to estimate the magnitude of H from spectroscopic data.[40] It should be noticed that the amount of electronic interaction required to promote electron transfer is very small in a common sense. In fact, it can be easily verified by substituting reasonable numbers for the parameters in eqs 2.11, 2.14, and 2.15 that, for an activationless reaction, H values of a few wavenumbers are sufficient to give rates in the subnanosecond time scale, and a few hundred wavenumbers may be sufficient to reach the limiting adiabatic regime.

In polynuclear metal complexes the bridging ligand is expected to play an important role in governing the electronic interaction. In fact, depending on its length and electronic structure, the bridging ligand can induce a more or less important degree of delocalization between the components, thus increasing H with respect to the corresponding intercomponent value at the same center-to-center distance. The role of the bridging ligand in enhancing the electronic coupling between the active components in a supramolecular system can be described in terms of *superexchange theory*.[50−58] This theory provides an approach where overlap between orbitals of the metal-based units is mediated by overlap with the orbitals of the bridging ligand (*through-bond* interaction). Within this approach, both bridge-mediated *electron-transfer* (which takes advantage of the lowest unoccupied molecular orbitals, LUMO's, of the bridge) and *hole-transfer* (which takes advantage of the highest occupied molecular orbitals, HOMO's, of the bridge) mechanisms can contribute to the electronic coupling between the two metal-based units. The parameters which govern the extent of the interaction are orbital overlap and energy gap between the relevant metal orbitals and LUMO/HOMO orbitals of the bridging ligand.

When a bridging ligand contains a spacer made of one or more subunits, the superexchange model has to be further elaborated to include interactions between the single subunits.[54−58] This translates into an exponential dependence of the electronic coupling on the number of subunits, i.e., on the through-bond length r of the spacer, as expressed by eq 2.18:

$$H = H(0)\ \mathrm{exp}\text{-}[(\beta/2(r - r_0)] \tag{2.18}$$

In eq 2.18 r_0 is the distance between the active components without the spacer, $H(0)$ is the corresponding electronic coupling value, and β is a term which contains the interactions between the subunits of the spacer.

It should also be noticed that the classical treatment neglects the role played by high-energy frequency vibrations as accepting modes. A simple quantum mechanical model treats the electron-transfer process as an activated radiationless transition between different electronic states of the supermolecule, leading to a golden-rule expression:[46]

$$k = (2\pi/\hbar)H^2\mathrm{FCWD} \tag{2.19}$$

where the FCWD term is the Franck−Condon weighted density of states. In a simple approximation in which the solvent modes (average frequency, ν_o) are thermally excited and treated classically ($h\nu_o \ll k_BT$), and the internal vibrations (average frequency, ν_i) are frozen and treated quantum mechanically ($k_BT \ll h\nu_i$), the FCWD term is given by[59]

$$\mathrm{FCWD} = \frac{1}{(4\pi\lambda_o RT)^{1/2}} e^{-S} \sum_m \frac{S^m}{m!} \exp\left[-\frac{(\Delta G^\circ + \lambda_o + mh\nu_i)^2}{4\lambda_o RT}\right] \tag{2.20}$$

$$S = \lambda_i/h\nu_i$$

In eq 2.20, λ_o and λ_i are the outer and inner reorganizational energies, and the summation extends over m, the number of quanta of the inner vibrational mode in the product state. It can be shown that, in the high-temperature limit, eqs 2.19 and 2.20 reduce to eq 2.21, where $\lambda = \lambda_o + \lambda_i$.

$$k = (2\pi/\hbar)H^2(4\pi\lambda RT)^{-1/2} \exp[-(\Delta G^\circ + \lambda)^2/4\lambda RT] \tag{2.21}$$

By comparison with eqs 2.11, 2.14, and 2.15 it is seen that the high-temperature limit of the quantum mechanical expression corresponds to the *nonadiabatic* limit of the classical Marcus theory, in which the electronic coupling is small and the rate-determining step is electron rather than nuclear motion. In this limit the FCWD term in eq 2.19 corresponds to the exponential term of the classic rate constant (eq 2.11). Besides the inherent nonadiabaticity of the quantum mechanical mode, an important difference between the quantum mechanical and the classical models is that eq 2.19 allows for *nuclear tunneling* between reactant and product levels at energies lower than that of the intersection point. This difference is especially relevant to the behavior predicted for highly exoergonic reactions, for which the parabolic behavior of the Marcus inverted region is substituted by a linear decrease of log k with increasing driving force (energy-gap law).[46,59]

2.2.3.2. Energy Transfer. Electronic energy-transfer processes (eq 2.22)[7,60] can occur by two mechanisms: the Förster-type mechanism,[61] based on Coulombic interactions, and the Dexter-type mechanism,[62] based on exchange interactions.

$$^*\mathrm{A{\sim}B} \rightarrow \mathrm{A{\sim}}^*\mathrm{B} \tag{2.22}$$

The Förster-type mechanism is a long-range mechanism (its rate falls off as r^6, where r is the separation distance between donor and acceptor), which is efficient when the radiative transitions corresponding to the deactivation and the excitation of the two partners have high oscillator strength. The Dexter-type mechanism is a short-range mechanism (its rate falls off as e^r) that requires orbital overlap between donor and acceptor. When the donor and acceptor are linked together by chemical bonds, the exchange interaction can be enhanced by the superexchange mechanism (section 2.2.3.1).

The rate of energy transfer according to the Förster mechanism can be calculated on the basis of spectroscopic quantities by eq 2.23:

$$k_{\mathrm{en}} = 5.87 \times 10^{-25}(\Phi_A/n^4\tau_A r^6)\int_0^\infty F_A(\bar\nu)\epsilon_B(\bar\nu)\ \mathrm{d}\bar\nu/\bar\nu^4 \tag{2.23}$$

where Φ_A and τ_A are the luminescence efficiency and lifetime of the donor excited state, and the integral is related to the overlap between donor emission and acceptor absorption.

The rate constant for electron-exchange energy transfer may be expressed in a semiclassical formalism[63−66] analogous to that used for electron-transfer processes. For a recent discussion of energy-transfer mechanisms in multichromophoric systems, see ref 67.

2.2.3.3. Optical Electron Transfer. The Marcus model makes it clear that reactants and products of an electron-transfer process are intertwined by a ground/excited state relationship. For example (Figure 2.3), for nuclear coordinates that correspond to the equilibrium geometry of the reactants (initial state, **i**), the product (final state, **f**) is an electronically excited state. Therefore, optical transitions connecting the two states are possible.

optical electron transfer

$$\mathrm{A{\sim}B} + h\nu \rightarrow \mathrm{A^+{\sim}B^-} \tag{2.24}$$

Such *optical electron-transfer* processes are a generalized version of the above discussed intervalence-transfer processes (eq 2.3, Figure 2.2).

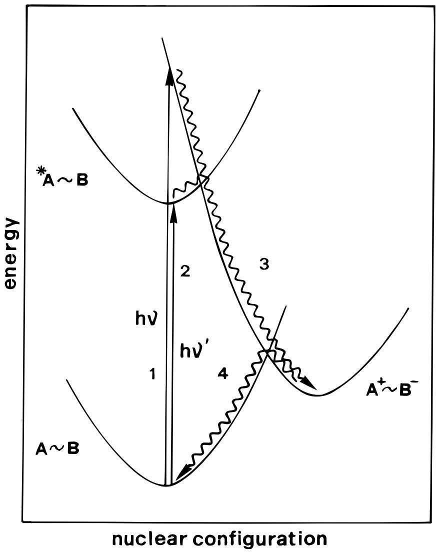


Figure 2.4. Relationships between optical (1), photoinduced (2 and 3), and thermal back (4) electron-transfer processes in supramolecular species. For the sake of simplicity, the vibrational levels are omitted.

Both optical electron transfer (eq 2.24) and photoinduced electron transfer (e.g., eq 2.5 *plus* eq 2.6a) may be followed by a thermal back-electron-transfer process:

thermal back-electron transfer

$$A^{+}{\sim}B^{-} \rightarrow A{\sim}B \qquad (2.25)$$

The relationships between optical, photoinduced and thermal back-electron-transfer processes in supramolecular species are schematized in Figure 2.4.

The Hush theory[40] correlates the parameters involved in the optical and thermal electron-transfer processes by means of eqs 2.26–2.28:

$$E_{\mathrm{op}} = \lambda + \Delta G^{\circ} \qquad (2.26)$$

$$\Delta\bar{\nu}_{1/2} = 48.06(E_{\mathrm{op}} - \Delta G^{\circ})^{1/2}\ (\mathrm{cm}^{-1}) \qquad (2.27)$$

$$\epsilon_{\max}\Delta\bar{\nu}_{1/2} = H^{2}\frac{r(\text{Å})^{2}}{4.20 \times 10^{-4}E_{\mathrm{op}}} \qquad (2.28)$$

where E_{op}, $\Delta\bar{\nu}_{1/2}$, and $\epsilon_{\max}$ are the energy, half-width, and maximum intensity of the optical electron-transfer band, and r the center-to-center distance. As shown by eqs 2.26–2.28, the energy of the optical transition depends on both reorganizational energy and thermodynamics, the half-width reflects the reorganizational energy, and the intensity of the transition is mainly related to the magnitude of the electronic coupling between the two redox centers.

In principle, therefore, important kinetic information on a thermal electron-transfer process can be obtained from the study of the corresponding optical transition. In practice, due to the dependence of the intensity on H, optical electron-transfer bands may only be observed in systems with relatively strong intercomponent electronic coupling (e.g., for H values of 10, 100, and 1000 cm^{-1}, $\epsilon_{\max}$ values of 0.2, 20, and 2000 $\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$, respectively, are obtained from eq 2.28 using $E_{\mathrm{op}} = 15000\ \mathrm{cm}^{-1}$, $\Delta\bar{\nu}_{1/2} = 4000\ \mathrm{cm}^{-1}$, and $r = 7$ Å). Since a few hundred wavenumbers of electronic interaction may be sufficient to reach the limiting adiabatic regime (section 2.2.3.1), it is clear that weakly coupled systems may undergo relatively fast electron-transfer processes without exhibiting appreciably intense optical electron-transfer transitions.

Besides optical electron-transfer absorption, the possibility of optical electron-transfer emission should also be considered in the case of an electron-transfer process in the inverted region. Emissions of this type have been reported for covalently bound organic donor–acceptor systems,[68] as well as for ion pairs.[69]

3. Bridging Ligands: Electronic and Structural Properties

In polynuclear complexes the metal-based components are linked together by bridging ligands. In several cases the coordinating moieties of the bridging ligands are linked together (and separated) by spacers (Figure 3.1a).

In the last few years the increasing interest in photoinduced energy- and electron-transfer processes in supramolecular systems has led to important progress in the design and preparation of new bridging ligands and in the development of versatile and selective synthetic strategies to assemble mononuclear complexes in supramolecular structures (section 4).

It should be pointed out that the role played by the bridging ligands in polynuclear complexes is extremely important for the following reasons: (i) with their coordinating sites they contribute (together with the "terminal" ligands) to determine the spectroscopic and redox properties of the active metal-based units;

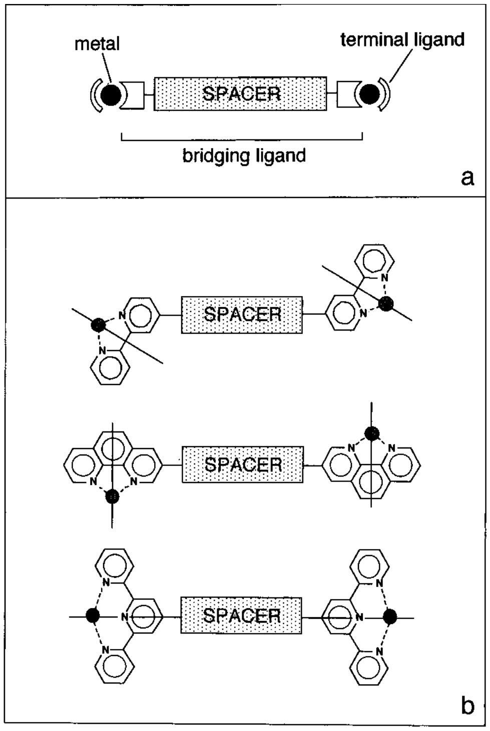


Figure 3.1. (a) Schematic representation of a dinuclear complex and (b) schemes showing the geometrical structure of representative examples of dinuclear complexes based on bpy, phen, and tpy bridging ligands.

(ii) their spacers and the connections between spacers and coordinating sites determine the structure of the supramolecular system; (iii) the chemical nature of the bridging ligand (coordinating sites and spacer) controls the electronic communication between the metal-based units. Therefore the choice of suitable bridging ligands is crucial to obtain polynuclear complexes capable to showing luminescence, exhibiting interesting electrochemical properties, and giving rise to photoinduced energy- and electron-transfer processes.

A wide range of bridging ligands have been used in recent years, as one can see looking at section 8. Some of them are very simple, like CN^-. In most cases the bridging ligands contain pyridine-type coordinating units (particularly chelating sites like bpy) either directly connected or separated by a variety of spacers.

When the spacer linking the coordinating sites of a bridging ligand is not rigid (i.e., a $-(CH_2)_n-$ chain), the discussion of the experimental results (particularly, the rates of energy- and electron-transfer processes in the frame of current theoretical treatments) can only be vague since the geometry of the system (e.g., the metal−metal distance) is not defined. Such systems are also of limited applicative interest because practical devices usually require the occurrence of vectorial energy or electron transfer over long distances.[7] Therefore rigid spacers, which are of course much more difficult to synthesize, have to be preferred.

To further illustrate the role of the bridging ligands consider, for example, dinuclear Ru(II) complexes based on bridging ligands containing bpy, phen, and tpy chelating units (Figure 3.1b).

From the viewpoint of the excited-state properties, bpy and phen are much better ligands than tpy for Ru(II). It is well know, in fact, that at room temperature in fluid solution $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ exhibit a strong and long-lived luminescence (^{3}MLCT lifetime of the order of 10^2−10^3 ns),[21] whereas $[Ru(tpy)_2]^{2+}$ does not show any luminescence (^{3}MLCT lifetime of the order of 250 ps, from transient absorption measurements).[70] The reason for this difference is the following. The main radiationless decay path at room temperature is in all cases an activated crossing to an upper lying, distorted ^{3}MC excited state.[71,72] Since tpy has a bad bite angle for octahedral Ru(II) coordination,[73−75] the ligand field strength in $[Ru(tpy)_2]^{2+}$ is weaker than in $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$. As a consequence, the energy gap between the ^{3}MLCT and ^{3}MC levels is smaller in $[Ru(tpy)_2]^{2+}$ and the activated radiationless deactivation through ^{3}MC is faster. At 77 K the activated radiationless decay through the ^{3}MC level is frozen and $[Ru(tpy)_2]^{2+}$ exhibits a strong and long-lived ($\tau = 10.6\ \mu$s) luminescence, comparable to that shown by $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$.[21]

From the viewpoint of structure, however, bridging ligands based on tpy are much more appealing than those based on bpy or phen. One reason is that there are differences concerning the coordination to the metal centers. This is apparent on looking at Figure 3.2, where the structure of $[M(bpy)_3]^{n+}$ and $[M(tpy)_2]^{n+}$ complexes and of their derivatives are illustrated:[76,77] 2,2′-bipyridine gives rise to stereoisomerism at six-coordinated centers due to its bidentate nature and therefore an $[M(bpy)_3]^{n+}$ complex exists in two enantiomeric forms. If the two coordinating nitrogens are not equivalent, as it happens for monosubstituted bpy (as well as for bridging ligands like 2,3-dpp) two geometrical isomers, *fac* and *mer*, are possible; furthermore each of them can exist as one of two enantiomers. In contrast to this behavior, a six-coordinate metal forms an achiral $[M(tpy)_2]^{n+}$ complex upon reaction with tpy. The introduction of a single substituent in the 4′-position of each tpy ligands presents no additional problems.

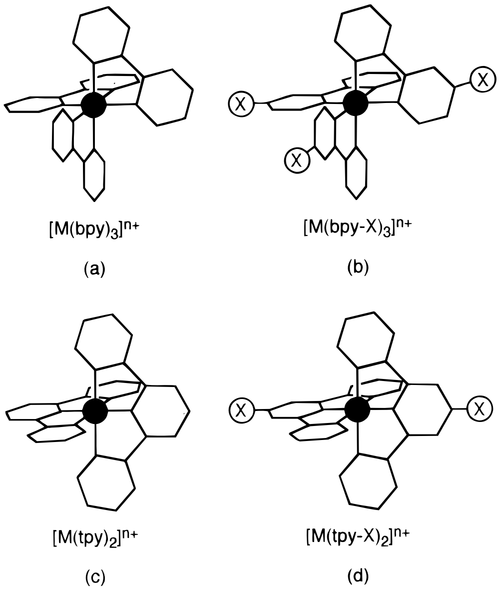


Figure 3.2. Schematic representations of (a) one of the two chiral isomers of an $[M(bpy)_3]^{n+}$ complex; (b) the *mer* geometrical isomer of an $[M(bpy\text{-}X)_3]^{n+}$ complex; (c) the unique (achiral) form of an $[M(tpy)_2]^{n+}$ complex; (d) the unique form of an $[M(tpy\text{-}X)_2]^{n+}$ complex.

Another important structural difference is illustrated in Figure 3.1b. Connection between bpy- or phen-type ligands with a spacer cannot occur along the coordination axis, whereas this can be obtained by 4′-substitution of the tpy ligand. The tridentate tpy ligand is therefore more appealing than the bidentate bpy and phen ligands from the point of view of constructing linear, rodlike polynuclear complexes.

From the above discussion, it is clear that one would need a ligand with the electronic properties of bpy or phen and, at the same time, the structural properties of tpy. To achieve this goal, two approaches have been recently attempted. On one side, the lifetime of the $[Ru(tpy)_2]^{2+}$-based chromophoric unit has been noticeably increased by electron-acceptor substituents on the 4′-position of the tpy ligand (for $[Ru(tpy\text{-}MeSO_2)(tpy)]^{2+}$, the luminescence lifetime at room temperature is 36 ns and the luminescence quantum yield is 4×10^{-4}).[78] On the other side, attempts have been made to construct bpy- and phen-based bridging ligands where the axis of the rigid spacer coincides with the coordination axes of the two bidentate ligands. Belser *et al.* have recently achieved this goal by preparing the bridging ligands FAF[79] and PAP[80] shown in Figure 3.3. In FAF the improvement of the structural properties has partially compromised the good electronic prop-

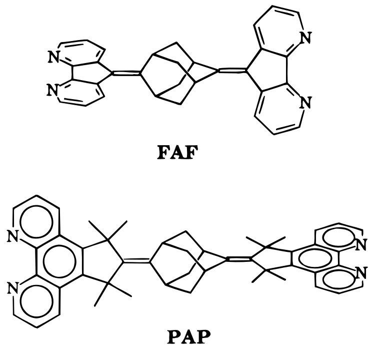


Figure 3.3. Structural formulas of the FAF[79] and PAP[80] bridging ligands.

erties of bpy because the five-membered ring constructed to obtain an anchoring point for the spacer along the metal–ligand coordination axis opens the bite angle of the metal coordination site and therefore reduces the ligand field strength, with the same consequences previously discussed for tpy. Nevertheless, FAF remains a useful linear bridging ligand based on a bis-chelating unit.[79] In PAP the construction of the anchoring point along the metal–ligand coordination axis has not affected the phenanthroline coordination sites, so that this bridging ligand combines the excellent electronic properties of phen and the possibility, typical of 4′-tpy derivatives, to give linear rodlike dinuclear complexes.[80]

Current developments in this field include the design of bridging ligands where the spacer is made of a progressive increasing number of rigid subunits (Figure 3.4). This allows one to obtain families of dinuclear compounds in which the metal–metal distance can be tuned without changing the nature of the active units. With such systems it is possible to perform systematic studies on the distance dependence of electron- and/or energy-transfer rates. Similar studies have already been performed on purely organic multicomponent systems.[47,49,52,53,55,81–86] Main difficulties in facing this kind of study are connected with the lowering of solubility on increasing the number of rigid subunits.

The importance of the bridging ligands in determining electronic coupling between metal-based components is well recognized.[46,87–94] As we have seen in section 2.2.3.1, the superexchange theory provides an approach where overlap between orbitals of the metal-based units is mediated by overlap with the orbitals of the bridging ligand (*through-bond* interaction). Within this approach, the parameters which govern the extent of the interaction are orbital overlap and energy gap between the relevant metal orbitals and LUMO/HOMO orbitals of the bridging ligand.[94] Bridging ligands with low-energy empty orbitals (usually, π^* orbitals for polypyridine bridges) maximize through-bond intercomponent interactions via electron-transfer pathways, whereas bridges with high-energy occupied orbitals (usually, π orbitals for polypyridine bridges) maximize through-bond intercomponent interactions via hole-transfer mechanism. Anionic bridges, for example, are expected to induce superexchange-assisted intercomponent interactions dominated by hole-transfer mechanism. It should also be noticed that (i) polynuclear complexes of the same bridging ligand experience different degrees of intercomponent interaction on changing the nature of the metals, even if the orbital energies of the bridge are not significantly affected by the nature of the metals; (ii) peripheral ligands can affect intercomponent interaction by modulating the energy levels of metal orbitals.

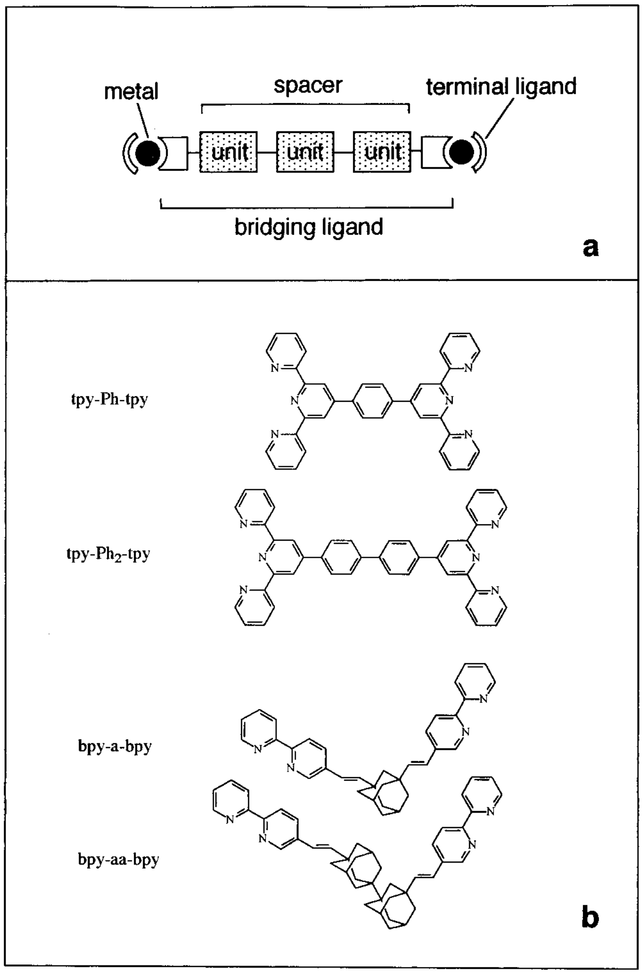


Figure 3.4. Schematic representation (a) and examples (b) of bridging ligands based on modular spacers. For references, see Tables 9.76, 9.26, and 9.27.

As we have seen in section 2.2.3.1, when a bridging ligand contains a spacer made of one or more subunits (Figure 3.4), the superexchange model has to be further elaborated to include interactions between the single subunits. It should also be noticed that in polynuclear complexes the spacer between two remote metal-based components can include other metal-based units. For example, the central $(\mu\text{-2,3-dpp})\text{Ru(bpy)}(\mu\text{-2,3-dpp})^{2+}$ component of the trinuclear species $[(\text{bpy})_2\text{Ru}(\mu\text{-2,3-dpp})\text{Ru(bpy)}(\mu\text{-2,3-dpp})\text{Ru(bpy)}_2]^{6+}$ can be considered a "bridge" connecting the peripheral $(\mu\text{-2,3-dpp})\text{Ru(bpy)}_2{}^{2+}$ chromophores.

For a more detailed discussion of the intercomponent interactions in dinuclear metal complexes, including representative examples, see ref 94.

4. Synthesis

4.1. Synthetic Strategies

The typical approach used to prepare polynuclear complexes is the so-called *complexes as metals and*

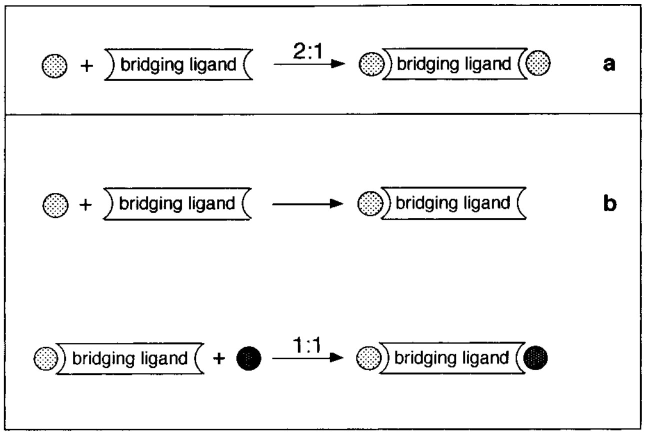


Figure 4.1. Schematic representation of the synthetic strategy used to prepare homodinuclear (a) and heterodinuclear (b) complexes.

complexes as ligands strategy,[95,96] briefly illustrated in the following.

Mononuclear complexes are synthesized by combining metal ion (M) and free ligands (L), as shown in eq 4.1:

$$M + nL \rightarrow M(L)_n \tag{4.1}$$

In the "complexes as metals/complexes as ligands" strategy one uses *complexes* (building blocks) in the place of the metal (M) and/or of the ligands (L). The place of M can be taken by mono- or oligonuclear complexes that possess easily replaceable ligands, and the place of L can be taken by mono- or oligonuclear complexes which contain free chelating sites. By using this strategy it was possible to obtain polynuclear complexes containing up to 13 metals.[95]

The application of this strategy to dinuclear complexes is briefly illustrated. If the target is the preparation of a dinuclear homometallic complex, the synthesis is particularly easy: it is sufficient to react a complex-metal with a bridging ligand in stoichiometric ratio, as illustrated in Figure 4.1a. To obtain a dinuclear heterometallic complex, the usual approach involves two steps (Figure 4.1b). First the preparation of a mononuclear complex–ligand is performed by reacting a metal precursor with an excess of the ligand. During this step dinuclear homometallic byproducts are unavoidably formed, but the desired mononuclear complex-ligand can be easily isolated by column chromatography (see below). In a following step, the second metal is added, so that only the dinuclear heterometallic species can be obtained. In the case of Ru(II) and Os(II) complexes of chelate polypyridine ligands, no scrambling of metals is usually found in the experimental conditions used for the synthesis. To obtain ruthenium–osmium heterometallic complexes of bpy-type bridging ligands, it is convenient to prepare in the first step the mononuclear osmium complex. There are at least two advantages in choosing this procedure: (i) as osmium is less reactive than ruthenium, in the first step the yield of unwanted dinuclear homometallic compounds is minimized; and (ii) the major reactivity of the ruthenium complex-metals allows the use of milder conditions to obtain the dinuclear species. With tpy-type ligands, the reverse order is employed, preparing at first the ruthenium mononuclear ligand complex.[71,97]

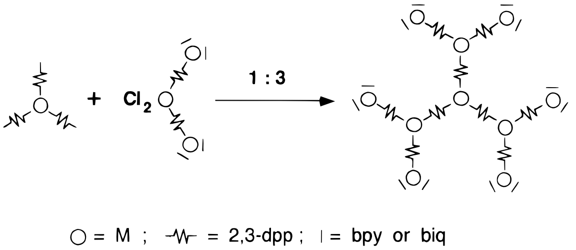


Figure 4.2. Schematic representation of the synthesis of decanuclear compounds.[96]

Polynuclear complexes of higher nuclearity can be obtained with this strategy if suitable polynuclear building blocks are available. An example is illustrated in Figure 4.2, where a mononuclear complex–ligand having three free chelating sites is reacted with 3 equiv of a trinuclear complex–metal, thus forming a decanuclear species. By a clever choice of the reaction partners it is possible to obtain compounds where different metals and ligands can be located in the desired position of the supramolecular structure (section 6.2.3).[95,96]

Recently the divergent iterative approach, well known in organic synthesis,[98–100] has been successfully extended to prepare polynuclear complexes containing up to 22 metal centers using 2,3-dpp as bridging ligand.[101,102] This kind of approach requires the availability of a bifunctional species; in the field of coordination chemistry, this species should be a complex which can behave both as a ligand and as a metal, such as $[Ru(2,3\text{-dpp})_2Cl_2]$ (Figure 4.3a). Unfortunately a species like this is unavoidably self-reactive under the preparative conditions because the free chelating sites of one molecule would substitute the labile ligands on another molecule, leading to compounds of uncontrolled nuclearity. The only safe way to carry on a divergent synthesis must be based on species where one of the two functions is temporarily blocked. This has been achieved by methylation of 2,3-dpp[103] at one pyridyl nitrogen, to obtain the "protected" ligand 2,3-$Medpp^+$. This allowed the easy, high yield (90%) preparation of the complex-metal $[Ru(2,3\text{-Medpp})_2Cl_2]^{2+}$, where the complex-ligand ability is inhibited (Figure 4.3a). The protection was proved to be stable under the conditions employed for the successive reactions of $[Ru(2,3\text{-Medpp})_2Cl_2]^{2+}$ as a complex-metal. Furthermore, it was possible to set up a demethylation procedure fully compatible with the stability of coordinate bonds,[103] in order to restore the presence of free chelating sites, that is the complex-ligand ability.

The divergent synthetic approach, summarized in Figure 4.3b, has allowed the preparation of large dendrimer-shaped polynuclear complexes.[102] Reaction of the mononuclear complex-ligand $[Ru(2,3\text{-dpp})_3]^{2+}$ with the complex-metal $[Ru(2,3\text{-Medpp})_2Cl_2]^{2+}$ in a 1:3 molecular ratio leads to a tetranuclear complex (first dendrimer generation) which in its periphery contains six protected chelating sites. Demethylation of this species restores its ligand ability and yields a tetranuclear complex which can play the role of complex-ligand. Further reaction with $[Ru(2,3\text{-Medpp})_2Cl_2]^{2+}$ in 1:6 molecular ratio

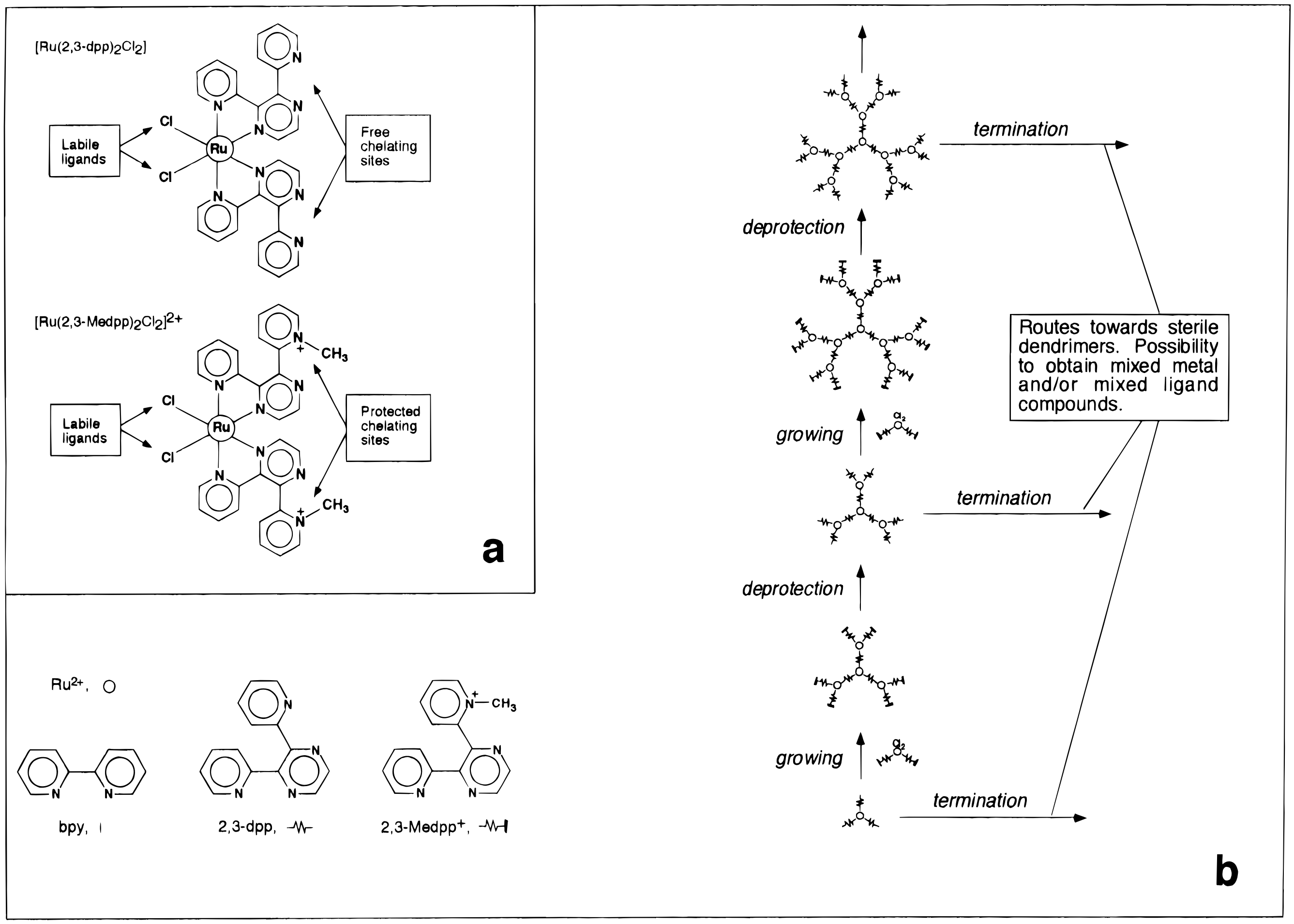


Figure 4.3. (a) Schematic representation of the bifunctional $[Ru(2,3\text{-}dpp)_2Cl_2]$ and monofunctional $[Ru(2,3\text{-}Medpp)_2Cl_2]^{2+}$ complexes and (b) divergent synthetic strategy to obtain polynuclear metal complexes of dendrimer shape.[101,102]

leads to a protected decanuclear compound (second dendrimer generation). The process in principle could lead to further generations, until eventual saturation[104] of the dendrimer surface takes place. This iterative synthetic strategy (Figure 4.3b) is characterized by a *full, step-by-step control of the growing process*. Therefore, different building blocks containing different metals and/or ligands can be introduced at each step. Moreover, each deprotected compound of the divergent synthetic approach can be used as a ligand core in convergent synthetic processes with complex-metals carrying terminal ligands, to yield *sterile* dendrimers of higher generation.[102]

4.2. Purification and Characterization

Chromatography is the best purification method for polynuclear complexes. The choice of the support depends on the desired product. Indeed one has to consider that in the synthesis of precursor complex-metal or complex-ligand species, byproducts of higher nuclearity are also formed, due to the presence in the target molecules of reactive sites (labile ligands or free chelating sites). On the other hand, in the reaction between complex-ligands and complex-metals, the byproducts (precursors and partially unreacted species) are constituted by lower nuclearity species with respect to the desired products. In any case the problem is the separation of species having different charge and/or size. If one needs the species of lower charge and/or smaller size, alumina and silica gel can be used; recently, also ion exchange resins have been profitably employed for complexes with charge up to 8+. Otherwise, if the target product is the higher charged and/or bigger species, size exclusion resins can be used.

Chromatographic techniques have been utilized so far mainly on column; the development of analogous HPLC methods[105] will certainly assist in solving the purification problems.

Characterization of very large molecules is always a difficult task.[104] For neutral compounds, techniques based on colligative properties can be used to determine the molecular mass. Polynuclear complexes like those reported in this review, however, are often charged species, and the use of the above techniques is not advisable, because of the presence of counterions. New mass spectrometry techniques, developed during the last few years, promise to be quite useful for the characterization of polynuclear transition metal complexes. In particular, fast-atom bombardment,[106,107] electrospray ionization,[108−110] and matrix-assisted laser desorption ionization mass spectrometry have been successfully employed.

The presence of geometrical and optical isomers in complexes containing bpy-type ligands (section 3) makes difficult the structural investigation of these species by NMR technique, because the numerous ^1H

and ^{13}C signals of the different ligands are multiplied by the number of isomers.

To some extent structural information can be obtained from the NMR spectrum of the transition metals, such as ^{99}Ru.[111,112] However, because the ruthenium NMR signals are very broad, the obtainable information will be limited in most of the cases to the knowledge of the number of metal ions in the molecule.

More information from NMR analysis can be obtained when the bpy-type ligands carry aliphatic substituents because the NMR signals of such groups are in a clear region of the spectrum and can be easily distinguished.[102,113]

5. Redox Behavior

As pointed out in section 2.2.1, a supramolecular polynuclear complex is made of molecular components with definite individual properties. To rationalize the redox behavior of these species it is therefore necessary to take into account the redox properties of the individual molecular components, how these properties are embodied in the supramolecular structure, and which new properties originate. Although only a few papers report accurate comparisons between the electrochemical properties of polynuclear complexes and those of the parent mononuclear units, some considerations can be made.

5.1. Properties of Molecular Components

From a general viewpoint, the redox processes featured by the molecular components are maintained in the supramolecular structure, although some changes in the potential values may occur. The extent of these changes depends on the communication ability of the bridging ligand. If the bridging ligand does not allow substantial electronic communication, the connected units maintain in the supramolecular structure their intrinsic redox properties. For example, in the ligand 4Mebpy-E4_A-bpy4Me (Table 9.20B) two bipyridines are weakly coupled by an ethylene spacer. As a consequence, the dinuclear complex $[(bpy)_2Os(\mu\text{-4Mebpy-E4}_A\text{-bpy-4Me})Os(bpy)_2]^{4+}$ features a two-electron oxidation wave due to simultaneous one-electron oxidation of the two osmium moieties at the same potential at which the mononuclear complex $[(bpy)_2Os(\text{4Mebpy-E4}_A\text{-bpy4Me})]^{2+}$ exhibits its one-electron, metal-centered oxidation wave. Analogously, the reduction potentials remain unchanged on passing from the mononuclear to the dinuclear species.[114]

When the bridging ligand allows substantial electronic communication, only an estimate of the redox properties of a polynuclear complex can be made from the properties of the mononuclear parent complexes. As an example, let us consider the bridging ligand bpym (Table 9.14B). The dinuclear complex $[(bpy)_2Ru(\mu\text{-bpym})Ru(bpy)_2]^{4+}$ features two distinct metal-centered one-electron oxidation waves at +1.53 and +1.69 V vs SSCE,[115] whereas the mononuclear complex $[(bpy)_2Ru(bpym)]^{2+}$ is oxidized at +1.40 V.[116] One can see that in the dinuclear complex (i) the first oxidation of ruthenium occurs at more positive potential than in the mononuclear parent compound, as coordination of a second ruthenium ion lowers the electronic density on the bridging ligand (and, as a consequence, on the coordinated metals) and (ii) the second oxidation is shifted to even more positive potential as oxidation of the first ruthenium ion further reduces the electronic density of the system. As far as the reduction of the bridging ligand is concerned, the potential shift is even larger, as indicated by the comparison between the reduction potential of bpym in the dinuclear (−0.41 V vs SSCE)[115] and in the mononuclear complex (−1.02 V).[116]

The bridging ligands discussed above represent two limiting cases of how the communication ability of the bridge may influence the redox behavior of the individual components in a supramolecular species. As mentioned in section 2.2.3.1, it should be recalled that even an electronic interaction not measurable from electrochemical experiments ($\Delta V \leq 10-20$ mV, i.e., 80−120 cm^{-1}) can be strong enough to permit very fast intercomponent energy- and/or electron-transfer processes (section 6).

5.2. Supramolecular Properties

Even a cursory examination of the electrochemical data reported in section 9 shows that processes involving more than one electron are very common in polynuclear species. This peculiarity originates from the fact that on increasing nuclearity several equivalent noninteracting units are often incorporated in the same supramolecular array. It has been shown[117] that species containing a number of identical noninteracting units exhibit current-potential responses having enhanced current intensity, but the same shape as that obtained with the parent isolated components.

The above-mentioned $[(bpy)_2Os(\mu\text{-4Mebpy-E4}_A\text{-bpy4Me})Os(bpy)_2]^{4+}$ complex is an example of a dinuclear species where the bridging ligand does not allow an electrochemically sizeable electronic interaction. In fact the two metal ions are oxidized at the same potential (bielectronic wave). Multielectron processes can also be observed in polynuclear complexes employing bridging ligands that allow electronic communication when the equivalent electroactive units do not share the same bridging ligand; indeed as a practical rule one can consider that components not sharing the same bridging ligand are substantially noninteracting. A remarkable example of a multielectron oxidation process is illustrated by the 22-nuclear complex $[Ru\{(\mu\text{-2,3-dpp})[Ru[(\mu\text{-2,3-dpp})\text{-}Ru\{(\mu\text{-2,3-dpp})Ru(bpy)_2\}_2]_2\}_3]^{44+}$ (Table 9.49B).[102] This complex exhibits a 12-electron oxidation wave attributed to the simultaneous one-electron oxidation of the 12 equivalent, noninteracting peripheral metal-based units. It is worth noting that the same peripheral unit, $(\mu\text{-2,3-dpp})Ru(bpy)_2^{2+}$, is oxidized at the same potential also in the analogous tetranuclear ($[Ru\{(\mu\text{-2,3-dpp})Ru(bpy)_2\}_3]^{8+}$) and decanuclear $[Ru\{(\mu\text{-2,3-dpp})Ru[(\mu\text{-2,3-dpp})Ru(bpy)_2]_2\}_3]^{20+}$ compounds (Table 9.49B).[102] This shows that the electrochemical properties of a certain unit depend only on the neighboring units, regardless of the nuclearity and of the overall electric charge of the supramolecular structure. The presence of multielectron processes makes such polynuclear complexes very attractive in view of their possible application as multielectron-transfer catalysts.[7,15]

6. Intercomponent Electron- and Energy-Transfer Processes. Representative Examples

In the polynuclear complexes dealt with in this review it is possible to identify components which can undergo photoexcitation independently from one another (Scheme 2.1). The excited component can then give rise to intercomponent energy- or electron-transfer processes, in competition with intracomponent decay. For most of the components which constitute the examined systems, the lifetime of the lowest excited state is long enough to allow the occurrence of energy or electron transfer to nearby components when suitable energetic and electronic conditions are satisfied. This is not usually the case for upper excited states, which decay very rapidly (picosecond time scale) to the lowest excited state within each component.

Photoinduced electron- or energy-transfer processes take place in several polynuclear complexes listed in section 9. Since a systematic discussion of these processes cannot be given in this article for space reasons, we will only present a few typical cases. For details and a more exhaustive treatment the reader can refer to the original papers or to some recent reviews.[4,7,118,119] General background on these processes has been presented in sections 2.2.3.1 and 2.2.3.2. We would also like to recall that intercomponent electron and energy transfer are very important processes for the design of devices capable to perform useful light-induced functions.[7,16]

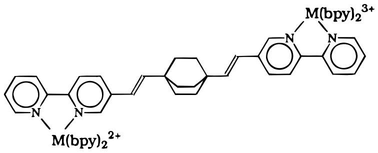
6.1. Intercomponent Electron Transfer

We present two recent, representative examples dealing with (i) the role played by electronic coupling and driving force in determining the rate constants of photoinduced electron transfer across a rigid spacer, and (ii) photogenerated electron collection at a single site of a polynuclear array.

6.1.1. Photoinduced Electron Transfer across a Rigid Spacer

The design of suitable systems for detailed mechanistic studies of photoinduced electron-transfer processes poses difficult problems. Since the parameters which govern the reaction rate (electronic coupling, reorganizational energy, free energy change) depend on the distance between donor and acceptor, one would need modular rigid structures, which are very difficult to synthesize. In recent years several efforts have been made in this direction and some interesting families of compounds have been studied (section 3).

A typical case is that of the dinuclear mixed-valence complexes based on the rigid bpy-E5$_A$-bpy bridging ligand.[120] The structural formulas of these complexes are shown in Figure 6.1. The electrochemical properties (Table 9.25B) show that in these mixed-valence systems (section 2.2.2) the energy of vibrational trapping noticeably exceeds the electronic interaction between the two metal-based chromophores, so that a $[(bpy)_2M^{II}(bpy\text{-}E5_A\text{-}bpy)]^{2+}$ and a $[(bpy\text{-}E5_A\text{-}bpy)M^{III}(bpy)_2)]^{3+}$ component can be identified. The M^{II}-based unit, when excited, plays the role of electron donor, and the M^{III}-based one plays the role of electron acceptor. The lowest excited state of the M(II)-based component is a long-lived, luminescent ^{3}MLCT level. Electron transfer from such an excited state to the M(III)-based component leads to the formation of the mixed-valence $M^{III}\cdot A\cdot M^{II}$ isomer of the $M^{II}\cdot A\cdot M^{III}$ starting compound (Figure 6.2).



$(bpy)_2Ru(bpy\text{-}E5_A\text{-}bpy)Ru(bpy)_2{}^{5+}$	**Ru^{II}.A.Ru^{III}**
$(bpy)_2Os(bpy\text{-}E5_A\text{-}bpy)Os(bpy)_2{}^{5+}$	**Os^{II}.A.Os^{III}**
$(bpy)_2Ru(bpy\text{-}E5_A\text{-}bpy)Os(bpy)_2{}^{5+}$	**Ru^{II}.A.Os^{III}**

Figure 6.1. Schematic representation of mixed-valence dinuclear complexes of the bpy-E5$_A$-bpy bridging ligand. The abbreviations used are also shown.[120]

The electron-transfer processes taking place in $*Ru^{II}\cdot A\cdot Os^{III}$, $*Ru^{II}\cdot A\cdot Ru^{III}$, and $*Os^{II}\cdot A\cdot Os^{III}$ are characterized by a different exoergonicity (1.62, 2.06, and 1.71 eV, respectively). The extent of the electronic coupling is very small and very similar for the three processes, since in each case a π* electron substantially localized on a bpy ligand of the M^{II}-based excited unit is transferred to a t_{2g} orbital of the oxidized metal of the other unit. The reorganizational barrier to electron transfer should also be the same in each case, since each process implies an electron transfer from a 2+ excited state to a 3+ ground state. Therefore, these three processes constitute a homogeneous family.

In the $Ru^{II}\cdot A\cdot Os^{III}$ mixed-metal compound (Figure 6.2a), a thermal back-electron-transfer reaction takes place after formation of the $Ru^{III}\cdot A\cdot Os^{II}$ isomeric species. In this reaction electron transfer takes place from a t_{2g} orbital of Os^{II} to a t_{2g} orbital of Ru^{III}, so that the electronic factor should be somewhat different from that of the electron-transfer quenching reactions in the $*M^{II}\cdot A\cdot M^{III}$ species. As far as the reorganizational barrier is concerned, the difference is expected to be very small.

The values of the experimental rate constants, free energy changes, and estimated intrinsic barriers for the four electron-transfer processes are gathered in Table 6.1, together with the calculated electronic factor ν (obtained from eq 2.16) and electronic interaction energy H (eq 2.15). One can see that the interaction energy is practically constant for the three "homogeneous" reactions, while it is considerably smaller for the back-electron-transfer reaction involving $Ru^{III}\cdot A\cdot Os^{II}$. Figure 6.3 shows a log k vs $\Delta G°$ plot for the four electron-transfer processes. A Marcus-type curve obtained from the classical eq 2.16 by using the parameters $\lambda = 1.4$ eV and $H = 8$ cm^{-1} is also shown (dashed line). It can be noticed that the fitting is not fully satisfactory even in the case of the three homogeneous excited-state electron-transfer processes a, b, and c. It is well known, in fact, that the classical treatment neglects the role played by

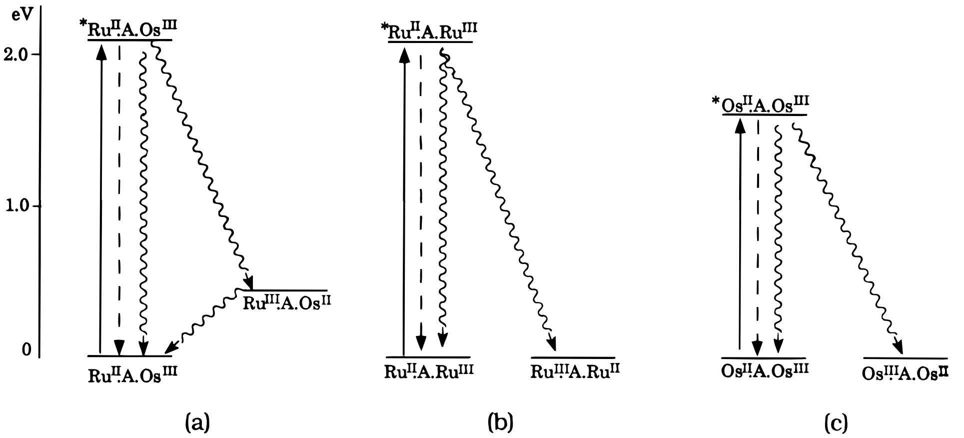


Figure 6.2. Energy level diagrams showing the photoinduced electron-transfer processes in $Ru^{II}{\cdot}A{\cdot}Os^{III}$ (a), $Ru^{II}{\cdot}A{\cdot}Ru^{III}$ (b), and $Os^{II}{\cdot}A{\cdot}Os^{III}$ (c). Key: full line, excitation; dashed line, luminescence; wavy line, radiationless decay.[120]

Table 6.1. Experimental Rate Constants and Related Parameters for Photoinduced Electron-Transfer Processes in the Compounds Shown in Figure 6.1

	k, s^{-1}	$\Delta G°$, eV	λ_i, eV	λ_o, eV	ν,[a] s^{-1}	H,[a] cm^{-1}
$^*Ru^{II}{\cdot}A{\cdot}Ru^{III} \rightarrow Ru^{III}{\cdot}A{\cdot}Ru^{II}$	1.1×10^9	−2.06	0.1	1.3	2.3×10^{10}	10
$^*Os^{II}{\cdot}A{\cdot}Os^{III} \rightarrow Os^{III}{\cdot}A{\cdot}Os^{II}$	5.0×10^9	−1.71	0.1	1.3	9.8×10^9	7
$^*Ru^{II}{\cdot}A{\cdot}Os^{III} \rightarrow Ru^{III}{\cdot}A{\cdot}Os^{II}$	8.7×10^9	−1.62	0.1	1.3	1.3×10^{10}	8
$Ru^{III}{\cdot}A{\cdot}Os^{II} \rightarrow Ru^{II}{\cdot}A{\cdot}Os^{III}$	1.0×10^6	−0.44	0	1.3	3.2×10^8	1

[a] Classical treatment, eqs 2.15 and 2.16.

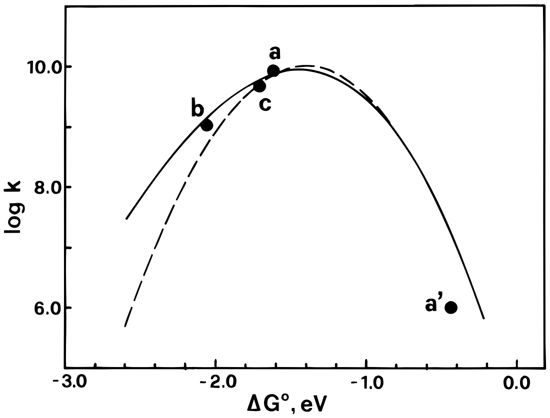


Figure 6.3. log k vs $\Delta G°$ for the electron-transfer reactions shown in Figure 6.2 (Table 6.1). Key: a, b, and c indicate the k values found for the excited-state electron-transfer processes shown in Figure 6.2a–c, respectively; a′ indicates the value found for the back-electron-transfer reaction shown in Figure 6.2a. The dashed curve has been obtained by using the classical Marcus treatment (eq 2.16). The full line curve corresponds to the treatment based on eq 2.19.

high-energy frequency vibrations as accepting modes (section 2.2.3.1). Equation 2.20 can be used to express the nuclear factor in order to better fit the experimental results. Using eqs 2.20 and 2.19 with $\lambda_o = 1.3$ eV, $H = 8$ cm^{-1}, and the average values $h\nu_i = 1400$ cm^{-1} and $S = 1.25$, the full line of Figure 6.3 has been obtained. The fitting is good for the three homogeneous excited-state electron-transfer reactions *a*, *b*, and *c*, whereas point *a′*, which corresponds to the back electron-transfer reaction in the $Ru^{II}{\cdot}A{\cdot}Os^{III}$ system, cannot be fit because of the different electronic factor.

6.1.2. Photoinduced Electron Collection

The design of an efficient photoinduced electron-transfer process in a supramolecular structure is only a step toward photochemical conversion of solar energy. Photoinduced electron transfer is in fact a *one-electron* process, whereas all the chemical reactions which are expected to be involved in artificial solar energy conversion schemes (e.g., water splitting) are *multielectron* processes.[16,119,121−123] Progress in this field is therefore related to the design of systems where components capable of causing photoinduced electron-transfer processes can be coupled with components capable of storing electrons and using them in multielectron redox processes.

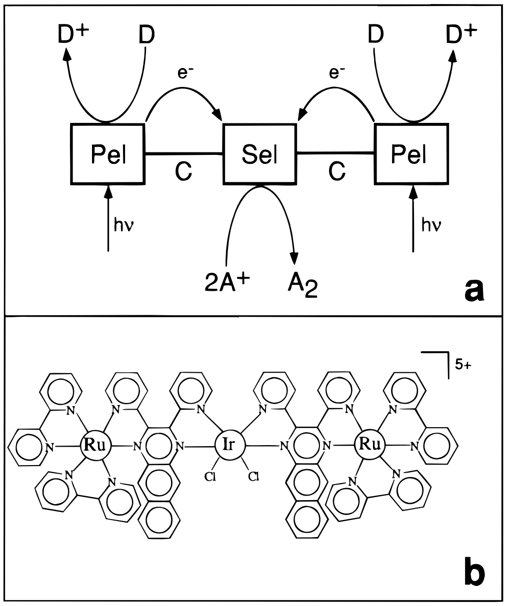


Figure 6.4. Schematic representation[1,124] (a) and an example[125] (b) of a photochemical molecular device for photoinduced electron collection.

The schematic diagram shown in Figure 6.4a shows a photochemical device for photoinduced electron collection.[1,124] In that scheme, Pel are electron-transfer photosensitizers, Sel an electron store component, D (sacrificial) electron donors, C rigid bridges, and A_2 a two-electron reduced product (e.g., H_2 starting from $2H^+$). The function of each Pel is that of harvesting light energy in order to transfer an electron to Sel, which must have the ability to store two electrons in order to perform the two-electron redox process that leads to the desired product.

A mixed-metal trinuclear complex capable of performing the above-mentioned function has recently been reported.[125] The trimetallic species has formula $[\{(bpy)_2Ru(\mu\text{-}dpb)\}_2IrCl_2]^{5+}$ (for a structural representation, see Figure 6.4b). In this compound, the two $(bpy)_2Ru(\mu\text{-}dpb)^{2+}$ moieties, which absorb in the visible spectral region, play the role of Pel and the $(\mu\text{-}dpb)_2IrCl_2^+$ unit can play the role of Sel. $[Ir(dpb)_2Cl_2]^+$ is in fact a catalyst for the electrochemical reduction of carbon dioxide to formate.[126] By using triphenylamine or dimethylaniline as sacrificial donors, it has been shown that $[\{(bpy)_2Ru(\mu\text{-}dpb)\}_2IrCl_2]^{5+}$ gives rise to a stable, reversible, doubly reduced species via the occurrence of two successive sequences of the following events: (i) light excitation of the peripheral Ru(II)-based chromophores; (ii) reduction of the central Ir(III)-based moiety by photoinduced electron transfer from the excited Ru(II)-based components; (iii) regeneration of the Ru(II)-based chromophores by oxidation of the sacrificial donor. In the doubly reduced species, the two added electrons are localized on the two bridging ligands of the central Ir(III)-based unit.

In spite of the low quantum yield of the photoreduction process (0.0015, in acetonitrile solution),[125] this system is interesting because it demonstrates the feasibility of photoinduced electron collection.

6.2. Intercomponent Energy Transfer

Electronic energy transfer in polynuclear metal complexes can be exploited for light harvesting (antenna effect). In this section we will briefly discuss this topic.

Generally speaking, an artificial antenna is a multicomponent system (Figure 6.5) in which several molecular components absorb the incident light and channel the excitation energy to a common acceptor component.[7]

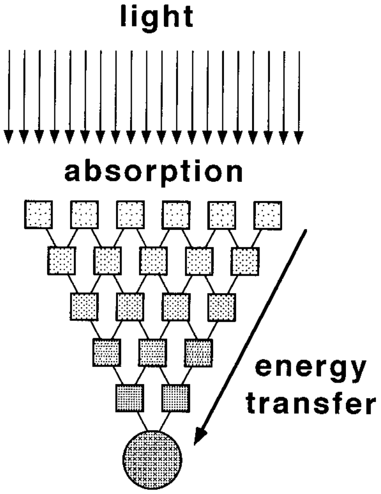


Figure 6.5. Schematic representation of an artificial antenna for light harvesting.[16]

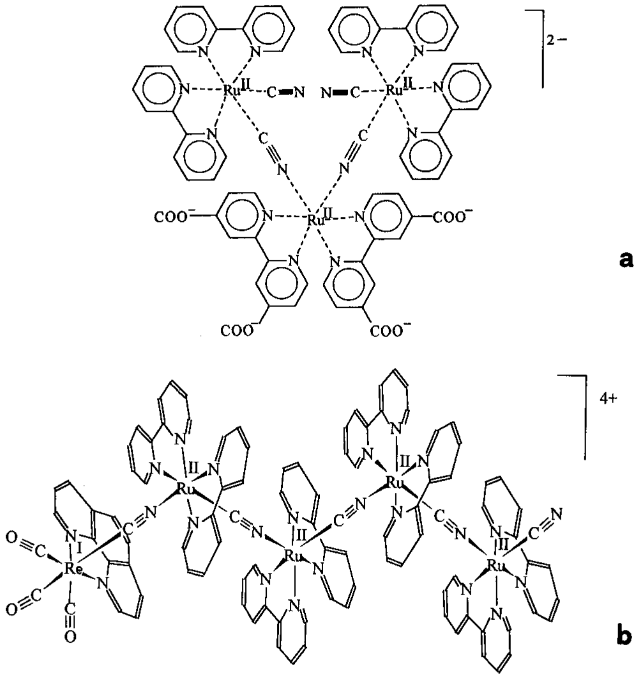


Figure 6.6. (a) A small antenna made of a trinuclear compound[131] and (b) a chainlike antenna.[132]

Toward the development of artificial antenna systems based on transition metal complexes, one line of trend is to assemble very large numbers of molecular components in more or less statistical ways. For example, photon-harvesting polymers are being developed[23,127] in which rapid energy migration among pendant chromophoric groups is observed under certain conditions. Although very interesting, such systems, as well as the beautiful porphyrin-based antenna arrays,[128,129] are outside the scope of this review.

Recent developments in the field of classic polynuclear complexes have shown that synthetic control of the position of the various components in the supramolecular array can be used to create a gradient for energy transfer in a predetermined direction. Most of the work in this area has been reviewed elsewhere.[4,16,130] We will only recall a few examples and some recent developments.

6.2.1. Small Antennas

Cyano-bridged complexes of d^6 metals have been used in the design of some simple antenna systems. An example is the trinuclear complex shown in Figure 6.6a.[118,131] In this system, because of the combined effects of the N-bonded bridging cyanides and of the carboxylate groups on the ligands, the lowest energy excited state is that of the central unit. Light energy absorbed by the peripheral units is efficiently funneled to the central one, as demonstrated by emission measurements[131] and by time-resolved resonance Raman techniques.[132] As simple as they are, antennas of this type have proven useful in a practical system for conversion of solar energy into electricity.[118,131,133,134]

6.2.2. Chainlike Systems

For some practical purposes (e.g., to bind at an interphase with good surface coverage), one-dimen-

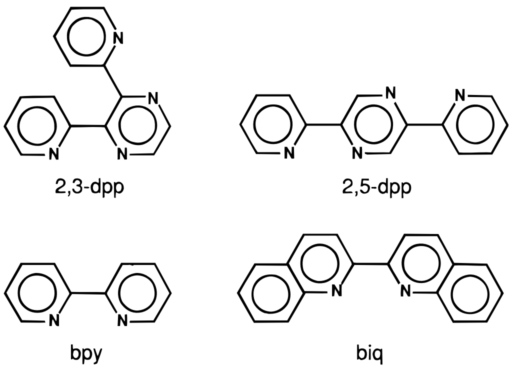


Figure 6.7. Ligands employed to obtain polynuclear complexes of large nuclearity.[95]

sional antenna systems might be more convenient than branched ones. A one-dimensional antenna requires stepwise energy transfer along a chain of molecular components, and the maximum length of the system (i.e., number of components) depends critically on the driving force demand of each energy-transfer step. The possibility of obtaining efficient energy migration along chainlike systems has been checked with the cyano-bridged pentanuclear species shown in Figure 6.6b.[135] This complex contains a Re(I)-based molecular component, three doubly bridged Ru(II)-based molecular components (Ru^1, Ru^2, and Ru^3), and a terminal Ru(II)-based molecular component (Ru^4), with all the bridging cyanides oriented in the same way (N-end pointing toward the terminal Ru(II) center). By molecular design, the relative MLCT excited-state energy ordering in this system is expected to be Re(I) $>$ Ru^1(II) $\geq$ Ru^2(II) $\approx$ Ru^3(II) $>$ Ru^4(II). Indeed, emission studies indicate that efficient energy transfer takes place from the Re(I)-based unit, presumably through several steps involving the intermediate units, down to the terminal Ru(II)-based unit.[135] Direct evidence for energy transfer between remote Re(I)- and Ru(II)-based chromophores has been obtained by time-resolved resonance Raman spectroscopy in a trinuclear analogue of the compound shown in Figure 6.6b, where labeling of the various components by isomorphous substitution of phen for bpy was used.[135] These results suggest that, in strongly coupled systems of this type, energy migration between *isoenergetic* adjacent molecular components takes place efficiently. The presence of (i) a higher-energy "stopper" on one end and (ii) a lower-energy "trap" at the other end are sufficient to give directionality to the overall process. Thus, relatively long-chain one-dimensional antenna systems can be conceived following these general design principles.

6.2.3. Dendrimers

An interesting series of polynuclear species of large nuclearity, which because of their shape can be called dendrimers or arborols, has been obtained using 2,3-dpp and/or 2,5-dpp as bridging ligands, Ru(II) and/or Os(II) as metal centers, and bpy or biq as terminal ligands (Figure 6.7).[95,102,136] The structure of a decanuclear complex of this family is schematized in Figure 6.8. Following the modular synthetic strategy known as "complexes-as-metals/complexes-as-ligands" (section 4),[95] such polynuclear species can be obtained with a high degree of synthetic control in terms of the nature and position of metal centers, bridging ligands, terminal ligands. The energy of the lowest metal-to-ligand charge transfer (MLCT) excited state of each unit depends on metal and ligands in a well-known and predictable way: $\mathrm{Os(bpy)_2(\mu\text{-}2,5\text{-}dpp)^{2+}} \leq \mathrm{Os(bpy)_2(\mu\text{-}2,3\text{-}dpp)^{2+}} < \mathrm{Os(biq)_2(\mu\text{-}2,5\text{-}dpp)^{2+}} \leq \mathrm{Os(biq)_2(\mu\text{-}2,3\text{-}dpp)^{2+}} < \mathrm{Os(\mu\text{-}2,5\text{-}dpp)_3{}^{2+}} < \mathrm{Os(\mu\text{-}2,3\text{-}dpp)_3{}^{2+}} < \mathrm{Ru(bpy)_2(\mu\text{-}2,5\text{-}dpp)^{2+}} \leq \mathrm{Ru(bpy)_2(\mu\text{-}2,3\text{-}dpp)^{2+}} < \mathrm{Ru(biq)_2(\mu\text{-}2,5\text{-}dpp)^{2+}} \leq \mathrm{Ru(biq)_2(\mu\text{-}2,3\text{-}dpp)^{2+}} < \mathrm{Ru(bpy)(\mu\text{-}2,5\text{-}dpp)_2{}^{2+}} \leq \mathrm{Ru(bpy)(\mu\text{-}2,3\text{-}dpp)_2{}^{2+}} < \mathrm{Ru(\mu\text{-}2,3\text{-}dpp)_3{}^{2+}}$. Thus, the synthetic control translates into a high degree of control on the direction of energy flow within these molecules.

In the case of the tetranuclear compounds, all the four possible energy-migration patterns, schematized in Figure 6.9, have been obtained. Pattern *i* is found

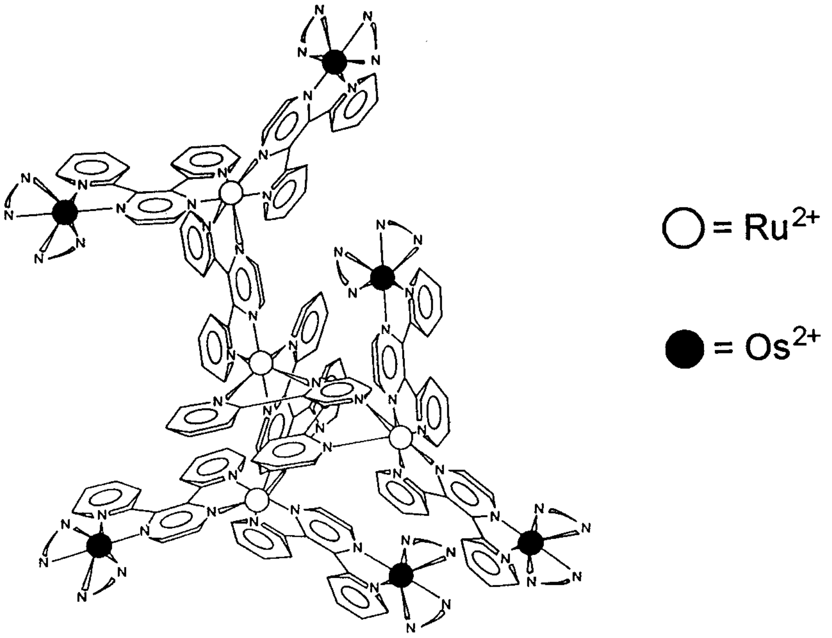


Figure 6.8. Schematic view of the structure of the $[\mathrm{Ru\{(\mu\text{-}2,3\text{-}dpp)Ru[(\mu\text{-}2,3\text{-}dpp)Os(bpy)_2]_2\}_3}]^{20+}$ decanuclear complex. N$-$N stands for bpy.[96]

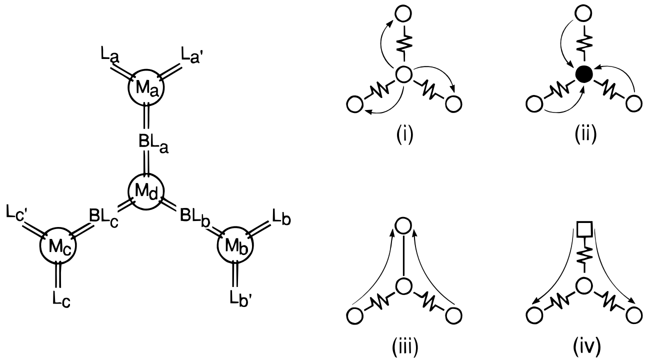


Figure 6.9. Energy-migration patterns in tetranuclear compounds.[137−140] Empty and full labels indicate Ru^{2+} and Os^{2+}, respectively. In the peripheral positions, circles and squares indicate $M(bpy)_2$ and $M(biq)_2$ components, respectively. For the bridging ligands: wavy lines, 2,3-dpp; straight lines, 2,5-dpp.

for L = bpy, BL = 2,3-dpp, and $M = Ru^{2+}$. In such a complex, the three peripheral units are equivalent and their lowest excited state lies at lower energy than the lowest excited state of the central unit.[137,138] The reverse symmetric pattern *ii* is observed for L = bpy, BL = 2,3-dpp, $M_d = Os^{2+}$, and $M_a = M_b = M_c = Ru^{2+}$. To channel energy toward a single peripheral unit (pattern *iii*) a compound with L = bpy, BL_a = 2,5-dpp, $BL_b = BL_c$ = 2,3-dpp, $M = Ru^{2+}$ was designed and synthesized.[139] Since 2,5-dpp is easier to reduce than 2,3-dpp, the Ru → BL CT excited state of the M_a-based building block is lower in energy than the Ru → BL CT state of the building blocks based on M_b and M_c. On the other hand, the lowest excited state of the central building block is higher in energy than the lowest excited state of all the peripheral ones. Thus, energy transfer from the M_d-, M_b-, and M_c-based building blocks to the M_a-based one is exoergonic, but the energy-transfer process from the M_b- and M_c-based units to the M_a-based one must either occur directly or overcome a barrier at M_d. The luminescence results show that the only emitting level is that based on M_a and that energy transfer is almost 100% efficient. The migration pattern shown by *iv* was obtained for a compound with $L_a = L_{a'}$ = biq, $L_b = L_{b'} = L_c = L_{c'}$ = bpy, BL = 2,3-dpp, and $M = Ru^{2+}$.[140] Since the energy level of the M_d-based building block is (slightly) higher than that of the M_a-based one, the migration process must again overcome an energy barrier.

A variety of energy-migration patterns have also been obtained for hexanuclear compounds of the same family.[141]

The decanuclear complex shown in Figure 6.8[96] is made so that the energy absorbed by all the units in the complex flows, via efficient intercomponent energy-transfer processes, from the center to the periphery of the complex, where it is reemitted by the Os(II)-containing units as near-infrared luminescence.[142] Several other synthetically predetermined energy-migration patterns have been obtained in similar decanuclear species, simply by using different combination of metals and ligands (Figure 6.10).[96]

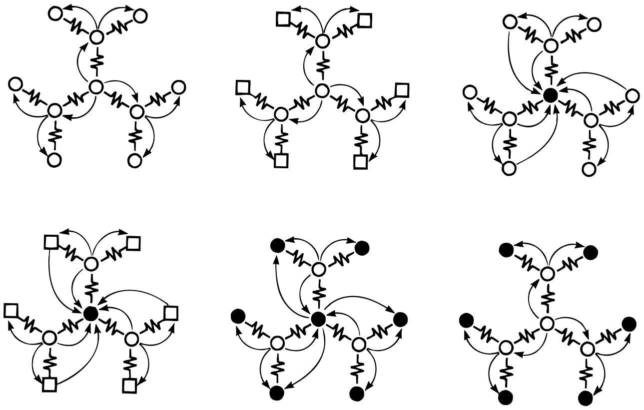


Figure 6.10. Schematic representation of the energy-transfer processes in decanuclear compounds.[96] For the graphic symbols, see caption to Figure 6.9.

As we have seen in section 4, the "complexes-as-metals/complexes-as-ligands" synthetic approach can be extended to obtain even larger dendrimers. Most of the work has so far been focused on compounds containing Ru(II) and Os(II). However, synthetic control of the energy gradient in larger structures, in order to obtain energy transfer according to predetermined patterns, will probably require the use of more than two different metals. This is a difficult task since for each family of metals, specific types of ligands must be chosen in order to assure chemical stability and to confer the desired excited-state and redox properties. For example, with metals like Rh(III), Ir(III), Pd(II), Pt(II), and Pt(IV), N−N (bipyridine-type) chelating ligands are not fully satisfactory, whereas $N-C^-$ (cyclometalating) chelating ligands give rise to stable and interesting species.[143] By using such cyclometalating ligands, the scope of the "complexes-as-metals/complexes-as-ligands" synthetic strategy can be noticeably extended. As a first step along this direction, the synthesis and characterization of some tetranuclear bimetallic complexes involving Rh(III)- and Ir(III)-based units which contain the cyclometalating phenylpyridine anion (ppy^-) as terminal ligand have been prepared.[144] Several other dendrimers based on metal complexes have also been prepared.[145−149]

7. Conclusions and Perspectives

In the last few years a great number of polynuclear transition metal complexes have been synthesized. Such compounds have usually well-defined composition and, in several cases, present a modular structure since they can contain repetitive metal-based components (see, e.g., Figures 4.3, 6.6, and 6.8) and/or spacers made of repetitive units (see, e.g., Figure 3.4). Research in the field of polynuclear transition metal complexes can give an important contribution to the development of modular chemistry[104,150−161] and to the bottom-up design of nanostructures.[162−164]

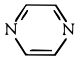
When interaction between the metal-based components is weak, polynuclear transition metal complexes belong to the field of supramolecular chemistry. At the roots of supramolecular chemistry is the concept that supramolecular species have the potential to achieve much more elaborated tasks than simple molecular components: while a molecular component can be involved in simple *acts*, supramolecular species can perform *functions*.[1,3,6,7,13,16] In other words, supramolecular species have the potentiality to behave as molecular devices. Particularly interesting molecular devices are those which use light to achieve their functions. Molecular devices which perform *light-induced functions* are called *photochemical molecular devices (PMD)*.[1,124] Luminescent and redox-active polynuclear complexes as those described in this article can play a role as PMDs operating by photoinduced energy- and electron-transfer processes.

The tables given in section 9 report the luminescence and redox properties of as many as 435 complexes, 110 of which have nuclearity equal or larger than three. These numbers are impressive, especially if we consider that only 15 dinuclear luminescent Ru(II) complexes were reported in a review article published in 1988,[21] and less than 70 luminescent polynuclear complexes (about 20 of which with nuclearity equal or larger than three) are listed in a 1990 review on the photochemistry and photophysics of polynuclear complexes.[4] A closer inspection of the compounds displayed in the tables of section 9, however, shows that this field is still in its infancy. In particular, most of the building blocks used so far are based on Ru, Re, and Os, and the ligands used are mainly of the polypyridine family. Furthermore in several cases the structure of the supramolecular array is not well defined because of the presence of flexible bridging ligands. Substantial progress has to be made in the design of new luminescent and redox-active building blocks and in the synthesis of new modules to construct spacers having well-defined structures (rods, rings, ribbons, etc.) and properties (insulating, conductive, photosensitive, etc.). The development of this field will be strictly connected with a more extensive use of theory and modeling of structural design and properties. Substantial benefit will also come from improvement of experimental techniques (like MS FAB, ESMS, etc.) capable of characterizing large and electrically charged arrays.

8. List of the Bridging Ligands

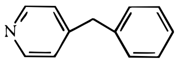
Cl^- (Table 9.1)

CN^- (Table 9.2)



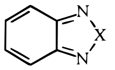
pyz

(Table 9.3)



4-benzyl-py

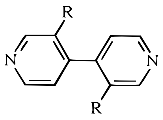
(Table 9.4)



btd, X = S

bsd, X = Se

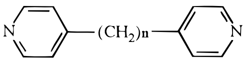
(Table 9.5)



4,4'-bpy, R = H

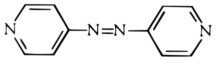
Me$_2$-4,4'-bpy, R = CH_3

(Table 9.6)



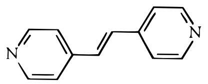
py-S4$_n$-py

(Table 9.7)



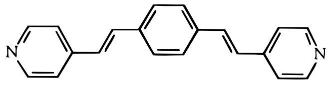
py-E4$_A$-py

(Table 9.8)



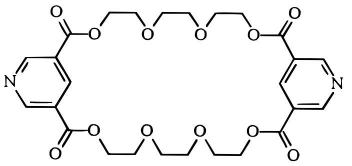
py-NN-py

(Table 9.9)



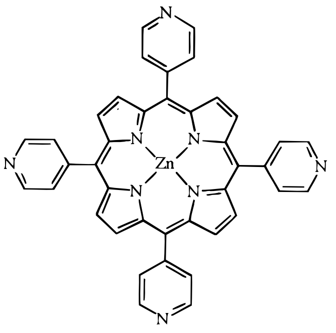
py-E4$_B$-py

(Table 9.10)



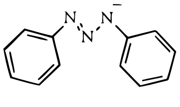
py-crown-py

(Table 9.11)



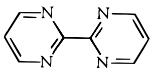
ZnTPyP

(Table 9.12)



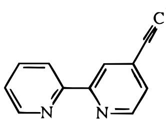
DPT$^-$

(Table 9.13)



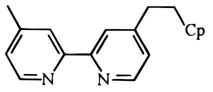
bpym

(Table 9.14)



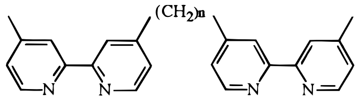
bpy-E4$_C$

(Table 9.15)



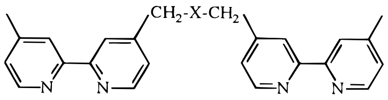
4Mebpy-S4$_2$-Cp

(Table 9.16)



4Mebpy-S4$_n$-bpy4Me

(Table 9.17)

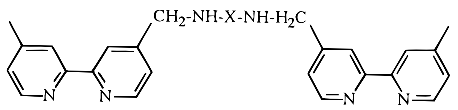


4Mebpy-S4$_A$-bpy4Me, X = CH(OH)

4Mebpy-S4$_B$-bpy4Me, X = O

4Mebpy-S4$_C$-bpy4Me, X = S

(Table 9.18)



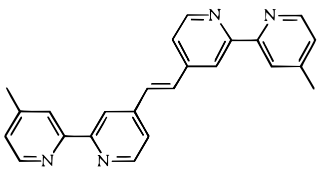
4Mebpy-S4$_D$-bpy4Me, X = $(CH_2)_8$

4Mebpy-S4$_E$-bpy4Me,

X = $(CH_2)_3$-N-$(CH_2)_3$

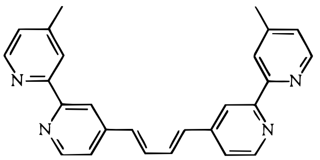
CH_3

(Table 9.19)



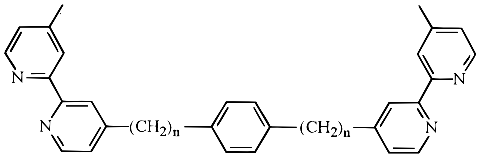
4Mebpy-E4$_A$-bpy4Me

(Table 9.20)



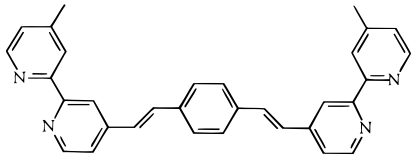
4Mebpy-bd4-bpy4Me

(Table 9.21)



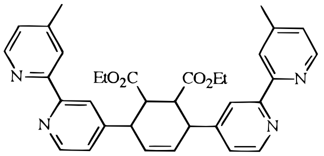
4Mebpy-P4$_n$-bpy4Me

(Table 9.22)



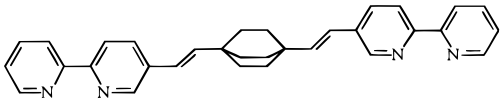
4Mebpy-E4$_B$-bpy4Me

(Table 9.23)



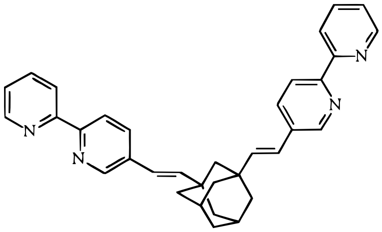
4Mebpy-ch4-bpy4Me

(Table 9.24)



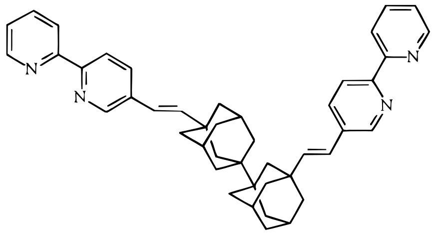
bpy-E5$_A$-bpy

(Table 9.25)



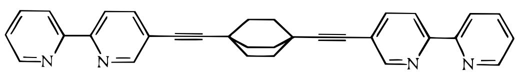
bpy-a-bpy

(Table 9.26)



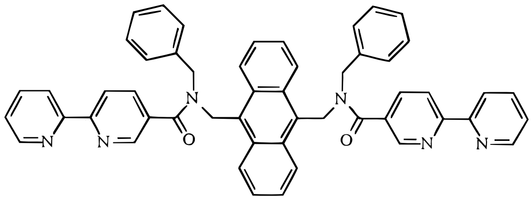
bpy-aa-bpy

(Table 9.27)



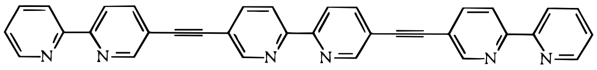
bpy-E5$_B$-bpy

(Table 9.28)



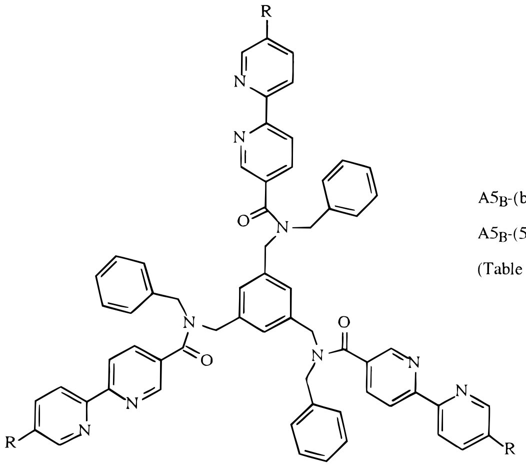
bpy-A5$_A$-bpy

(Table 9.29)



bpy-bpy-bpy

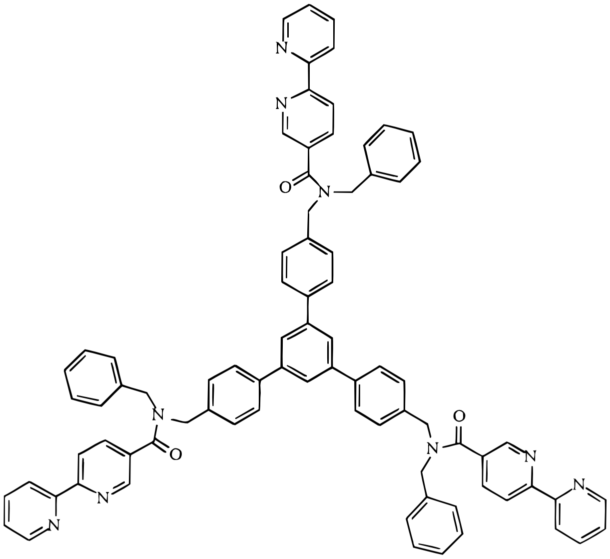
(Table 9.30)



A5$_B$-(bpy)$_3$, R = H

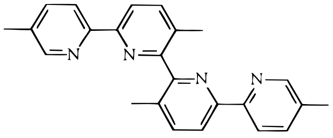
A5$_B$-(5CE-bpy)$_3$, R = $COOC_2H_5$

(Table 9.31)



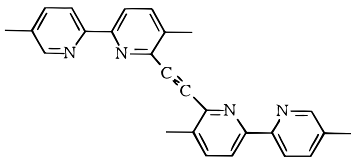
A5$_C$-(bpy)$_3$

(Table 9.32)



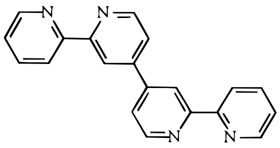
QP

(Table 9.33)



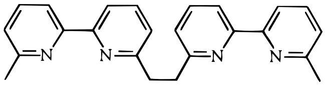
5,5'-dmbpy-E6-5,5'-dmbpy

(Table 9.34)



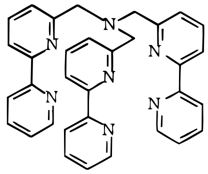
QP$_B$

(Table 9.35)



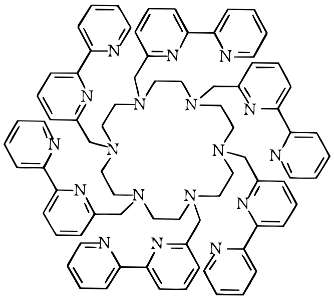
6Mebpy-S6$_2$-bpy6Me

(Table 9.36)



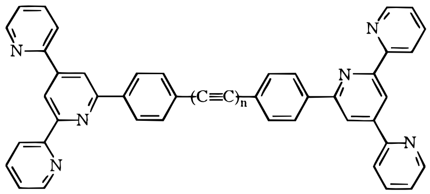
N-bpy$_3$

(Table 9.37)



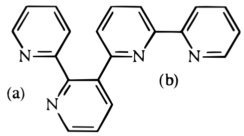
hacod-bpy$_6$

(Table 9.38)



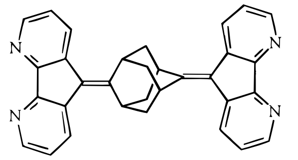
pbpy-Ph-E$_n$-Ph-pbpy

(Table 9.39)



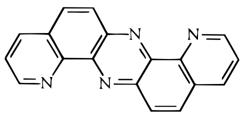
bpy$_a$-bpy$_b$

(Table 9.40)



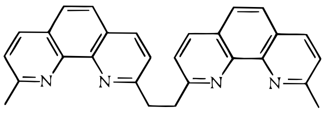
FAF

(Table 9.41)



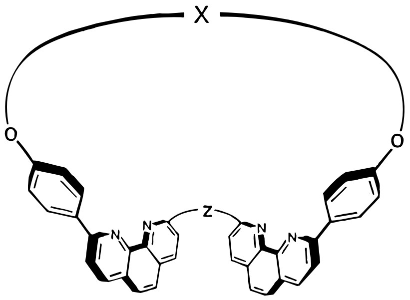
dpop

(Table 9.42)



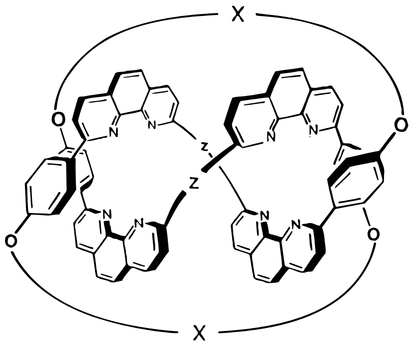
9Mephen-S2$_2$-phen9Me

(Table 9.43)



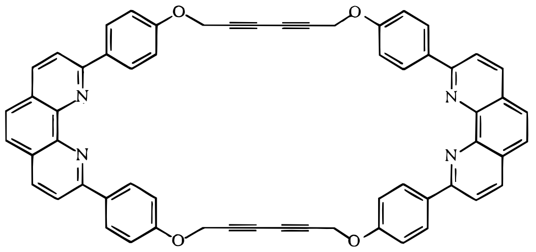
m-nn

(Table 9.44)



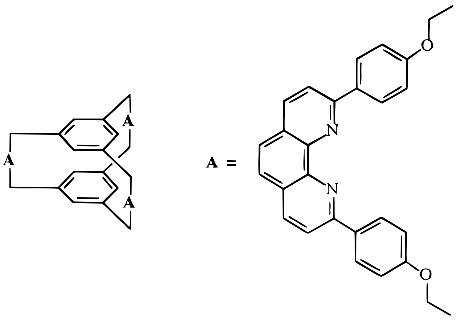
knot -k-nn

(Table 9.45)



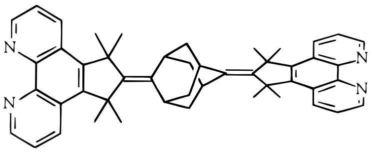
caten

(Table 9.46)



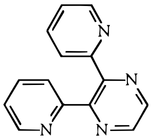
cage-phen$_3$

(Table 9.47)



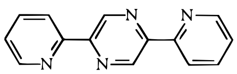
PAP

(Table 9.48)



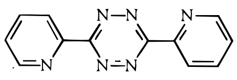
2,3-dpp

(Tables 9.49, 9.51, 9.67)



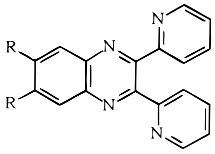
2,5-dpp

(Tables 9.50, 9.51)



BPTZ

(Table 9.52)

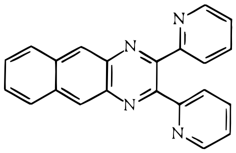


dpq, R = H

Me$_2$dpq, R = CH$_3$

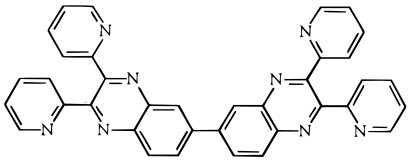
Cl$_2$dpq, R = Cl

(Table 9.53)



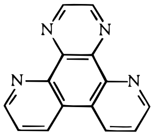
dpbq

(Table 9.54)



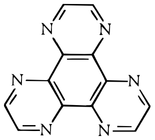
dpq-dpq

(Table 9.55)



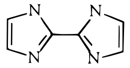
ppz

(Table 9.56)



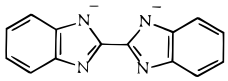
HAT

(Table 9.57)



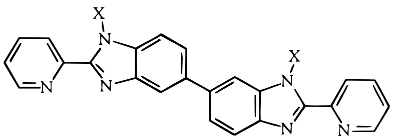
BiIm^{2-}

(Table 9.58)



BiBzIm^{2-}

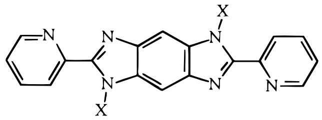
(Table 9.59)



bpbimH$_2$, X = H

dimbpbim, X = CH$_3$

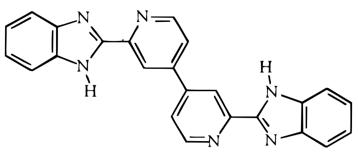
(Table 9.60)



dpimbH$_2$, X = H

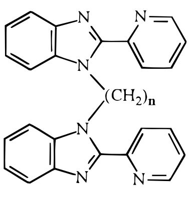
bptb, X = S

(Table 9.61)



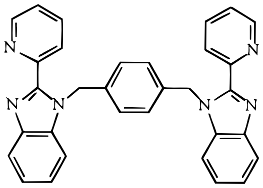
bbbpyH$_2$

(Table 9.62)



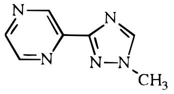
pbim-S$_n$-pbim

(Table 9.63)



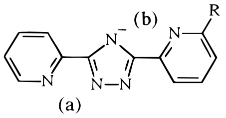
pbim-S$_B$-pbim

(Table 9.64)



mpzt

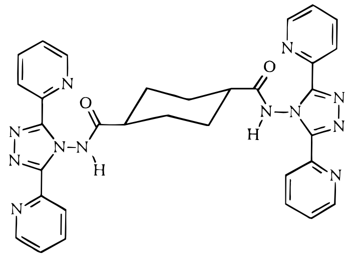
(Table 9.65)



a-bpt-b$^-$, R = H

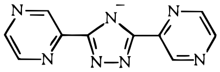
a-mbpt-b$^-$, R = CH

(Tables 9.66, 9.67)^3



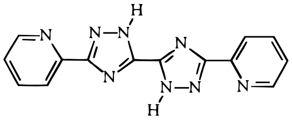
bpt-A10$_D$-bpt

(Table 9.68)



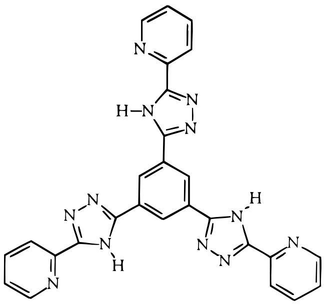
bpzt$^-$

(Table 9.69)



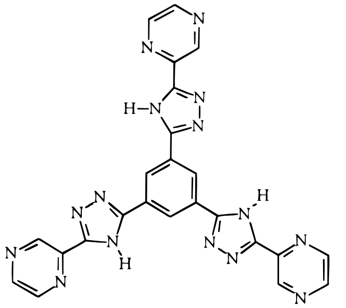
bpbtH$_2$

(Table 9.70)



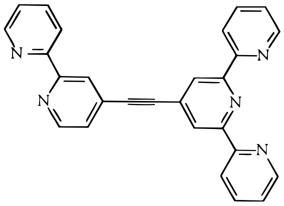
tpbH3

(Table 9.71)



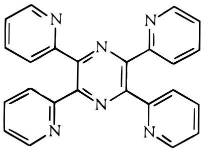
tpzbH$_3$

(Table 9.72)



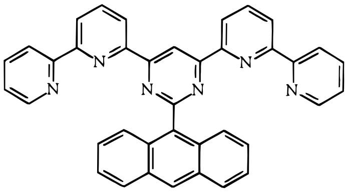
bpy-E4C-tpy

(Table 9.73)



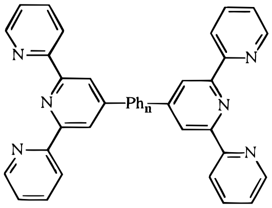
tpp

(Table 9.74)



tpy-A-tpy

(Table 9.75)

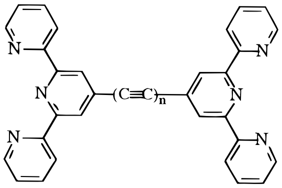


tpy-tpy, n = 0

tpy-Ph-tpy, n = 1

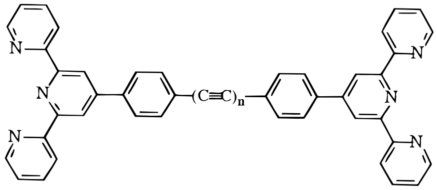
tpy-Ph$_2$-tpy, n = 2

(Table 9.76)



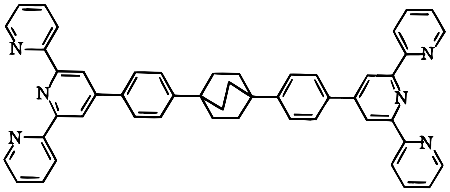
tpy-E$_n$-tpy

(Table 9.77)



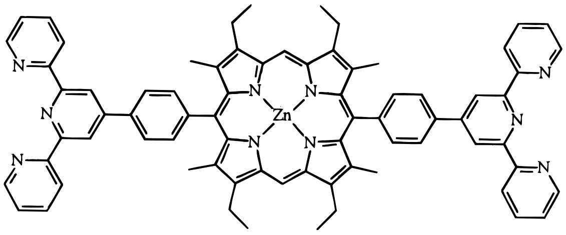
tpy-Ph-E$_n$-Ph-tpy

(Table 9.78)



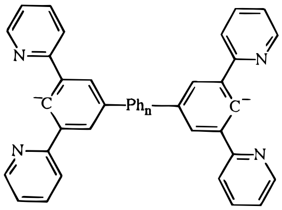
tpy-Ph-bco-Ph-tpy

(Table 9.79)



tpy-ZnP-tpy

(Table 9.80)



(dpb-dpb)$^{-2}$, n = 0

(dpb-Ph-dpb)$^{-2}$, n = 1

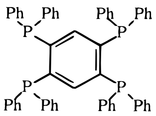
(dpb-Ph$_2$-dpb)$^{-2}$, n = 2

(Table 9.81)

P(Ph)$_2$-CH$_2$-P(Ph)$_2$

dppm

(Table 9.82)



tppb

(Table 9.83)

S(C$_2$H$_5$)$_2$

(Table 9.84)

9. Tables of Photophysical and Electrochemical Data

This section contains tables on the photophysical and electrochemical data. Each table (part A, photophysical data, and part B, electrochemical data) refers to the complexes of a specific bridging ligand, whose structural formula and abbreviations are shown at the top of the table.

The succession of the tables is the same as that of the bridging ligands listed in section 8. In the formulas of the complexes the bridging ligand is shown in bold. For the sake of clarity, the μ symbol has been omitted. Within each table, the complexes are ordered by increasing nuclearity and atomic number of the metals.

The abbreviations used for the ligands, solvents, etc. are shown in section 10. Moreover, the following abbreviations are used: a = aerated solution; d = deareated solution; c = corrected spectrum; u = uncorrected spectrum; f = value estimated from a figure; i = irreversible process; [n] = number of exchanged electrons; BL = bridging ligand.

Table 9.1

Cl$^-$

A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Rh$_2$									
[(ppy)$_2$Rh(**Cl**)$_2$Rh(ppy)$_2$]	CH$_2$Cl$_2$	393	7700						165
	Et/Met						461	93	165
[(bzq)$_2$Rh(**Cl**)$_2$Rh(bzq)$_2$]	CH$_2$Cl$_2$	410	8200						165
	Et/Met						484	2600	165
RhPd									
[(ppy)$_2$Rh(**Cl**)$_2$Pd(ppy)$_2$]	CH$_2$Cl$_2$	455							165
	Et/Met						498	13.2	165
[(ppy)$_2$Rh(**Cl**)$_2$Pd(bzq)$_2$]	CH$_2$Cl$_2$	408							165
	Et/Met						460	237	165
							484	2500	
Ir$_2$									
[(ppy)$_2$Ir(**Cl**)$_2$Ir(ppy)$_2$]	CH$_2$Cl$_2$	484	1100	518 c	140 d				166
	Et/Met						483 c	4.8	166
[(bzq)$_2$Ir(**Cl**)$_2$Ir(bzq)$_2$]	CH$_2$Cl$_2$	480	3100	550 c	1400 d				167
	Et/Met						510 c	30	167
[(ptpy)$_2$Ir(**Cl**)$_2$Ir(ptpy)$_2$]	CH$_2$Cl$_2$	482	1000	510 c	150 d				166
	Et/Met						490 c	5.2	166
[(mppy)$_2$Ir(**Cl**)$_2$Ir(mppy)$_2$]	CH$_2$Cl$_2$	484	1400	520 c	60 d				166
	Et/Met						497 c	5.0	166

Table 9.2

CN$^-$

A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
CrRu									
[(NC)$_5$Cr(**CN**)Ru(bpy)$_2$(CN)]$^{2-}$	DMF	496		≈805 f	1.1×10^6 d	8.5×10^{-4} d			168
RuRh									
[(NC)(bpy)$_2$Ru(**CN**)Rh(NH$_3$)$_5$]$^{3+}$	DMSO/H$_2$O†	430	8470	604 c	310		556 c	5.7	169
	DMF/CHCl$_3$	457		626 c	610		577 c	6.1	169
[(NC)(bpy)$_2$Ru(**CN**)-Rh(NH$_3$)$_4$(CN)]$^{2+}$	DMSO/H$_2$O†	430	8940	606 c	400		556 c	6.0	169
	DMF/CHCl$_3$	455		630 c	630		578 c	6.25	169
[(NC)(bpy)$_2$Ru(**CN**)-Rh(NH$_3$)$_4$(Br)]$^{2+}$	DMSO/H$_2$O†	429	10400	620 c	40, 220‡		554 c	5.0	169
	DMF/CHCl$_3$	453		632 c	220		577 c	5.8	169
[(NC)(bpy)$_2$Ru(**CN**)-Rh(NH$_3$)$_4$(I)]$^{2+}$	DMSO/H$_2$O†	433	11700	631 c	350§		572 c	3.9§	169
	DMF/CHCl$_3$	458		650 c	60		590 c	5.3	169
Ru$_2$									
[(NC)(bpy)$_2$Ru(**CN**)-Ru(bpy)$_2$(CN)]$^+$	AN	488	15400	714 c	120 d		630 c	1.6	170,171
[(NC)(bpy)$_2$Ru(**CN**)-Ru(phen)$_2$(CN)]$^+$	AN	483	17600	700 c	400 d		592 c	4.6	170,171
[(NC)(phen)$_2$Ru(**CN**)-Ru(bpy)$_2$(CN)]$^+$	AN	480	16600	715 c	95				132
RuRe									
[(NC)(bpy)$_2$Ru(**CN**)-Re(phen)(CO)$_3$]$^+$	AN	482		667	422	0.020			135
RuPt									
[(NC)(bpy)$_2$Ru(**CN**)Pt(dien)]$^{2+}$	DMF	460	≈7500	630	630 d				172
	H$_2$O	416		590	140 d				172
Re$_2$									
[(CO)$_3$(bpy)Re(**CN**)-Re(bpy)(CO)$_3$]$^+$	AN			580 c	245				173
	CH$_2$Cl$_2$	370	6610	571 c	395				173
	EtOH			580 c					173
	Et/Met						530 c	3.92	173
	MeOH			581 c	190				173

Table 9.2 (Continued)

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
$\mathbf{Cr_2Ru}$									
$[\{(NH_3)_5Cr(\mathbf{NC})\}_2\text{-}Ru(bpy)_2]^{6+}$	$DMSO/H_2O^{\dagger}$	390	12600	no emission			738		169
	$DMF/CHCl_3$	408		not reported	≤40		680	78	169
$[\{(NC)_5Cr(\mathbf{CN})\}_2\text{-}Ru(bpy)_2]^{4-}$	DMF	490	≈8500	≈810	1.3×10^3 d	9.2×10^{-4} d			168
	H_2O	454							168
$[\{(NC)(cyclam)Cr(\mathbf{CN})\}_2\text{-}Ru(bpy)_2]^{4+}$	$H_2O^{\dagger}$	440 sh	≈10000	727 c	2.60×10^5 d	5.3×10^{-3} d			174,175
	$H_2O^{\square}$	≈390	≈8000	722 c	2.40×10^5 d	4.4×10^{-3} d			175
$[\{(NC)(cyclam)\text{-}Cr(\mathbf{CN})\}_2Ru(CN)_4]$	DMF	370	≈7000 f	723 c	9.6×10^4 a	7.9×10^{-3} a			176
	H_2O	338	6500	722 c	3.00×10^5 a	1.3×10^{-2} a			176
$\mathbf{Ru_3}$									
$[\{(NC)(bpy)_2Ru(\mathbf{CN})\}_2\text{-}Ru(bpy)_2]^{2+}$	AN	478	21600	735 c	90 d				170,171
	EtOH						685 c	1.3	170,171
$[\{(CN)(bpy)_2Ru(\mathbf{CN})\}_2\text{-}Ru(dcbpyH_2)_2]^{2+}$	AN	536	10800	793 c	30 d				177,178
	EtOH	540	11400	795 c	30 d				177,178
	H_2O (pH = 1)	542	10400	820 c	20 d				177,178
	MeOH	536	10300	781 c	48 d				177,178
$[\{(CN)(bpy)_2Ru(\mathbf{CN})\}_2\text{-}Ru(dcbpy)_2]^{2-}$	AN	482	18300	723 c	122 d				177,178
	AN	485	22000	720 c	140 d		710 c		131,171
	EtOH	474	19900	724 c	145 d				177,178
	H_2O	526		760 c					131,171
	H_2O (pH = 11)	520	13500	752 c	38 d				177,178
	MeOH	466	18300	733 c					177,178
$[\{(H_2O)(bpy)_2Ru(\mathbf{NC})\}_2\text{-}Ru(dcbpyH_2)_2]^{4+}$	AN	486	10900	737 c	24 d				178
$[\{(HO)(bpy)_2Ru(\mathbf{NC})\}_2\text{-}Ru(dcbpy)_2]^{2-}$	AN	498	16400	749 c	24 d				178
$[\{(CN)(dmbpy)_2Ru(\mathbf{CN})\}_2\text{-}Ru(dcbpyH_2)_2]^{2+}$	AN	540	11900	802 c	23 d				178
$[\{(CN)(dmbpy)_2Ru(\mathbf{CN})\}_2\text{-}Ru(dcbpy)_2]^{2-}$	AN	498	16300	728 c	83 d				178
$[\{(CN)((MeO)_2\text{-}bpy)_2Ru\text{-}(\mathbf{CN})\}_2Ru(dcbpyH_2)_2]^{2+}$	AN	510	8300	743 c					178
$[\{(CN)((MeO)_2\text{-}bpy)_2Ru\text{-}(\mathbf{CN})\}_2Ru(dcbpy)_2]^{2-}$	AN	498	11000	718 c					178
$[\{(CN)(phen)_2Ru(\mathbf{CN})\}_2\text{-}Ru(dcbpyH_2)_2]^{2+}$	AN	514	10000	750 c					178
$[\{(CN)(phen)_2Ru(\mathbf{CN})\}_2\text{-}Ru(dcbpy)_2]^{2-}$	AN	500	19400	764 c	45 d				178
$[\{(CN)(dcbpy)_2Ru(\mathbf{CN})\}_2\text{-}Ru(dcbpyH_2)_2]^{2-}$	EtOH	480	29000	700 c					178
$\mathbf{Ru_2Re}$									
$[(NC)(bpy)_2Ru(\mathbf{NC})Ru\text{-}(bpy)_2(\mathbf{NC})Re(phen)\text{-}(CO)_3]^{2+}$	AN	480		694	133	4.7×10^{-3}			135
$\mathbf{RuRh_2}$									
$[(bpy)_2Ru\{(\mathbf{CN})\text{-}Rh(NH_3)_5\}_2]^{6+}$	$DMSO/H_2O^{\dagger}$	413	8160	576	40		543	8.4	169
	$DMF/CHCl_3$	428		589	50		553	7.6	169
$\mathbf{RuRe_2}$									
$[(bpy)_2Ru\{(\mathbf{CN})\text{-}Re(bpy)(CO)_3\}_2]^{2+}$	AN			645 c	330	≈0.01			173
	CH_2Cl_2	442	8060	643 c	465				173
	Et/Met						592 c	4.09	173
	MeOH			639 c	310				173
$[(dcbpyH_2)_2Ru\{(\mathbf{NC})\text{-}Re(bpy)(CO)_3\}_2]^{2+}$ ¶	DMF			670 c					173
	EtOH	492	12600	661 c	<40	≈0.002			173
	Et/Met						655 c		173
	H_2O	500		702 c					173
$\mathbf{RuOs_2}$									
$[(dcbpy)_2Ru\{(\mathbf{NC})\text{-}Os(bpy)_2(CN)\}_2]^{2-}$	AN	518	17400	≈900					178
$[(dcbpy)_2Ru\{(\mathbf{CN})\text{-}Os(bpy)_2(H_2O)\}_2]^{2-}$	AN	510	20000	≈860					178
$\mathbf{RuPt_2}$									
$[(bpy)_2Ru\{(\mathbf{CN})\text{-}Pt(dien)\}_2]^{4+}$	DMF	426	≈8000 f	580	90 d		≈530 f		172
	H_2O	408		580	60 d				172
$\mathbf{Ru_3Re}$									
$[(NC)(bpy)_2Ru\{(\mathbf{NC})Ru\text{-}(bpy)_2\}_2(\mathbf{NC})Re(phen)\text{-}(CO)_3]^{3+}$	AN	479		694	149	4.5×10^{-3}			135
$\mathbf{Zn_2Ru_3}$									
$[\{Zn(\mathbf{NC})Ru(bpy)_2(\mathbf{CN})\}_2\text{-}Ru(bpy)_2]^{6+}$	AN			690 c	160 d				132
$\mathbf{Ru_4Re}$									
$[(NC)(bpy)_2Ru\{(\mathbf{NC})Ru\text{-}(bpy)_2\}_3(\mathbf{NC})Re(phen)\text{-}(CO)_3]^{3+}$	AN	477		694	127	3.9×10^{-3}			135

Table 9.2 (Continued)

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [*n*] (site)	E_{red}, V [*n*] (site)	ref(s)
CrRu					
$[(NC)_5Cr(\mathbf{CN})Ru(bpy)_2(CN)]^{2-}$	DMF	SCE	+0.89 (Ru)	≈−1.4 i (Cr)	168
Ru_2					
$[(NC)(bpy)_2Ru(\mathbf{CN})Ru(bpy)_2(CN)]^{+}$	AN	SCE	+0.74 (Ru-N), +1.35 (Ru-C)	−1.54 [2]	38,132, 170
	DMF	SCE		−1.54 [2]	170
	DMF (−54 °C)	SCE		−1.47 [1], −1.53 [1], −1.74 [1], −1.83 [1], −2.44 [1], −2.52 [1], −2.78 [1] (all bpy)	38
	H_2O	SCE	+0.64		170
$[(NC)(bpy)_2Ru(\mathbf{CN})Ru(phen)_2(CN)]^{+}$	AN	SCE	+0.75, +1.35	−1.54 [2]	132,170
	DMF	SCE		−1.54 [2]	170
	H_2O	SCE	+0.64		170
$[(NC)(phen)_2Ru(\mathbf{CN})Ru(bpy)_2(CN)]^{+}$	AN	SCE	+0.72, +1.35	−1.56 [2]	132
RuRh					
$[(NC)(bpy)_2Ru(\mathbf{CN})Rh(NH_3)_5]^{3+}$	AN	SSCE	+1.00 [1] (Ru)	−1.695, −1.931	169
$[(NC)(bpy)_2Ru(\mathbf{CN})Rh(NH_3)_4(I)]^{2+}$	AN	SCE	+0.923		169
RuRe					
$[(NC)(bpy)_2Ru(\mathbf{CN})Re(phen)(CO)_3]^{+}$	AN	SCE	0.94, +1.78 i		135
RuPt					
$[(NC)(bpy)_2Ru(\mathbf{CN})Pt(dien)]^{2+}$	DMF	SCE	+1.03	−1.62	172
Re_2					
$[(CO)_3(bpy)Re(\mathbf{CN})Re(bpy)(CO)_3]^{+}$	AN	SCE	+1.35 i (Re-N), +1.60 i (Re-C)	−1.29 (bpyRe-C), −1.41 (bpyRe-N)	173
Cr_2Ru					
$[\{(NC)_5Cr(\mathbf{CN})\}_2Ru(bpy)_2]^{4-}$	DMF	SCE	+0.84 (Ru)	≈−1.4 i (Cr)	168
$[\{(NC)(cyclam)Cr(\mathbf{CN})\}_2Ru(bpy)_2]^{4+}$	DMSO	SCE	+1.35 i (Ru)	−1.44 (bpy), −1.58 (bpy), −1.82 i (Cr)	174
$[\{(NC)(cyclam)Cr(\mathbf{CN})\}_2Ru(CN)_4]$	H_2O	SCE	+1.13 i (Ru)	−1.34 i (Cr)	176
Ru_3					
$[\{(NC)(bpy)_2Ru(\mathbf{CN})\}_2Ru(bpy)_2]^{2+}$	AN	SCE	+0.66 (Ru_c), +1.19 (Ru_t), +1.46 (Ru_t)$^{\nabla}$	−1.53 [3]	38,132, 170
	AN (−30 °C)	SCE		−1.54 [2], −1.65	131
	DMF	SCE		−1.51	170
	DMF (−54 °C)	SCE		−1.52 [1], −1.57 [1], −1.63 [1], −1.80 [1], −1.84 [1], −2.02 [1], −2.57 [1], −2.62 [1], −2.83 [1], −2.90 [1] (all bpy)	38
	H_2O	SCE	+0.53		170
$[\{(CN)(bpy)_2Ru(\mathbf{CN})\}_2Ru(dcbpyH_2)_2]^{2+}$	AN/H_2SO_4	SCE	+0.65 (Ru_c), +1.20 (Ru_t)$^{\nabla}$	<−1.4	177,178
$[\{(CN)(bpy)_2Ru(\mathbf{CN})\}_2Ru(dcbpy)_2]^{2-}$	AN	SCE	+0.68 (Ru_c), +1.20 (Ru_t)$^{\nabla}$	<−1.4	177,178
	AN (−30 °C)	SCE	+0.54, +1.24, +1.58 i	−1.61 [2], −1.74	131
$[\{(H_2O)(bpy)_2Ru(\mathbf{NC})\}_2Ru(dcbpyH_2)_2]^{4+}$	AN/H_2SO_4	SCE	+0.69 (Ru_c), +0.97 (Ru_t)$^{\nabla}$	<−1.4	178
$[\{(HO)(bpy)_2Ru(\mathbf{NC})\}_2Ru(dcbpy)_2]^{2-}$	AN	SCE	+0.30 (Ru_c), ≈+1.0 (Ru_t)$^{\nabla}$	<−1.4	177,178
$[\{(CN)(dmbpy)_2Ru(\mathbf{CN})\}_2Ru(dcbpyH_2)_2]^{2+}$	AN/H_2SO_4	SCE	+0.68 (Ru_c), +0.98 (Ru_t)$^{\nabla}$	<−1.4	178
$[\{(CN)(dmbpy)_2Ru(\mathbf{CN})\}_2Ru(dcbpy)_2]^{2-}$	AN	SCE	≈+0.80 (Ru_c), ≈+1.00 (Ru_t)$^{\nabla}$	<−1.4	178
$[\{(CN)((MeO)_2\text{-}bpy)_2Ru(\mathbf{CN})\}_2Ru(dcbpyH_2)_2]^{2+}$	H_2SO_4 4 M	SCE	≈+0.70 (Ru_c), ≈+0.90 (Ru_t)$^{\nabla}$	<−1.4	178
$[\{(CN)(phen)_2Ru(\mathbf{CN})\}_2Ru(dcbpyH_2)_2]^{2+}$	AN/H_2SO_4	SCE	+0.70 (Ru_c), ≈+1.20 (Ru_t)$^{\nabla}$		178
$[\{(CN)(dcbpy)_2Ru(\mathbf{CN})\}_2Ru(dcbpyH_2)_2]^{2-}$	AN	SCE	+0.73 (Ru_c)$^{\nabla}$		178
$RuRh_2$					
$[(bpy)_2Ru\{(\mathbf{CN})Rh(NH_3)_5\}_2]^{6+}$	AN	SSCE	+1.188 [1] (Ru)	−1.695, −1.931	169
Ru_2Re					
$[(NC)(bpy)_2Ru(\mathbf{NC})Ru(bpy)_2\text{-}(\mathbf{NC})Re(phen)(CO)_3]^{2+}$	AN	SCE	+0.76, +1.37, +1.74 i		135
$RuRe_2$					
$[(bpy)_2Ru\{(\mathbf{CN})Re(bpy)(CO)_3\}_2]^{2+}$	DMF	SCE	≈+1.0 i (Ru), ≥+1.4 i (Re)	−1.23 [2] (bpy-Re), −1.57 (bpy-Ru)	173
$[(dcbpyH_2)_2Ru\{(\mathbf{NC})Re(bpy)(CO)_3\}_2]^{2+}$	DMF	SCE	+0.75 i (Ru) ≥+1.4 i (Re)	−1.30 [2] (bpy-Re), −1.70 (dcbpy)	173
$RuPt_2$					
$[(bpy)_2Ru\{(\mathbf{CN})Pt(dien)\}_2]^{4+}$	DMF	SCE	+0.86	−1.50	172
Ru_3Re					
$[(NC)(bpy)_2Ru\{(\mathbf{NC})Ru(bpy)_2\}_2\text{-}(\mathbf{NC})Re(phen)(CO)_3]^{3+}$	AN	SCE	+0.75, +1.10, +1.63 i, +1.77 i		135
Zn_2Ru_3					
$[\{Zn(\mathbf{NC})Ru(bpy)_2(\mathbf{CN})\}_2Ru(bpy)_2]^{6+}$	AN	SCE	+0.75, +1.47, +1.64		132

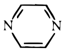
Table 9.2 (Continued)

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_4$Re					
[(NC)(bpy)$_2$Ru{(**NC**)Ru(bpy)$_2$}$_3$-(**NC**)Re(phen)(CO)$_3$]$^{3+}$	AN	SCE	+0.73, +1.08, +1.34, +1.60 i, +1.77 i		135

† Absorption data in other solvent mixtures are given in the original papers. ‡ Biphasic decay. § Weak emission, probably due to Ru(bpy)$_2$(CN)$_2$. $^{\square}$ **NC** isomer. ¶ Or its deprotonated forms. $^{\nabla}$ Ru$_c$ and Ru$_t$ stand for central and terminal Ru, respectively.

Table 9.3

pyz



A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Cr$_2$									
[(CO)$_5$Cr(**pyz**)Cr(CO)$_5$]	C_6H_6†	516		702 c		0.6×10^{-4} d‡			179,180
CrMo									
[(CO)$_5$Cr(**pyz**)Mo(CO)$_5$]	C_6H_6†	504		687 c		1.4×10^{-4} d‡			179,180
CrW									
[(CO)$_5$Cr(**pyz**)W(CO)$_5$]	C_6H_6†	514		707 c		1.5×10^{-4} d‡			179,180
Mo$_2$									
[(CO)$_5$Mo(**pyz**)Mo(CO)$_5$]	C_6H_6†	484		675 c		3.9×10^{-4} d‡			179,180
MoW									
[(CO)$_5$Mo(**pyz**)W(CO)$_5$]	C_6H_6†	498		712 c		4.6×10^{-4} d‡			179,180
W$_2$									
[(CO)$_5$W(**pyz**)W(CO)$_5$]	$CHCl_3$	539	13600	741 c	153 d	2.9×10^{-4} d			181
	CH_2Cl_2	521	12800	730 c	103 d	1.6×10^{-4} d			181,182
	C_6H_6†	510		722 c		5.0×10^{-4} d‡			179,180
	C_6H_6	510	12000	721 c	186 d	4.4×10^{-4} d			183,184
	C_6H_6	510	12000	721 c	206 d	5.0×10^{-4} d			181
	C_7H_{14}/C_6H_6	534	13500	759 c	284 d	7.0×10^{-4} d			181
	2-Me-THF§	455					562 c	1.7, 11.3	184
							700 c	8.7	
WRe									
[(CO)$_5$W(**pyz**)Re(CO)$_4$Cl]	CH_2Cl_2	486 sh		688 c	196 d	1.59×10^{-4} d			182
Re$_2$									
[Cl(CO)$_4$Re(**pyz**)Re(CO)$_4$Cl]	CH_2Cl_2	466 sh		688 c	137 d	3.03×10^{-4} d			182
[(CO)$_3$(bpy)Re(**pyz**)Re(bpy)(CO)$_3$]$^{2+}$	AN	380		703	<20	$<5 \times 10^{-4}$			185
[(CO)$_3$(Me$_4$phen)Re(**pyz**)-Re(Me$_4$phen)(CO)$_3$]$^{2+}$	AN	380		694	60	$<5 \times 10^{-4}$			185

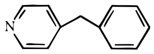
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
W$_2$					
[(CO)$_5$W(**pyz**)W(CO)$_5$]	CH_2Cl_2	SCE	+1.26 i (W)	−1.21 [1] (BL), <−2.3 [1] (BL)	181−183
	CH_2Cl_2/DMF	SCE	+1.14 i (W), +1.26 i (W)	−0.94 [1] (BL), −1.45 [1] (BL)	181
	DMF	SCE	+1.00 i (W), +1.16 i (W)	−0.84 [1] (BL), −1.34 [1] (BL), −2.09 i (BL)	181
WRe					
[(CO)$_5$W(**pyz**)Re(CO)$_4$Cl]	CH_2Cl_2	SCE	+1.16 i (W), +1.82 (Re)	−0.90 [1] (BL), −1.24 [1] (BL)	182
Re$_2$					
[Cl(CO)$_4$Re(**pyz**)Re(CO)$_4$Cl]	CH_2Cl_2	SCE	+1.73 (Re)	−0.47 i [1] (BL), −0.89 [1] (BL), −1.23 [1] (BL)	182
[(CO)$_3$(bpy)Re(**pyz**)Re(bpy)(CO)$_3$]$^{2+}$	DMSO	SCE	+1.78 i (Re)	−0.66 [1] (BL), −1.12 [2] (bpy), −1.28 [2] (Re)	185
[(CO)$_3$(Me$_4$phen)Re(**pyz**)-Re(Me$_4$phen)(CO)$_3$]$^{2+}$	DMSO	SCE	+1.69 i (Re)	−0.69 [1] (BL), −1.35 i (Re)	185

† Absorption data in other solvents are given in the original papers. ‡ Excitation wavelength dependent. § At 80 K.

Table 9.4

4-benzyl-py



A. Photophysical Data

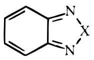
compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
FeRe									
[(Cp)Fe(**4-benzyl-py**)Re(bpy)(CO)$_3$]$^{2+}$	AN			586 c	2.9 d				186

Table 9.4 (Continued)

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
RuRe									
$[(Cp)Ru($**4-benzyl-py**$)Re(bpy)(CO)_3]^{2+}$	AN	≈326 f	≈18600 f	586 c	225 d	0.051 d			186
$[(Cp)Ru($**4-benzyl-py**$)Re(5,5'\text{-dmbpy})(CO)_3]^{2+}$	AN			561 c	960 d	0.16 d			186
$[(Cp)Ru($**4-benzyl-py**$)Re(Me_4bpy)(CO)_3]^{2+}$	AN			540 c	907 d	0.15 d			186
$[(Cp)Ru($**4-benzyl-py**$)Re(deabpy)(CO)_3]^{2+}$	AN			523 c	890 d	0.041 d			186

Table 9.5

btd, X = S
bsd, X = Se



A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
W_2									
$[(CO)_5W($**btd**$)W(CO)_5]$	C_6H_6†	648		>750	<5				187
$[(CO)_5W($**bsd**$)W(CO)_5]$	C_6H_6†	670		>750	<5				187

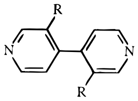
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [*n*] (site)	E_{red}, V [*n*] (site)	ref(s)
W_2					
$[(CO)_5W($**btd**$)W(CO)_5]$	AN	SCE		−0.53 [1] (BL)	187
$[(CO)_5W($**bsd**$)W(CO)_5]$	AN	SCE		−0.47 [1] (BL)	187

† Absorption data in other solvents are given in the original paper.

Table 9.6

4,4'-bpy, R = H
Me_2-4,4'-bpy, R = CH_3



A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
CrMo									
$[(CO)_5Cr($**4,4′-bpy**$)Mo(CO)_5]$	C_6H_6	432 sh		602 c	767 d	4.0×10^{-5} d			183
CrW									
$[(CO)_5Cr($**4,4′-bpy**$)W(CO)_5]$	C_6H_6	436 sh		642 c	368 d	6.2×10^{-5} d			183
Mo_2									
$[(CO)_5Mo($**4,4′-bpy**$)Mo(CO)_5]$	C_6H_6	430 sh		606 c	547 d	9.9×10^{-5} d			183
MoW									
$[(CO)_5Mo($**4,4′-bpy**$)W(CO)_5]$	C_6H_6	432 sh		651 c	428 d	1.23×10^{-4} d			183
Ru_2									
$[Cl(dpte)_2Ru($**4,4′-bpy**$)\text{-}Ru(bpy)_2Cl]^{2+}$	AN/CH_2Cl_2	≈440 f†	≈15000 f†	706	51 d‡	$<2 \times 10^{-4}$ d			188
$[Cl(dpte)_2Ru($**4,4′-bpy**$)\text{-}Ru^{III}(bpy)_2Cl]^{3+}$	AN/CH_2Cl_2	≈833 f†	≈100 f†	708	54 d‡	$<2 \times 10^{-4}$ d			188
RuOs									
$[(H_2O)(bpy)_2Ru($**4,4′-bpy**$)\text{-}Os(tpy)(bpy)]^{4+}$	H_2O (pH = 5)	≈460 f	≈25000 f	798 c	31 d	8.5×10^{-3} d			189
$[(HO)(bpy)_2Ru($**4,4′-bpy**$)\text{-}Os(tpy)(bpy)]^{3+}$	H_2O (pH = 11.9)			798 c	30 d	1.1×10^{-3} d			189
$[(H_2O)(bpy)_2Ru($**4,4′-bpy**$)\text{-}Os^{III}(tpy)(bpy)]^{5+}$	H_2O (pH = 1)			795 c	34 d	2.2×10^{-3} d			189
$[(HO)(bpy)_2Ru^{III}($**4,4′-bpy**$)\text{-}Os(tpy)(bpy)]^{4+}$	H_2O (pH = 10.9)			795 c	24 d	2.5×10^{-3} d			189
Pd_2									
$[(CNN)Pd($**4,4′-bpy**$)Pd(CNN)]^{2+}$	AN	446	7200	606	<1.0	7×10^{-4} a§			190
	BuCN						≈545	<0.001	190
W_2									
$[(CO)_5W($**4,4′-bpy**$)W(CO)_5]$	$CHCl_3$	432	9400	660 c	220 d	0.95×10^{-4} d			181
	CH_2Cl_2	431	11400	678 c	121 d	0.38×10^{-4} d			181
	C_6H_6	438	10800	654 c	394 d	1.59×10^{-4} d			181,183, 184
	C_7H_{14}/C_6H_6	446	11100	649 c	429 d	1.60×10^{-4} d			181
	2Me-THF						488	1.8, 10.2	184
							596	5.2	

Table 9.6 (Continued)

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Re$_2$									
[(CO)$_3$(bpy)Re(**4,4′-bpy**)-Re(bpy)(CO)$_3$]$^{2+}$	AN	350		578 c	365 d				185
	AN	340	17600	585 c	365 d	0.0332 d			191,192
	DCE			570 c	870 d	0.170 d			191,192
	Et/Met				321 d			4.65	191,192
	PC			590 c	325 d	0.0267 d			191,192
[(CO)$_3$(bpy)Re(**Me$_2$-4,4′-bpy**)-Re(4DCE-bpy)(CO)$_3$]$^{2+}$	AN	380	7300	620 c§	126, 300 d	0.0185 d			191
	DCE			612 c§		0.16 d			191
	PC			630 c§		0.0141 d			191
[(CO)$_3$(dmbpy)Re(**4,4′-bpy**)-Re(dmbpy)(CO)$_3$]$^{2+}$	AN	340	18800	585 c	432 d	0.0094 d			191
	DCE			565 c	1980 d	0.090 d			191
	Et/Met				595 d				191
	PC			585 c	335 d	0.0068 d			191
[(CO)$_3$(dabpy)Re(**4,4′-bpy**)-Re(dabpy)(CO)$_3$]$^{2+}$	AN	345	17500	660 c	64 d	0.007 d			191
	DCE			510 c	690 d	0.0015 d			191
	Et/Met				89 d				191
	PC			650 c	49 d	0.006 d			191
[(CO)$_3$(4DCE-bpy)Re(**4,4′-bpy**)-Re(4DCE-bpy)(CO)$_3$]$^{2+}$	AN	350	16500	650 c	118 d	0.0119 d			191
	DCE			625 c	314 d	0.085 d			191
	Et/Met				78 d				191
	PC			650 c	100 d	0.0102 d			191
[(CO)$_3$(bpy)Re(**4,4′-bpy**)-Re(dmbpy)(CO)$_3$]$^{2+}$	AN	340	17900	585 c	388 d	0.0224 d			191
	DCE			570 c	1060 d	0.145 d			191
	PC			585 c	328 d	0.0199 d			191
[(CO)$_3$(bpy)Re(**4,4′-bpy**)-Re(dabpy)(CO)$_3$]$^{2+}$	AN	340	19700	605 c	42, 360 d	0.0042 d			191
	DCE			590 c		0.020 d			191
	PC			598 c		0.0019 d			191
[(CO)$_3$(bpy)Re(**4,4′-bpy**)-Re(4DCE-bpy)(CO)$_3$]$^{2+}$	AN	380	9100	650 c	116 d	0.0119 d			191
	DCE			625 c	340 d	0.095 d			191
	Et/Met				74 d				191
	PC			650 c	100 d	0.0102 d			191
[(CO)$_3$(dabpy)Re(**4,4′-bpy**)-Re(4DCE-bpy)(CO)$_3$]$^{2+}$	AN	350	16400	650 c	99 d	0.0102 d			191
	DCE			620 c	261 d	0.060 d			191
	Et/Met				60 d				191
	PC			650 c	80 d	0.0050 d			191
[(CO)$_3$(biq)Re(**4,4′-bpy**)-Re(biq)(CO)$_3$]$^{2+}$	AN	382		687 c	<20 d	4.0×10^{-3} d			185
[(CO)$_3$(Me$_4$phen)Re(**4,4′-bpy**)-Re(Me$_4$phen)(CO)$_3$]$^{2+}$	AN	340		630 c	595 d				185
Os$_2$									
[(CO)(bpy)$_2$Os(**4,4′-bpy**)-Os(phen)(dppe)Cl]$^{3+}$	CH_2Cl_2	510	9000						193
	Et/Met						550	<0.01	193
							625	3.93	
[(CO)(bpy)$_2$Os(**4,4′-bpy**)-Os^{III}(phen)(dppe)Cl]$^{4+}$	AN	≈1700	<200	600 c	1970 d				193

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
CrMo					
[(CO)$_5$Cr(**4,4′-bpy**)Mo(CO)$_5$]	CH_2Cl_2	SCE	+1.06 i	−1.43 [1] (BL), −1.78 [1] (BL)	183
CrW					
[(CO)$_5$Cr(**4,4′-bpy**)W(CO)$_5$]	CH_2Cl_2	SCE	+1.06 i	−1.37 [1] (BL), −1.70 [1] (BL)	183
Mo$_2$					
[(CO)$_5$Mo(**4,4′-bpy**)Mo(CO)$_5$]	CH_2Cl_2	SCE	+1.16 i	−1.38 [1] (BL), −1.67 [1] (BL)	183
MoW					
[(CO)$_5$Mo(**4,4′-bpy**)W(CO)$_5$]	CH_2Cl_2	SCE	+1.07 i	−1.32 [1] (BL), −1.68 [1] (BL)	183
Ru$_2$					
[Cl(dpte)$_2$Ru(**4,4′-bpy**)Ru(bpy)$_2$Cl]$^{2+}$	AN	SCE	+0.81, +1.20		188
[Cl(dpte)$_2$Ru(**4,4′-bpy**)Ru^{III}(bpy)$_2$Cl]$^{3+}$	AN	SCE	+1.20	+0.82	188
W$_2$					
[(CO)$_5$W(**4,4′-bpy**)W(CO)$_5$]	CH_2Cl_2	SCE	+1.09 i (W)	−1.30 [1] (BL), −1.80 [1] (BL)	181,183
	CH_2Cl_2/DMF	SCE	+1.12 i (W), +1.32 i (W)	−1.20 [1] (BL), −1.47 [1] (BL), −1.90 i (BL)	181
	DMF	SCE	+1.07 i (W)	−1.13 [1] (BL), −1.42 [1] (BL), −1.85 [1] (BL)	181
Re$_2$					
[(CO)$_3$(bpy)Re(**4,4′-bpy**)-Re(bpy)(CO)$_3$]$^{2+}$	AN	SSCE	+1.90 [2]	−1.06 [1] (BL), −1.20 [2] (bpy)	191
	DMSO	SCE	+1.78 i (Re)	−0.96 [1] (BL), −1.10 [2] (bpy), −1.26 [2] (Re)	185
[(CO)$_3$(bpy)Re(**Me$_2$-4,4′-bpy**)-Re(4DCE-bpy)(CO)$_3$]$^{2+}$	AN	SSCE	+1.90	−0.82 (4DCE-bpy), −1.17 (bpy)	191
[(CO)$_3$(dmbpy)Re(**4,4′-bpy**)-Re(dmbpy)(CO)$_3$]$^{2+}$	AN	SSCE	+1.85 [2]	−1.04 [1] (BL), −1.3 i (dmbpy)	191
[(CO)$_3$(dabpy)Re(**4,4′-bpy**)-Re(dabpy)(CO)$_3$]$^{2+}$	AN	SSCE	+1.62 [2]	−1.09 [1] (BL), −1.65 i (dabpy)	191
[(CO)$_3$(4DCE-bpy)Re(**4,4′-bpy**)-Re(4DCE-bpy)(CO)$_3$]$^{2+}$	AN	SSCE	≈+2.0	−0.82 (4DCE-bpy), −1.18 (4DCE-bpy), −1.25 i (BL)	191
[(CO)$_3$(bpy)Re(**4,4′-bpy**)-Re(dmbpy)(CO)$_3$]$^{2+}$	AN	SSCE	+1.92 [2]	−1.05 (BL), −1.2 (bpy), −1.34 i (dmbpy)	191

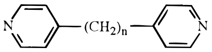
Table 9.6 (Continued)

compound	solvent	RE	E_{ox}, V [*n*] (site)	E_{red}, V [*n*] (site)	ref(s)
Re$_2$					
[(CO)$_3$(bpy)Re(**4,4′-bpy**)-Re(dabpy)(CO)$_3$]$^{2+}$	AN	SSCE	+1.64, +1.9	−1.06 (BL), −1.21 (bpy), −1.62 i (dabpy)	191
[(CO)$_3$(bpy)Re(**4,4′-bpy**)-Re(4DCE-bpy)(CO)$_3$]$^{2+}$	AN	SSCE	+1.90, ≈+2.0	−0.80 (4DCE-bpy), −1.20 [2] (BL and bpy)	191
[(CO)$_3$(dabpy)Re(**4,4′-bpy**)-Re(4DCE-bpy)(CO)$_3$]$^{2+}$	AN	SSCE	+1.64, ≈+2.0	−0.82 (4DCE-bpy), −1.15 (BL), −1.63 i (dabpy)	191
[(CO)$_3$(biq)Re(**4,4′-bpy**)Re(biq)(CO)$_3$]$^{2+}$	DMSO	SCE	+1.84 i (Re)	−0.59 [2] (biq), −1.16 [2] (biq)	185
[(CO)$_3$(Me$_4$phen)Re(**4,4′-bpy**)-Re(Me$_4$phen)(CO)$_3$]$^{2+}$	DMSO	SCE	+1.68 i (Re)	−0.99 [1] (BL), −1.36 i (Re)	185
Os$_2$					
[(CO)(bpy)$_2$Os(**4,4′-bpy**)-Os(phen)(dppe)Cl]$^{3+}$	AN	SCE	+0.95 [1] (Os-phen), +1.67 [1] (Os-bpy)		194
	AN	SSCE	+1.03 [1] (Os-phen), +1.75 [1] (Os-bpy)		193
	DMF	SSCE		−1.02 [1] (bpy), −1.16 [1] (bpy), −1.29 [1] (phen), −1.45 i (BL)	193

† Numerical values are reported in a supplementary table in the original paper. ‡ From transient excited state absorption, 280 K. § Excitation wavelength dependent.

Table 9.7

py-S4$_n$-py



A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[(NH$_3$)$_5$Ru(**py-S4$_2$-py**)Ru(bpy)$_2$Cl]$^{3+}$	AN/CH$_2$Cl$_2$	†	†	711	74 d‡	<2 × 10^{-4} d			188
[(NH$_3$)$_5$Ru^{III}(**py-S4$_2$-py**)Ru(bpy)$_2$Cl]$^{4+}$	AN/CH$_2$Cl$_2$	†	†	713		<5 × 10^{-4} d			188
[Cl(dpte)$_2$Ru(**py-S4$_2$-py**)Ru(bpy)$_2$Cl]$^{2+}$	AN/CH$_2$Cl$_2$	†	†	706	64 d‡	<5 × 10^{-4} d			188
[Cl(dpte)$_2$Ru(**py-S4$_2$-py**)Ru^{III}(bpy)$_2$Cl]$^{3+}$	AN/CH$_2$Cl$_2$	†	†	704		<5 × 10^{-4} d			188
RuRe									
[(NH$_3$)$_5$Ru(**py-S4$_2$-py**)Re(bpy)(CO)$_3$]$^{3+}$	AN	410	4830	564	0.23 d				195
[(NH$_3$)$_5$Ru(**py-S4$_2$-py**)-Re(Me$_4$bpy)(CO)$_3$]$^{3+}$	AN	410	5200	521	0.28 d				195
[(NH$_3$)$_5$Ru(**py-S4$_2$-py**)-Re(DCO-bpy)(CO)$_3$]$^{3+}$	AN	410	4500	629	0.15 d				195
[(NH$_3$)$_5$Ru(**py-S4$_3$-py**)-Re(bpy)(CO)$_3$]$^{3+}$	AN	410	4900	567	0.20 d				195
[(NH$_3$)$_5$Ru(**py-S4$_3$-py**)-Re(Me$_4$bpy)(CO)$_3$]$^{3+}$	AN	410	5200	523	0.25 d				195
[(NH$_3$)$_5$Ru(**py-S4$_3$-py**)-Re(DCO-bpy)(CO)$_3$]$^{3+}$	AN	410	4620	629	0.14 d				195
W$_2$									
[(CO)$_5$W(**py-S4$_2$-py**)W(CO)$_5$]	CH$_2$Cl$_2$§	379	15000						181
	2Me-THF						522 c	1.8	184
Re$_2$									
[(CO)$_3$(bpy)Re(**py-S4$_2$-py**)-Re(bpy)(CO)$_3$]$^{2+}$	AN	347		580	210	0.13			185
	AN	352	6700	590 c	200 d	0.0325 d			191,192
	DCE			575 c	510 d	0.135 d			191,192
	Et/Met				180 d			4.62	191,192
	PC			596 c	175 d	0.0264 d			191,192
[(CO)$_3$(biq)Re(**py-S4$_2$-py**)-Re(biq)(CO)$_3$]$^{2+}$	AN	380		687	<20	2.8 × 10^{-3}			185
[(CO)$_3$(Me$_4$phen)Re(**py-S4$_2$-py**)-Re(Me$_4$phen)(CO)$_3$]$^{2+}$	AN	340		529	10550	0.54			185
[(CO)$_3$(bpy)Re(**py-S4$_3$-py**)-Re(bpy)(CO)$_3$]$^{2+}$	AN	349		580	170				185
[(CO)$_3$(biq)Re(**py-S4$_3$-py**)-Re(biq)(CO)$_3$]$^{2+}$	AN	380		687	<20				185
[(CO)$_3$(Me$_4$phen)Re(**py-S4$_3$-py**)-Re(Me$_4$phen)(CO)$_3$]$^{2+}$	AN	340		528	10500				185
Os$_2$									
[(CO)(bpy)$_2$Os(**py-S4$_2$-py**)-Os(phen)(dppe)Cl]$^{3+}$	CH$_2$Cl$_2$	520	1500	688 c					193
	Et/Met	515			<10		550	0.045	193,194
					160		640	3.74	
[(CO)(bpy)$_2$Os(**py-S4$_2$-py**)-Os^{III}(phen)(dppe)Cl]$^{4+}$	AN			607 c					193
	CH$_2$Cl$_2$	≈1700	<200						193
	Et/Met				1620				193

Table 9.7 (Continued)

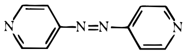
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[(NH$_3$)$_5$Ru(**py-S4$_2$-py**)Ru(bpy)$_2$Cl]$^{3+}$	AN	SCE	+0.38, +0.79		188
[(NH$_3$)$_5$Ru^{III}(**py-S4$_2$-py**)Ru(bpy)$_2$Cl]$^{4+}$	AN	SCE	+0.79	+0.38	188
[Cl(dpte)$_2$Ru(**py-S4$_2$-py**)Ru(bpy)$_2$Cl]$^{2+}$	AN	SCE	+0.78, +1.18		188
[Cl(dpte)$_2$Ru(**py-S4$_2$-py**)Ru^{III}(bpy)$_2$Cl]$^{3+}$	AN	SCE	+1.18	+0.78	188
RuRe					
[(NH$_3$)$_5$Ru(**py-S4$_2$-py**)Re(bpy)(CO)$_3$]$^{3+}$	AN	SSCE	+0.30 [1] (Ru), +1.76 i [1] (Re)	−1.09 [1] (bpy), −1.30 [1] (Re)	195
[(NH$_3$)$_5$Ru(**py-S4$_2$-py**)Re(Me$_4$bpy)(CO)$_3$]$^{3+}$	AN	SSCE	+0.30 [1] (Ru), +1.66 i [1] (Re)	−1.40 [1] (Re)	195
[(NH$_3$)$_5$Ru(**py-S4$_2$-py**)Re(DCO-bpy)(CO)$_3$]$^{3+}$	AN	SSCE	+0.30 [1] (Ru), +1.88 i [1] (Re)	−0.83 [1] (bpy), −1.24 [1] (Re)	195
[(NH$_3$)$_5$Ru(**py-S4$_3$-py**)Re(bpy)(CO)$_3$]$^{3+}$	AN	SSCE	+0.30 [1] (Ru), +1.75 i [1] (Re)	−1.09 [1] (bpy), −1.30 [1] (Re)	195
[(NH$_3$)$_5$Ru(**py-S4$_3$-py**)Re(Me$_4$bpy)(CO)$_3$]$^{3+}$	AN	SSCE	+0.30 [1] (Ru), +1.67 i [1] (Re)	−1.40 [1] (Re)	195
[(NH$_3$)$_5$Ru(**py-S4$_3$-py**)Re(DCO-bpy)(CO)$_3$]$^{3+}$	AN	SSCE	+0.30 [1] (Ru), +1.88 i [1] (Re)	−0.83 [1] (bpy), −1.24 [1] (Re)	195
W$_2$					
[(CO)$_5$W(**py-S4$_2$-py**)W(CO)$_5$]	CH$_2$Cl$_2$	SCE	+1.16 i (W)	<-2.30	181,183
	CH$_2$Cl$_2$/DMF	SCE	+1.11 i (W), + 1.34 i (W)	<-2.30	181
	DMF	SCE	+1.10 i (W)	−1.84 [1] (BL), −2.17 i (BL)	181
Re$_2$					
[(CO)$_3$(bpy)Re(**py-S4$_2$-py**)Re(bpy)(CO)$_3$]$^{2+}$	AN	SSCE	+1.85 [2]	−1.17 [2] (bpy)	191
	DMSO	SCE	+1.73 i (Re)	−1.08 [2] (bpy), −1.30 [2] (Re)	185
[(CO)$_3$(biq)Re(**py-S4$_2$-py**)Re(biq)(CO)$_3$]$^{2+}$	DMSO	SCE	+1.82 i (Re)	−0.59 [2] (biq), −1.16 [2] (biq)	185
[(CO)$_3$(Me$_4$phen)Re(**py-S4$_2$-py**)Re(Me$_4$phen)(CO)$_3$]$^{2+}$	DMSO	SCE	+1.66 i (Re)	−1.36 i (Re)	185
[(CO)$_3$(bpy)Re(**py-S4$_3$-py**)Re(bpy)(CO)$_3$]$^{2+}$	DMSO	SCE	+1.73 i (Re)	−1.08 [2] (bpy), −1.30 [2] (Re)	185
[(CO)$_3$(biq)Re(**py-S4$_3$-py**)Re(biq)(CO)$_3$]$^{2+}$	DMSO	SCE	+1.83 i (Re)	−0.59 [2] (biq), −1.16 [2] (biq)	185
[(CO)$_3$(Me$_4$phen)Re(**py-S4$_3$-py**)Re(Me$_4$phen)(CO)$_3$]$^{2+}$	DMSO	SCE	+1.66 i (Re)	−1.36 i (Re)	185
Os$_2$					
[(CO)(bpy)$_2$Os(**py-S4$_2$-py**)Os(phen)(dppe)Cl]$^{3+}$	AN	SCE	+0.95 [1] (Os-phen), +1.67 [1] (Os-bpy)		194
	AN	SSCE	+0.93, +1.64		193
	DMF	SSCE		−1.02 [1] (bpy), −1.19 [1] (bpy), −1.37 i (phen)	193

† Numerical values are reported in a supplementary table in the original paper. ‡ From transient excited state absorption, 280 K. § Data in other solvents are given in the original papers.

Table 9.8

py-NN-py

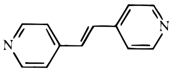


A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Re$_2$									
[(CO)$_3$(bpy)Re(**py-NN-py**)Re(bpy)(CO)$_3$]$^{2+}$	CH$_2$Cl$_2$	366	4085	535	1040				196

Table 9.9

py-E4$_A$-py



A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[Cl(dpte)$_2$Ru(**py-E4$_A$-py**)Ru(bpy)$_2$Cl]$^{2+}$	AN/CH$_2$Cl$_2$	†	†	700	60 d‡	$<1 \times 10^{-4}$ d			188
[Cl(dpte)$_2$Ru(**py-E4$_A$-py**)Ru^{III}(bpy)$_2$Cl]$^{3+}$	AN/CH$_2$Cl$_2$	†	†	704	50 d‡	$<1 \times 10^{-4}$ d			188
W$_2$									
[(CO)$_5$W(**py-E4$_A$-py**)W(CO)$_5$]	C$_6$H$_6$	450	15500	560 c	123 d	1.3×10^{-5} d			183,184
	2Me-THF						464	1.6, 9.3	184
							521	8.9	

Table 9.9 (Continued)

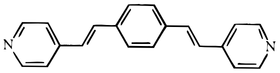
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[Cl(dpte)$_2$Ru(**py-E4$_A$-py**)Ru(bpy)$_2$Cl]$^{2+}$	AN	SCE	+0.79, +1.21		188
[Cl(dpte)$_2$Ru(**py-E4$_A$-py**)Ru^{III}(bpy)$_2$Cl]$^{3+}$	AN	SCE	+1.21	+0.79	188
W$_2$					
[(CO)$_5$W(**py-E4$_A$-py**)W(CO)$_5$]	CH$_2$Cl$_2$	SCE	+1.09 i	−1.20 [1] (BL), −1.46 [1] (BL), −1.80 [1] (BL)	183

[†] Numerical values are reported in a supplementary table in the original paper. [‡] From transient excited state absorption, 280 K.

Table 9.10

py-E4$_B$-py



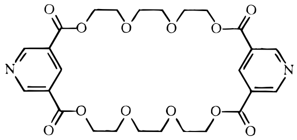
A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Re$_2$									
[(CO)$_3$(bpy)Re(**py-E4$_B$-py**)Re(bpy)(CO)$_3$]$^{2+}$	AN	347	6710	586	200		508[†]		196
[(CO)$_3$(phen)Re(**py-E4$_B$-py**)Re(phen)(CO)$_3$]$^{2+}$	AN			570	1500		540[†]		196
	CH$_2$Cl$_2$	383 sh	5825	550	2500				196

[†] Solid sample.

Table 9.11

py-crown-py

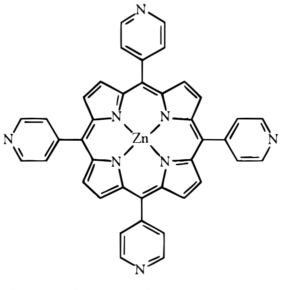


A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Re$_2$									
[(CO)$_3$(bpy)Re(**py-crown-py**)Re(bpy)(CO)$_3$]$^{2+}$	nitromethane			556 c	520 d				197

Table 9.12

ZnTPyP



A. Photophysical Data

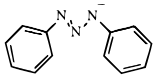
compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_4$									
[{Cl(bpy)$_2$Ru}$_4$**ZnTpyP**]$^{4+}$	DMF	606	≈32000 f						198
	EtOH			606 d	900 d		597		198
				655 d			652		
							770		

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_4$					
[{Cl(bpy)$_2$Ru}$_4$**ZnTPyP**]$^{4+}$	DMF	NHE	+0.92 [4] (Ru), +1.50 i (porphyrin)	−0.93 (Zn), −1.14 (porphyrin), −1.35 (bpy + porphyrin), −1.67 i (bpy)	198

Table 9.13

DPT⁻

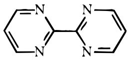


A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Cu_2									
$[Cu_2($**DPT**$)_2]$	2Me-THF	392	7720				≈570 f	2.23×10^{-3}	199
Ag_2									
$[Ag_2($**DPT**$)_2]$	2Me-THF	374	12600				610	2.73×10^{-3}	199

Table 9.14

bpym



A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru_2									
$[(bpy)_2Ru($**bpym**$)Ru(bpy)_2]^{4+}$	AN	594	6900	790 u	<20 d	$\leq 10^{-4}$	702 c	0.36	200
	AN	594	8130						201
	CH_2Cl_2	588	7200	770 u	<20 d	$\leq 10^{-4}$			200
	H_2O	608	6900	824 c	<15 d	$\leq 10^{-4}$			200
	H_2O	606	7600				769[§]		202
RuRh									
$[(bpy)_2Ru($**bpym**$)RhH_2(PPh_3)_2]^{3+}$	acetone	551	4900	767	41	1.9×10^{-3}			203
RuRe									
$[(bpy)_2Ru($**bpym**$)Re(CO)_3Cl]^{2+}$	AN	558	4500						204
	DMSO	556	2167				774		205
	Et/Met						630		204
$RuRe_2$									
$[(bpy)Ru\{($**bpym**$)Re(CO)_3Cl\}_2]^{2+}$	AN	531	6800	630	942	2.7×10^{-5}			204
	Et/Met						616		204
$RuRe_3$									
$[Ru\{($**bpym**$)Re(CO)_3Cl\}_3]^{2+}$	AN	501	11000	640	847	2.6×10^{-5}			204
	Et/Met						586		204

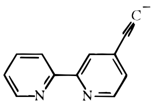
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru_2					
$[(bpy)_2Ru($**bpym**$)Ru(bpy)_2]^{4+}$	AN	SCE	+1.44 [1] (Ru), +1.62 [1] (Ru)		206
	AN	SSCE	+1.53 [1] (Ru), +1.69 [1] (Ru)	−0.41 [1] (BL), −1.08 [1] (BL)	115
RuRh					
$[(bpy)_2Ru($**bpym**$)RhH_2(PPh_3)_2]^{3+}$	AN	SCE	+1.65 i (overlapping Ru + Rh)	−0.47 [1] (BL), −1.26, −1.52, −1.77	203
RuRe					
$[(bpy)_2Ru($**bpym**$)Re(CO)_3Cl]^{2+}$	AN	SSCE	+1.58 [1] (Ru), +1.76 i (Re)	−0.41 [1] (BL), −1.10 [1] (BL), −1.56 (bpy), −1.75 (Re)	204
$RuRe_2$					
$[(bpy)Ru\{($**bpym**$)Re(CO)_3Cl\}_2]^{2+}$	AN	SSCE	+1.61 (Ru + Re)	−0.33 [1] (BL), −0.48 [1] (BL), −1.09 [1] (BL), −1.23 [1] (BL), −1.80 i (Re)	204
$RuRe_3$					
$[Ru\{($**bpym**$)Re(CO)_3Cl\}_3]^{2+}$	AN	SSCE	+1.59 (Ru + Re)	−0.21 [1] (BL), −0.35 [1] (BL), −0.53 [1] (BL), −1.24 (BL), −1.29 (BL), −1.35 (BL)	204

[§] Solid, 15 K.

Table 9.15

bpy-E4$_C$



A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
RuPt									
$[(bpy)_2Ru($**bpy-E4$_C$**$)Pt(E4_C\text{-}bpy)(PBu^n{}_3)_2]^{2+}$	AN	458	15200	620					207
RePt									
$[Cl(CO)_3Re($**bpy-E4$_C$**$)Pt(E4_C\text{-}bpy)(PBu^n{}_3)_2]$	AN	364	19700	620					207

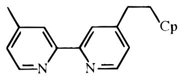
Table 9.15 (Continued)

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
OsPt									
[(bpy)$_2$Os(**bpy-E4$_C$**)Pt(E4$_C$-bpy)(PBu$^n_3$)$_2$]$^{2+}$	AN	627	1800	733					207
Ru$_2$Pt									
[{(bpy)$_2$Ru(**bpy-E4$_C$**)}$_2$Pt(PBu$^n_3$)$_2$]$^{4+}$ §	AN	456	31200	618					208
Re$_2$Pt									
[{Cl(CO)$_3$Re(**bpy-E4$_C$**)}$_2$Pt(PBu$^n_3$)$_2$]	AN	393	36200	603					208
Os$_2$Pt									
[{(bpy)$_2$Os(**bpy-E4$_C$**)}$_2$Pt(PBu$^n_3$)$_2$]$^{2+}$	AN	481	15600	733					208
FeRu$_3$Pt$_3$									
[Fe{(**bpy-E4$_C$**)Pt(PBu$^n_3$)$_2$(**E4$_C$-bpy**)Ru(bpy)$_2$}$_3$]$^{8+}$	acetone	530	15200	620					207

§ The *cis*- and *trans*-Pt(II) isomers have been prepared and show identical absorption and emission properties.

Table 9.16

4Mebpy-S4$_2$-Cp

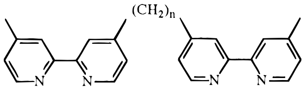


A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
FeRu									
[CpFe(**Cp-S4$_2$-4Mebpy**)Ru(bpy)$_2$]$^{2+}$	AN	≈452 f	≈13500 f		0.110	$<10^{-4}$			209

Table 9.17

4Mebpy-S4$_n$-bpy4Me



A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
FeRu									
[Fe(**4Mebpy-S4$_2$-bpy4Me**)$_3$Ru]$^{4+}$	DCE			≈630	0.41 d				210
[Fe(**4Mebpy-S4$_3$-bpy4Me**)$_3$Ru]$^{4+}$	DCE			≈630	0.35 d				210
[Fe(**4Mebpy-S4$_4$-bpy4Me**)$_3$Ru]$^{4+}$	DCE			≈630	2.7 d				210
[Fe(**4Mebpy-S4$_5$-bpy4Me**)$_3$Ru]$^{4+}$	DCE			≈630	13.3 d				210
CoRu									
[(bpy)$_2$Co-(**4Mebpy-S4$_2$-bpy4Me**)-Ru(bpy)$_2$]$^{5+}$	AN	453	11700	623 c	0.3 a				211
	DMSO/H$_2$O						590 c	0.45	211
Ru$_2$									
[(bpy)$_2$Ru-(**4Mebpy-S4$_2$-bpy4Me**)-Ru(bpy)$_2$]$^{4+}$	AN	454	19400						211
	H$_2$O	455	27100	614 u	630 d				212,213
	PC	457		620 u	1037 d	0.06			214
[(bpy)$_2$Ru-(**4Mebpy-S4$_3$-bpy4Me**)-Ru(bpy)$_2$]$^{4+}$	H$_2$O	455	27800	616 u	520 d				212,213
[(bpy)$_2$Ru-(**4Mebpy-S4$_{10}$-bpy4Me**)-Ru(bpy)$_2$]$^{4+}$	AN	454		617 u	1140 d				215
RuRh									
[(dmphen)$_2$Ru-(**4Mebpy-S4$_2$-bpy4Me**)-Rh(dmbpy)$_2$]$^{5+}$ ‡	AN	≈450	≈20000	610 c	6 (85%), >30 (15%)	≈0.001			216
	Et/Met						575 c	6.8	216
RuRe									
[(bpy)$_2$Ru-(**4Mebpy-S4$_2$-bpy4Me**)-Re(CO)$_3$py]$^{3+}$	AN	454			942 d§	0.072 d§			217
	CH$_2$Cl$_2$	≈455 f	≈13000 f	540		0.011 d			218
				610		0.149 d			
	CH$_2$Cl$_2$	456	14000	610 c	1001 d§	0.164 d§			219
	CH$_2$Cl$_2$	456			1148 d§	0.105 d§			217
	DCE	456			989 d§	0.102 d§			217
	EtOH	453			617 d§	0.035 d§			217
	THF	455			803 d§	0.060 d§			217

Table 9.17 (Continued)

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
RuOs									
[(bpy)$_2$Ru-(**4Mebpy-S4$_2$-bpy4Me**)-Os(bpy)$_2$]$^{4+}$	AN			≈615 u,f ≈730 u,f	1.2 d 55 d				220
	EtOH				1.9 d 52 d				220
	H_2O				0.86 d 23 d				220
	MeOH	≈660 sh f	≈4500 f						220
[(bpy)$_2$Ru-(**4Mebpy-S4$_3$-bpy4Me**)-Os(bpy)$_2$]$^{4+}$	AN			≈615 u,f ≈730 u,f	2.5 d 44 d				220
	EtOH				3.0 d 37 d				220
	H_2O				2.2 d 18 d				220
	MeOH	≈660 sh f	≈4500 f	615 u 730 u					220
[(bpy)$_2$Ru-(**4Mebpy-S4$_5$-bpy4Me**)-Os(bpy)$_2$]$^{4+}$	AN			≈615 u,f ≈730 u,f	7.9 d 48 d				220
	EtOH				8.0 d 42 d				220
	H_2O				5.8 d 19 d				220
	MeOH	≈660 sh f	≈4500 f						220
[(bpy)$_2$Ru-(**4Mebpy-S4$_7$-bpy4Me**)-Os(bpy)$_2$]$^{4+}$	AN			≈615 u,f ≈730 u,f	12.1 d 56 d				220
	EtOH				9.6 d 42 d				220
	H_2O				8.1 d 20 d				220
	MeOH	≈660 sh f	≈4500 f						220
RuPt									
[(bpy)$_2$Ru-(**4Mebpy-S4$_2$-bpy4Me**)-PtCl$_2$]$^{2+}$	PC	457	13000	620 u	1034 d	0.06			214
Re$_2$									
[Cl(CO)$_3$Re-(**4Mebpy-S4$_2$-bpy4Me**)-Re(CO)$_3$Cl]	AN	368	7900	603	30 d	1.56×10^{-3}			221
	Et/Met						450 540		221
FeRu$_3$									
[Fe{(**4Mebpy-S4$_2$-bpy4Me**)-Ru(bpy)$_2$}$_3$]$^{8+\,\dagger}$	MeOH/H_2O			610 u	6 a	0.0052 a		0.045	222
[Fe{(**4Mebpy-S4$_5$-bpy4Me**)-Ru(bpy)$_2$}$_3$]$^{8+\,\dagger}$	MeOH/H_2O			610 u	52 a	0.016 a		0.110	222
[Fe{(**4Mebpy-S4$_{12}$-bpy4Me**)-Ru(bpy)$_2$}$_3$]$^{8+\,\dagger}$	MeOH/H_2O			610 u	92 a	0.015 a		0.085	222

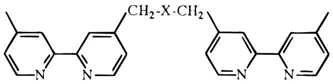
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
CoRu					
[(bpy)$_2$Co(**4Mebpy-S4$_1$-bpy4Me**)Ru(bpy)$_2$]$^{5+}$	AN	SSCE	+1.183 [1] (Ru)	−0.227 [1] (Co$^{3+/2+}$), −0.99 [1] (Co$^{2+/+}$), −1.35, −1.55, −1.81	211
Ru$_2$					
[(bpy)$_2$Ru(**4Mebpy-S4$_2$-bpy4Me**)Ru(bpy)$_2$]$^{4+}$	AN	SCE	+1.21	−1.38, −1.57, −1.81	212,213
	AN	SSCE	+1.184 [2] (Ru)		211
	PC	SSCE	+1.19 (Ru)	−1.38 [1] (bpy)	214
[(bpy)$_2$Ru(**4Mebpy-S4$_3$-bpy4Me**)Ru(bpy)$_2$]$^{4+}$	AN	SCE	+1.21	−1.38, −1.56, −1.82	212,213
RuRh					
[(dmphen)$_2$Ru(**4Mebpy-S4$_2$-bpy4Me**)Ru(dmbpy)$_2$]$^{5+}$	AN	SCE	+1.13 (Ru)	−0.92 (Rh), −1.45, −1.66	216
RuRe					
[(bpy)$_2$Ru(**4Mebpy-S4$_2$-bpy4Me**)Re(CO)$_3$py]$^{3+}$	AN	SSCE	+1.25, +1.78 i	−1.36, −1.60, −1.81	218
	AN	SSCE	+1.25 [1] (Ru), +1.78 i (Re)	−1.36 [2] (BL + bpy), −1.60 [2] (Re + bpy), −1.81 [1] (BL)	219
RuOs					
[(bpy)$_2$Ru(**4Mebpy-S4$_2$-bpy4Me**)Os(bpy)$_2$]$^{4+}$	AN	SCE	+0.78 [1] (Os), +1.22 [1] (Ru)		220
[(bpy)Ru(**4Mebpy-S4$_3$-bpy4Me**)Os(bpy)$_2$]$^{4+}$	AN	SCE	+0.78 [1] (Os), +1.22 [1] (Ru)		220
[(bpy)$_2$Ru(**4Mebpy-S4$_5$-bpy4Me**)Os(bpy)$_2$]$^{4+}$	AN	SCE	+0.78 [1] (Os), +1.22 [1] (Ru)		220
[(bpy)$_2$Ru(**4Mebpy-S4$_7$-bpy4Me**)Os(bpy)$_2$]$^{4+}$	AN	SCE	+0.78 [1] (Os), +1.22 [1] (Ru)		220
RuPt					
[(bpy)$_2$Ru(**4Mebpy-S4$_2$-bpy4Me**)PtCl$_2$]$^{2+}$	PC	SSCE	+1.19 (Ru)	−1.27 [1] (BL), −1.38 [1] (bpy)	214
Re$_2$					
[Cl(CO)$_3$Re(**4Mebpy-S4$_2$-bpy4Me**)Re(CO)$_3$Cl]	DMF	SSCE		−1.29 [1] (BL)	221

‡ The Ru-based emission is strongly quenched at room temperature. § Excitation wavelength dependent. † Prepared in situ.

Table 9.18

4Mebpy-S4$_A$-bpy4Me, X = CH(OH);
4Mebpy-S4$_B$-bpy4Me, X = O;
4Mebpy-S4$_C$-bpy4Me, X = S



A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
FeRu									
[Fe(**4Mebpy-S4$_B$-bpy4Me**)$_3$Ru]$^{4+}$	DCE			≈630	0.34 d				210
[Fe(**4Mebpy-S4$_C$-bpy4Me**)$_3$Ru]$^{4+}$	DCE			≈630	0.37 d				210
Ru$_2$									
[(bpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Ru(bpy)$_2$]$^{4+}$	H$_2$O	455		615 u	481 d				213
RuRh									
[(bpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Rh(bpy)$_2$]$^{5+}$	AN	456							223
	H$_2$O				59.9 d 527 d				223
[(bpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Rh(phen)$_2$]$^{5+}$	AN	≈455 f	≈13000 f						223
	H$_2$O				71.3 d 543 d				223
RuRe									
[(bpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Re(CO)$_3$Cl]$^{2+}$	AN	≈450 f	≈13000 f		6.0 d				224
[(bpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Re(CO)$_3$(AN)]$^{3+}$	AN				0.80 d				224
[(bpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Re(CO)$_3$(4-Mepy)]$^{3+}$	AN			550 u 613 u	1.4 d				224
[(bpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Re(CO)$_3$(1-MeIm)]$^{3+}$	AN				4.0 d				224
RuOs									
[(bpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Os(bpy)$_2$]$^{4+}$	AN				2.5 d 41 d				220
	BuOH			630 u 750 u					225
	EtOH				3.0 d 41 d				220
	H$_2$O				2.2 d 19 d				220
	MeOH	≈650 sh f	≈4600 f	615 u 720 u	2.1 d 18.5 d				226
[(dmbpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Os(bpy)$_2$]$^{4+}$	AN				1.4 d 63 d				220
	EtOH				1.9 d 53 d				220
	H$_2$O				1.1 d 22 d				220
[(BTMFbpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Os(bpy)$_2$]$^{4+}$	BuOH			630 u 750 u					225
	MeOH	≈640 sh f	≈4100 f		2.3 d† 40.5 d†				225

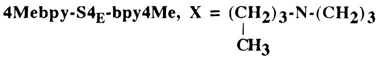
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[(bpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Ru(bpy)$_2$]$^{4+}$	AN	SCE	+1.21	−1.38	213
RuRh					
[(bpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Rh(bpy)$_2$]$^{5+}$	AN	SCE	+1.27 [1] (Ru)	≈−0.7 i (Rh)	223
[(bpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Rh(phen)$_2$]$^{5+}$	AN	SCE	+1.27 [1] (Ru)	≈−0.7 i (Rh)	223
RuRe					
[(bpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Re(CO)$_3$Cl]$^{2+}$	AN	SCE	+1.23 [1] (Ru), +1.36 [1] (Re)	≈−1.3 [1] (BL), ≈−1.5 [1] (bpy)	224
[(bpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Re(CO)$_3$(AN)]$^{3+}$	AN	SCE	+1.24 [1] (Ru), +1.59 [1] (Re)	≈−1.3 [1] (BL), ≈−1.5 [1] (bpy)	224
[(bpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Re(CO)$_3$(4-Mepy)]$^{3+}$	AN	SCE	+1.24 [1] (Ru), +1.72 [1] (Re)	≈−1.3 [1] (BL), ≈−1.5 [1] (bpy)	224
[(bpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Re(CO)$_3$(1-MeIm)]$^{3+}$	AN	SCE	+1.24 [1] (Ru), +1.60 [1] (Re)	≈−1.3 [1] (BL), ≈−1.5 [1] (bpy)	224
RuOs					
[(bpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Os(bpy)$_2$]$^{4+}$	AN	SCE	+0.77 [1] (Os), +1.21 [1] (Ru)		226
[(BTMFbpy)$_2$Ru(**4Mebpy-S4$_A$-bpy4Me**)Os(bpy)$_2$]$^{4+}$	AN	SCE	+0.76 [1] (Os), +1.48 [1] (Ru)	−0.94 [1] (BTFMbpy), −1.14 [1] (BTFMbpy), −1.33 [1] (bpy), −1.51 [1] (bpy)	225

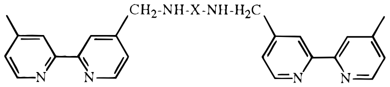
† At 273 K.

Table 9.19

4Mebpy-S4$_D$-bpy4Me, X = $(CH_2)_8$



4Mebpy-S4$_E$-bpy4Me, X = $(CH_2)_3\text{-}\underset{\displaystyle CH_3}{\underset{|}{N}}\text{-}(CH_2)_3$

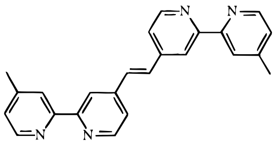


A. Photophysical Data

compound	solvent	Abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru_2									
$[(bpy)_2Ru($**4Mebpy-S4$_D$-bpy4Me**$)Ru(bpy)_2]^{4+}$	AN	455		619 u	1150 d				215
$[(bpy)_2Ru($**4Mebpy-S4$_E$-bpy4Me**$)Ru(bpy)_2]^{4+}$	AN	455		618 u	960 d				215

Table 9.20

4Mebpy-E4$_A$-bpy4Me



A. Photophysical Data

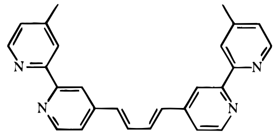
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Re_2									
$[(dmbpy)_2Ru($**4Mebpy-E4$_A$-bpyMe**$)Ru(dmbpy)_2]^{4+}$	AN	500	25810	750 c	1310 d	0.005 d			227
	Et/Met			730 c	1500 d	0.008 d			227
Re_2									
$[(CO)_3(PTZ\text{-}py)Re($**4Mebpy-E4$_A$-bpy4Me**$)\text{-}Re(PTZ\text{-}py)(CO)_3]^{2+}$	AN	384	14000					5.29	114
	Et/Met						600	20.1	114
Os_2									
$[(bpy)_2Os($**4Mebpy-E4$_A$-bpy4Me**$)Os(bpy)_2]^{4+}$	AN	682	8520	>850					227
	Et/Met			>850	37 d		>850		227

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru_2					
$[(dmbpy)_2Ru($**4Mebpy-E4$_A$-bpy4Me**$)Ru(dmbpy)_2]^{4+}$	AN	SSCE	+1.16 [2] (Ru)	−1.07 [1] (BL), −1.33 [1] (BL), −1.65 [2] (dmbpy)	227
Re_2					
$[(CO)_3(PTZ\text{-}py)Re($**4Mebpy-E4$_A$-bpy4Me**$)\text{-}Re(PTZ\text{-}py)(CO)_3]^{2+}$	AN	SSCE	+0.76 (PTZ)	−1.05 (BL)	114
Os_2					
$[(bpy)_2Os($**4Mebpy-E4$_A$-bpy4Me**$)Os(bpy)_2]^{4+}$	AN	SSCE	+0.80 [2] (Os)	−1.07 [1] (BL), −1.22 [1] (BL), −1.60 [2] (bpy)	227

Table 9.21

4Mebpy-bd4-bpy4Me



A. Photophysical Data

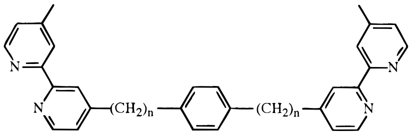
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru_2									
$[(dmbpy)_2Ru($**4Mebpy-bd4-bpy4Me**$)Ru(dmbpy)_2]^{4+}$	AN	496	18200	780 c		<0.001 d			228

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru_2					
$[(dmbpy)_2Ru($**4Mebpy-bd4-bpy4Me**$)Ru(dmbpy)_2]^{4+}$	AN	SSCE	+1.14 [2] (Ru)	−1.05 (BL), −1.16 (BL), −1.57	228

Table 9.22

4Mebpy-P4$_n$-bpy4Me



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
FeRu									
[Fe(**4Mebpy-P4$_1$-bpy4Me**)$_3$Ru]$^{4+}$	DCE			≈630	34.5 d				210
Ru$_2$									
[(dmbpy)$_2$Ru(**4Mebpy-P4$_0$-bpy4Me**)-Ru(dmbpy)$_2$]$^{4+}$	AN	468	31600	641 c	1570 d	0.125 d			228
	Et/Met						613 c	5.09	228
[(bpy)$_2$Ru(**4Mebpy-P4$_2$-bpy4Me**)Ru(biq)$_2$]$^{4+}$	AN	550	9400	620 c 748 c		0.008			229
	Et/Met						586 c 739 c	298 2300	229
[(dmbpy)$_2$Ru(**4Mebpy-P4$_2$-bpy4Me**)-Ru(dmbpy)(CN)$_2$]$^{2+}$	AN	462		687 c	894 d				230
	DMA	464		697 c	800 d				230
	DMF	464		690 c	808 d				230
	DMSO	466		685 c	804 d				230
	EtOH	460		649 c	805 d				230
	HMPA	466		700 c	800 d				230
	NMF	462		649 c	800 d				230
	py	466		695 c	924 d				230
[(dmbpy)$_2$Ru(**4Mebpy-P4$_2$-bpy4Me**)-Ru(dmbpy)$_2$]$^{4+}$	AN	471	27540	617 c	820 d	0.066 d			231
	Et/Met						602 c	4.19	231
[(dmbpy)$_2$Ru(**4Mebpy-P4$_2$-bpy4Me**)-Ru(4DCE-bpy)$_2$]$^{4+}$	AN	463	21480	658 c	1140 d	0.076 d			231
	Et/Met						634 c	5.31	231
FeRu$_3$									
[Fe{(**4Mebpy-P4$_2$-bpy4Me**)Ru(bpy)$_2$}$_3$]$^{8+}$ †	MeOH/H$_2$O			610 u	38 a	0.0173 a		0.100	222
Ru$_4$									
[Ru{(**4Mebpy-P4$_2$-bpy4Me**)-Ru(dmbpy)$_2$}$_3$]$^{8+}$	AN	417	60260	599 c	770 d	0.041 d			231
	Et/Met						621 c	4.10	231
[Ru{(**4Mebpy-P4$_2$-bpy4Me**)-Ru(4DCE-bpy)$_2$}$_3$]$^{8+}$	AN	483	72440	662 c	970 d	0.044 d			231
	Et/Met						641 c	4.74	231

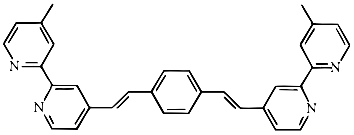
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[(dmbpy)$_2$Ru(**4Mebpy-P4$_0$-bpy4Me**)Ru(dmbpy)$_2$]$^{4+}$	AN	SSCE	+1.13 [2] (Ru)	−1.28 (BL), −1.40, −1.58	228
[(bpy)$_2$Ru(**4Mebpy-P4$_2$-bpy4Me**)Ru(biq)$_2$]$^{4+}$	AN	SSCE	+1.22 [1] (Ru-bpy), +1.35 [1] (Ru-biq)	−0.85 [1] (biq), −1.08 [1] (biq), −1.38 [1] (bpy)	229
[(dmbpy)$_2$Ru(**4Mebpy-P4$_2$-bpy4Me**)Ru(dmbpy)$_2$]$^{4+}$	AN	SSCE	+1.11 [2] (Ru)	−1.46, −1.65	231
[(dmbpy)$_2$Ru(**4Mebpy-P4$_2$-bpy4Me**)Ru(4DCE-bpy)$_2$]$^{4+}$	AN	SSCE	+1.11 [1] (Ru), +1.42 [1] (Ru)	−0.96, −1.15, −1.46	231
Ru$_4$					
[Ru{(**4Mebpy-P4$_2$-bpy4Me**)Ru(dmbpy)$_2$}$_3$]$^{8+}$	AN	SSCE	+1.11 [4] (Ru)	−1.46, −1.63	231
[Ru{(**4Mebpy-P4$_2$-bpy4Me**)Ru(4DCE-bpy)$_2$}$_3$]$^{8+}$	AN	SCE	+1.11 [3] (Ru$_p$), +1.42 [1] (Ru$_c$)§	overlapping waves	231

† Prepared in situ. § Ru$_c$ and Ru$_p$ indicate central and peripheral Ru, respectively.

Table 9.23

4Mebpy-E4$_B$-bpy4Me



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[(dmbpy)$_2$Ru(**4Mebpy-E4$_B$-bpy4Me**)Ru(dmbpy)$_2$]$^{4+}$	AN	460	37150	617 c	820 d	0.001 d			232
Re$_2$									
[(CO)$_3$(AN)Re(**4Mebpy-E4$_B$-bpy4Me**)Re(AN)(CO)$_3$]$^{2+}$	AN	400	25550	695 c	4680 d	$<10^{-4}$			233
	Et/Met	443					695 c 22.7†	1.5	233

Table 9.23 (Continued)

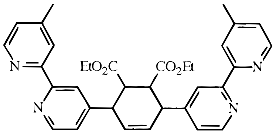
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[(dmbpy)$_2$Ru(**4Mebpy-E4$_B$-bpy4Me**)Ru(dmbpy)$_2$]$^{4+}$	AN	SSCE	+1.10 [2] (Ru)	−1.26 [1] (BL)	232
Re$_2$					
[(CO)$_3$(AN)Re(**4Mebpy-E4$_B$-bpy4Me**)Re(AN)(CO)$_3$]$^{2+}$	AN	SSCE	+1.84 i [1] (Re)	−1.09 [1] (BL)	233

[†] Biexponential decay.

Table 9.24

4Mebpy-ch4-bpy4Me



A. Photophysical Data

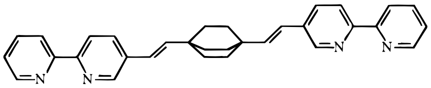
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[(dmbpy)$_2$Ru(**4Mebpy-ch4-bpy4Me**)Ru(dmbpy)$_2$]$^{4+}$	AN	460	25700	628 c	1060 d	0.092 d			228
	Et/Met						593 c	4.61	228

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[(dmbpy)$_2$Ru(**4Mebpy-ch4-bpy4Me**)Ru(dmbpy)$_2$]$^{4+}$	AN	SSCE	+1.13 [2] (Ru)	−1.37 (BL), −1.59, −1.82	228

Table 9.25

bpy-E5$_A$-bpy



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[(bpy)$_2$Ru(**bpy-E5$_A$-bpy**)Ru(bpy)$_2$]$^{4+}$	AN	451	26800	628 u	209 a	0.014 a			120,234,235
	BuCN						604 u	4.46	120,234,235
[(bpy)$_2$Ru^{III}(**bpy-E5$_A$-bpy**)Ru(bpy)$_2$]$^{5+}$	AN			628 u	0.94 a				120
RuOs									
[(bpy)$_2$Ru(**bpy-E5$_A$-bpy**)Os(bpy)$_2$]$^{4+}$	AN	595	3500	625 u	18 a	0.0014 a			120,234,235
			740 u	39 a	0.0023 a				
	BuCN						601 u	0.031	120, 234, 235
							723 u	1.0	
[(bpy)$_2$Ru(**bpy-E5$_A$-bpy**)Os^{III}(bpy)$_2$]$^{5+}$	AN			625 u	0.115 a				120
Os$_2$									
[(bpy)$_2$Os(**bpy-E5$_A$-bpy**)Os(bpy)$_2$]$^{4+}$	AN	595	6100	740 u	40 a	0.0023 a			120,234,235
	BuCN						727 u	0.89	120,234,235
[(bpy)$_2$Os(**bpy-E5$_A$-bpy**)Os^{III}(bpy)$_2$]$^{5+}$	AN			740 u	0.200 a				120

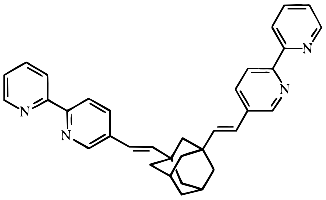
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[(bpy)$_2$Ru(**bpy-E5$_A$-bpy**)Ru(bpy)$_2$]$^{4+}$	AN	SCE	+1.25 [2] (Ru)	−1.31 [2] (bpy)[†]	120,234,235
RuOs					
[(bpy)$_2$Ru(**bpy-E5$_A$-bpy**)Os(bpy)$_2$]$^{4+}$	AN	SCE	+0.81 [1] (Os), +1.25 [1] (Ru)	−1.30 [2] (bpy)[†]	120,234,235
Os$_2$					
[(bpy)$_2$Os(**bpy-E5$_A$-bpy**)Os(bpy)$_2$]$^{4+}$	AN	SCE	+0.81 [2] (Os)	−1.25 [2] (bpy)[†]	120,234,235

[†] Two irreversible processes follow at more negative potential.

Table 9.26

bpy-a-bpy



A. Photophysical Data

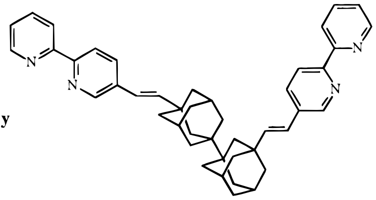
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru_2									
$[(bpy)_2Ru($**bpy-a-bpy**$)Ru(bpy)_2]^{4+}$	AN	≈460 f		625 u	210 a	1.6×10^{-2} a			236
	BuCN						598 u	4.8	236
RuOs									
$[(bpy)_2Ru($**bpy-a-bpy**$)Os(bpy)_2]^{4+}$	AN	≈670 sh f		626 u	1.7 a	1.3×10^{-4} a			236
				736 u	38 a	2.4×10^{-3} a			
	BuCN						595 u	0.05	236
							720 u	1.1	
$[(bpy)_2Ru($**bpy-a-bpy**$)Os^{III}(bpy)_2]^{5+}$	AN			620 u	0.35 a				236
Os_2									
$[(bpy)_2Os($**bpy-a-bpy**$)Os(bpy)_2]^{4+}$	AN	≈670 sh f		738 u	39 a	2.4×10^{-3} a			236
	BuCN						725 u	1.0	236
$[(bpy)_2Os($**bpy-a-bpy**$)Os^{III}(bpy)_2]^{5+}$	AN			735 u	0.25 a				236

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru_2					
$[(bpy)_2Ru($**bpy-a-bpy**$)Ru(bpy)_2]^{4+}$	AN	SCE	+1.27 [2] (Ru)	−1.29 [2]	236
RuOs					
$[(bpy)_2Ru($**bpy-a-bpy**$)Os(bpy)_2]^{4+}$	AN	SCE	+0.80 [1] (Os), +1.26 [1] (Ru)	−1.27 [2]	236
Os_2					
$[(bpy)_2Os($**bpy-a-bpy**$)Os(bpy)_2]^{4+}$	AN	SCE	+0.80 [2] (Os)	−1.25 [2]	236

Table 9.27

bpy-aa-bpy



A. Photophysical Data

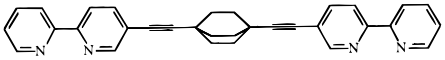
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru_2									
$[(bpy)_2Ru($**bpy-aa-bpy**$)Ru(bpy)_2]^{4+}$	AN	≈460		621 u	217 a	1.4×10^{-2} a			236
	BuCN						600 u	4.6	236
Os_2									
$[(bpy)_2Os($**bpy-aa-bpy**$)Os(bpy)_2]^{4+}$	AN	≈670 sh		732 u	44 a	2.4×10^{-3} a			236
	BuCN						723 u	1.1	236
$[(bpy)_2Os($**bpy-aa-bpy**$)Os^{III}(bpy)_2]^{5+}$	AN			735 u	1.1 a				236

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru_2					
$[(bpy)_2Ru($**bpy-aa-bpy**$)Ru(bpy)_2]^{4+}$	AN	SCE	+1.25 [2] (Ru)	−1.29 [2]	236
Os_2					
$[(bpy)_2Os($**bpy-aa-bpy**$)Os(bpy)_2]^{4+}$	AN	SCE	+0.81 [2] (Os)	−1.21 [2]	236

Table 9.28

bpy-E5$_\mathrm{B}$-bpy



A. Photophysical Data

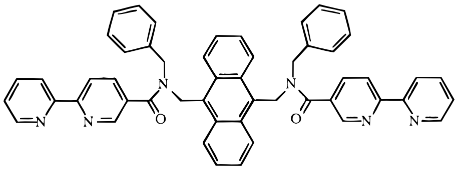
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_\mathrm{RT}$ (nm)	τ_RT (ns)	Φ_RT	Em$_\mathrm{77K}$ (nm)	τ_77K (μs)	ref(s)
Ru$_2$									
[(bpy)$_2$Ru(**bpy-E5$_\mathrm{B}$-bpy**)Ru(bpy)$_2$]$^{4+}$	AN	452		635 c	231 a	0.015 a			235,237
RuOs									
[(bpy)$_2$Ru(**bpy-E5$_\mathrm{B}$-bpy**)Os(bpy)$_2$]$^{4+}$	AN	484 sh		638 c	22 a	0.0013 a			235,237
				787 c	29 a	0.0018 a			
Os$_2$									
[(bpy)$_2$Os(**bpy-E5$_\mathrm{B}$-bpy**)Os(bpy)$_2$]$^{4+}$	AN	484		787 c	29 a	0.0018 a			235,237

B. Electrochemical Data

compound	solvent	RE	E_ox, V [n] (site)	E_red, V [n] (site)	ref(s)
Ru$_2$					
[(bpy)$_2$Ru(**bpy-E5$_\mathrm{B}$-bpy**)Ru(bpy)$_2$]$^{4+}$	AN	SCE	+1.28 [2] (Ru)		235,237
RuOs					
[(bpy)$_2$Ru(**bpy-E5$_\mathrm{B}$-bpy**)Os(bpy)$_2$]$^{4+}$	AN	SCE	+0.84 [1] (Os), +1.27 [1] (Ru)		235,237
Os$_2$					
[(bpy)$_2$Os(**bpy-E5$_\mathrm{B}$-bpy**)Os(bpy)$_2$]$^{4+}$	AN	SCE	+0.84 [2] (Os)		235,237

Table 9.29

bpy-A5$_\mathrm{A}$-bpy

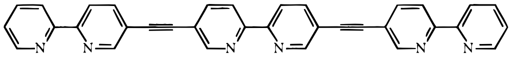


A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_\mathrm{RT}$ (nm)	τ_RT (ns)	Φ_RT	Em$_\mathrm{77K}$ (nm)	τ_77K (μs)	ref(s)
RuOs									
[(bpy)$_2$Ru(**bpy-A5$_\mathrm{A}$-bpy**)Os(bpy)$_2$]$^{4+}$	AN	451	2058	640 u	2.1 d				238,239
				770 u	16 d				
Os$_2$									
[(bpy)$_2$Os(**bpy-A5$_\mathrm{A}$-bpy**)Os(bpy)$_2$]$^{4+}$	AN			770 u	18 d				238

Table 9.30

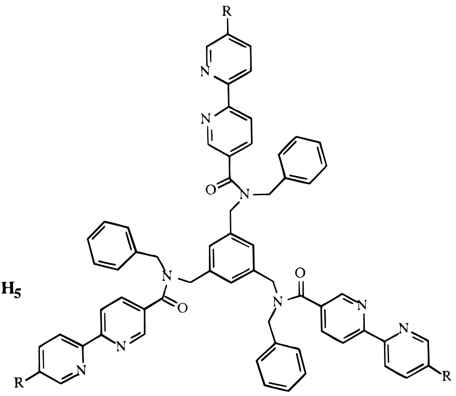
bpy-bpy-bpy



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_\mathrm{RT}$ (nm)	τ_RT (ns)	Φ_RT	Em$_\mathrm{77K}$ (nm)	τ_77K (μs)	ref(s)
Ru$_3$									
[{Ru(bpy)$_2$}$_3$(**bpy-bpy-bpy**)]$^{6+}$	AN	470		715					240

Table 9.31



A5$_B$-(bpy)$_3$, R = H

A5$_B$-(5CE-bpy)$_3$, R = COOC$_2$H$_5$

A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[{Ru(bpy)$_2$(**bpy-**)}$_2$**A5$_B$-bpy**]$^{4+}$	AN	451	24700	640 u	200 a				241,242
	AN			650 u	205 a				243
	BuCN						595 u	3.7	243
[{Ru(bpy)$_2$(**5CE-bpy-**)}$_2$**A5$_B$-(5CE-bpy)**]$^{4+}$	AN	488 sh	16000						113,244
	nitrile			702 u	60 a	0.0036 a	654 u	1.3	113,244
Ru$_3$									
[{Ru(bpy)$_2$(**bpy-**)}$_3$**A5$_B$**]$^{6+}$	AN	450	38100	640 u	200 a				241,242
	BuCN						595 u	3.8	243
	nitrile						595 u	4.2	241,242
[{Ru(bpy)$_2$(**5CE-bpy-**)}$_3$**A5$_B$**]$^{6+}$	AN	489 sh	20600						113,244
	nitrile			702 u	60 a	0.0032 a	654 u	1.3	113,244
Ru$_2$Os									
[{Ru(bpy)$_2$(**bpy-**)}$_2$**A5$_B$-(bpy)**Os(bpy)$_2$]$^{6+}$	AN	450	36300	642 u	185 a				241,242
				780 u	24 a				
	nitrile						595 u	†	241,242
							720 u	0.70	
Os$_3$									
[{Os(bpy)$_2$(**bpy-**)}$_3$**A5$_B$**]$^{6+}$	AN	642	9500	780 u	25 a				241,242
	BuCN						720	0.68	243
	nitrile						720 u	0.68	241,242

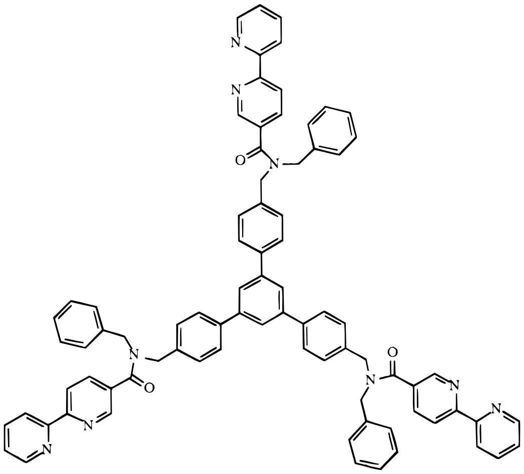
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[{Ru(bpy)$_2$(**bpy-**)}$_2$**A5$_B$-bpy**]$^{4+}$	AN	SCE	+1.30 [2] (Ru)	−1.19 (BL)§	241,242
[{Ru(bpy)$_2$(**5CE-bpy-**)}$_2$**A5$_B$-(5CE-bpy)**]$^{4+}$	AN	SCE	+1.36 [2] (Ru)	−0.91 (BL)‡	113
Ru$_3$					
[Ru(bpy)$_2$(**bpy-**)}$_3$**A5$_B$**]$^{6+}$	AN	SCE	+1.31 [3] (Ru)	−1.18 (BL)§	241,242
[{Ru(bpy)$_2$(**5CE-bpy-**)}$_3$**A5$_B$**]$^{6+}$	AN	SCE	+1.35 [3] (Ru)	−0.90 (BL)‡	113
Ru$_2$Os					
[{Ru(bpy)$_2$(**bpy-**)}$_2$**A5$_B$-(bpy)**Os(bpy)$_2$]$^{6+}$	AN	SCE	+0.865 [1] (Os), +1.30 [2] (Ru)	−1.16 (BL)§	241,242
Os$_3$					
[{Os(bpy)$_2$(**bpy-**)}$_3$**A5$_B$**]$^{6+}$	AN	SCE	+0.870 [3] (Os)	−1.14 (BL)§	241,242

† Not measurable because of strong overlap with the more intense Os-based emission. § Two irreversible processes follow at more negative potential. ‡ Other irreversible processes follow at more negative potential, due to terminal bpy ligands.

Table 9.32

$\mathbf{A5_C\text{-}(bpy)_3}$



A. Photophysical Data

compound	solvent	abs (nm)	ϵ ($M^{-1}\ cm^{-1}$)	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
$\mathbf{Ru_3}$									
$[\{Ru(bpy)_2(\mathbf{bpy\text{-}})\}_3\mathbf{A5_C}]^{6+}$	AN	450	37300	640 u	210 a				241,242
	nitrile						595 u	4.4	241,242
$[\{Ru(bpy)_2(\mathbf{bpy\text{-}})\}_2\mathbf{A5_C\text{-}(bpy)}Ru^{III}(bpy)_2]^{7+}$	AN			640 u					241
$\mathbf{Ru_2Os}$									
$[\{Ru(bpy)_2(\mathbf{bpy\text{-}})\}_2\mathbf{A5_C\text{-}(bpy)}Os(bpy)_2]^{6+}$	AN	450	35330	640 u†	200 a†				241,242
	nitrile						595 u	4.0	241,242
							720 u	0.60	
$\mathbf{Os_3}$									
$[\{Os(bpy)_2(\mathbf{bpy\text{-}})\}_3\mathbf{A5_C}]^{6+}$	AN	642	8800	780 u	25 a				241,242
	nitrile						720 u	0.67	241,242
$[\{Os(bpy)_2(\mathbf{bpy\text{-}})\}_2\mathbf{A5_C\text{-}(bpy)}Os^{III}(bpy)_2]^{7+}$	AN			780 u					241

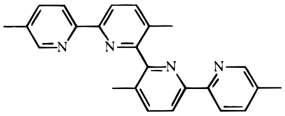
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
$\mathbf{Ru_3}$					
$[\{Ru(bpy)_2(\mathbf{bpy\text{-}})\}_3\mathbf{A5_C}]^{6+}$	AN	SCE	+1.31 [3] (Ru)	−1.17 (BL)‡	241,242
$\mathbf{Ru_2Os}$					
$[\{Ru(bpy)_2(\mathbf{bpy\text{-}})\}_2\mathbf{A5_C\text{-}(bpy)}Os(bpy)_2]^{6+}$	AN	SCE	+0.880 [1] (Os), +1.31 [2] (Ru)	−1.14 (BL)‡	241,242
$\mathbf{Os_3}$					
$[\{Os(bpy)_2(\mathbf{bpy\text{-}})\}_3\mathbf{A5_C}]^{6+}$	AN	SCE	+0.865 [3] (Os)	−1.15 (BL)‡	241,242

† Emission from Os-based unit not measurable because it is covered by the much more intense Ru-based emission. ‡ Two irreversible processes follow at more negative potential.

Table 9.33

QP



A. Photophysical Data

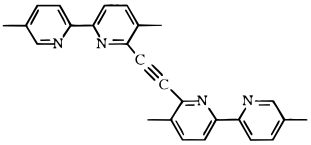
compound	solvent	abs (nm)	ϵ ($M^{-1}\ cm^{-1}$)	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
$\mathbf{Re_2}$									
$[Br(CO)_3Re(\mathbf{QP})Re(CO)_3Br]$	DMF	370 sh		583 u	96 d	0.016 d	520 u	7.0	245

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
$\mathbf{Re_2}$					
$[Br(CO)_3Re(\mathbf{QP})Re(CO)_3Br]$	AN	SCE	+0.98		245
	DMF	SCE		−1.45 (BL)	245

Table 9.34

5,5'-dmbpy-E6-5,5'-dmbpy

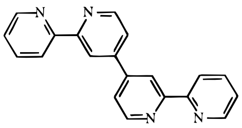


A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[(bpy)$_2$Ru(**5,5′-dmbpy-E6-5,5′-dmbpy**)Ru(bpy)$_2$]$^{4+}$	AN	445	23000	618 u					246

Table 9.35

QP$_B$



A. Photophysical Data

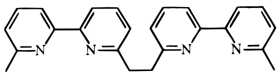
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[(bpy)$_2$Ru(**QP$_B$**)Ru(bpy)$_2$]$^{4+}$	AN	471	22000	685	2000				247

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[(bpy)$_2$Ru(**QP$_B$**)Ru(bpy)$_2$]$^{4+}$	AN	SCE	+1.24 [2] (Ru)	−1.10 [1] (BL), −1.44 [1] (bpy), −1.57 [1] (bpy), −1.64 [1] (adsorption)	247

Table 9.36

6Mebpy-S6$_2$-bpy6Me



A. Photophysical Data

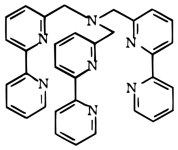
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Cu$_2$									
[Cu(**6Mebpy-S6$_2$-bpy6Me**)$_2$Cu]$^{2+}$	CH_2Cl_2	445	8760	670 u	13 d	4×10^{-5} d	690 u	0.335	248

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Cu$_2$					
[Cu(**6Mebpy-S6$_2$-bpy6Me**)$_2$Cu]$^{2+}$	AN	SCE	+0.88 [2]	−1.68 i	249

Table 9.37

N-bpy$_3$



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru$_3$									
[{Ru(bpy)$_2$}$_3$(**N-bpy$_3$**)]$^{6+}$	AN	446	33000	610 u					250
Re$_3$									
[{Cl(CO)$_3$Re}$_3$(**N-bpy$_3$**)]	AN	360	6490	598 u					250

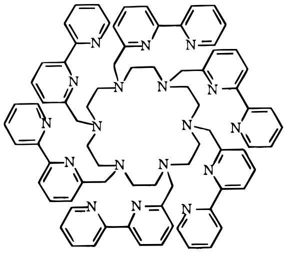
Table 9.37 (Continued)

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru₃					
$[\{Ru(bpy)_2\}_3($**N-bpy₃**$)]^{6+}$	AN	SCE	+1.36	−1.20, −1.41, −1.68	250
Re₃					
$[\{Cl(CO)_3Re\}_3($**N-bpy₃**$)]$	AN	SCE	+1.37 i (Re)	−1.44	250

Table 9.38

hacod-bpy₆



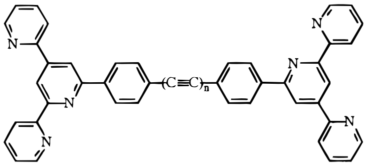
A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Eu₂									
$[Eu_2($**hacod-bpy₆**$)]^{6+}$	AN	306	49000	578 u	730 a†	0.020 a		1020†	251
	D_2O				1890 a†			1780†	251
	H_2O	285	54000		230 a†	0.002 a		300†	251
Gd₂									
$[Gd_2($**hacod-bpy₆**$)]^{6+}$	AN	306	52000				455 u	1800§	251
	Et/Met	286	51000				455 u	3900§	251
	H_2O	285	51000				455 u	2400§	251
Tb₂									
$[Tb_2($**hacod-bpy₆**$)]^{6+}$	AN	306	60400	488 u	1360 a†	0.015 a		1740†	251
	D_2O				1560 a†			2120†	251
	H_2O	285	59200		700 a†	0.003 a		710†	251

† Metal centered excited state. § Ligand centered excited state.

Table 9.39

pbpy-Ph-Eₙ-Ph-pbpy

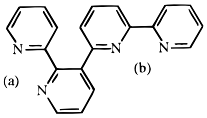


A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru₂									
$[(bpy)_2Ru($**pbpy-Ph-E₁-Ph-pbpy**$)Ru(bpy)_2]^{4+}$	AN	455	19300	639 u					246
$[(bpy)_2Ru($**pbpy-Ph-E₂-Ph-pbpy**$)Ru(bpy)_2]^{4+}$	AN	455	24900	640 u					246
CuRu₂									
$[Cu\{($**pbpy-Ph-E₁-Ph-pbpy**$)Ru(bpy)_2\}_2]^{5+}$	MeOH	455	28200	639 u					246
$[Cu\{($**pbpy-Ph-E₂-Ph-pbpy**$)Ru(bpy)_2\}_2]^{5+}$	MeOH	454	28600	643 u					246

Table 9.40

bpyₐ-bpy_b



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru₂									
$[(bpy)_2Ru($**bpyₐ-bpy_b**$)Ru(bpy)_2]^{4+}$	AN	448	21000	674 u	232 a	1.9×10^{-2} a			252
	BuCN						612 u	5.7	252
	DMF/CH_2Cl_2	452	23000	656 u	340 a	2.2×10^{-2} a	615 u	5.3	253

Table 9.40 (Continued)

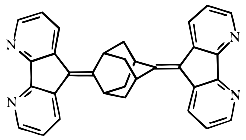
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
RuRe									
$[(bpy)_2Ru(\mathbf{bpy_a\text{-}bpy_b})Re(CO)_3Cl]^{2+}$	DMF/CH_2Cl_2	456	14000	644 u	410 a	2.8×10^{-2} a	607 u	4.7	253
$[(bpy)_2Ru(\mathbf{bpy_b\text{-}bpy_a})Re(CO)_3Cl]^{2+}$	DMF/CH_2Cl_2	453	13000	623 u	23 a	1.4×10^{-3} a	590 u	5.8	253
RuOs									
$[(bpy)_2Ru(\mathbf{bpy_a\text{-}bpy_b})Os(bpy)_2]^{4+}$	AN	646	2700	756 u	41 a	3.2×10^{-3} a			252
	BuCN						716 u	1.5	252
$[(bpy)_2Ru(\mathbf{bpy_b\text{-}bpy_a})Os(bpy)_2]^{4+}$	AN	690	2800	808 u	26 a	1.3×10^{-3} a			252
	BuCN						756 u	1.0	252
Re_2									
$[Cl(CO)_3Re(\mathbf{bpy_a\text{-}bpy_b})Re(CO)_3Cl]$	DMF/CH_2Cl_2	385	8000	622 u	9 a	5.3×10^{-4} a	548 u	2.7	253
Os_2									
$[(bpy)_2Os(\mathbf{bpy_a\text{-}bpy_b})Os(bpy)_2]^{4+}$	AN	650	5700	814 u	21 a	8.8×10^{-4} a			252
	BuCN						756 u	1.2	252

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru_2					
$[(bpy)_2Ru(\mathbf{bpy_a\text{-}bpy_b})Ru(bpy)_2]^{4+}$	AN	Fc/Fc^+	+0.99 [1] (Ru), +1.06 [1] (Ru)	−1.46 (BL), −1.73 (bpy), −1.86 (bpy)	252
RuRe					
$[(bpy)_2Ru(\mathbf{bpy_a\text{-}bpy_b})Re(CO)_3Cl]^{2+}$	AN	Fc/Fc^+	+0.93 [1] (Ru), +1.17 [1] (Re)	−1.56, −1.77, −1.99	253
$[(bpy)_2Ru(\mathbf{bpy_b\text{-}bpy_a})Re(CO)_3Cl]^{2+}$	AN	Fc/Fc^+	+1.04 [2] (Ru + Re)	−1.49, −1.77, −1.98	253
RuOs					
$[(bpy)_2Ru(\mathbf{bpy_a\text{-}bpy_b})Os(bpy)_2]^{4+}$	AN	Fc/Fc^+	+0.60 [1] (Os), +1.05 [1] (Ru)	−1.43 (BL), −1.66 (bpy), −1.85 (bpy)	252
$[(bpy)_2Ru(\mathbf{bpy_b\text{-}bpy_a})Os(bpy)_2]^{4+}$	AN	Fc/Fc^+	+0.57 [1] (Os), +1.09 [1] (Ru)	−1.42 (BL), −1.71 (bpy), −1.83 (bpy)	252
Re_2					
$[Cl(CO)_3Re(\mathbf{bpy_a\text{-}bpy_b})Re(CO)_3Cl]$	AN	Fc/Fc^+	+0.98 [1] (Re), +1.10 [1] (Re)	−1.55 i (BL), −1.66 i (BL)	253
Os_2					
$[(bpy)_2Os(\mathbf{bpy_a\text{-}bpy_b})Os(bpy)_2]^{4+}$	AN	Fc/Fc^+	+0.56 [1] (Os), +0.65 [1] (Os)	−1.39 (BL), −1.63 (bpy), −1.81 (bpy)	252

Table 9.41

FAF



A. Photophysical Data

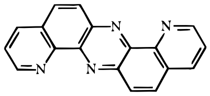
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru_2									
$[(bpy)_2Ru(\mathbf{FAF})Ru(bpy)_2]^{4+}$	AN	≈450 f	≈22100 f	605 u	0.300 a				79
	BuCN						577 u	5.5	79
RuOs									
$[(bpy)_2Ru(\mathbf{FAF})Os(bpy)_2]^{4+}$	AN	≈655 f	≈2600 f	605 u	0.290 a				79
				720 u	40 a				
	BuCN						577 u	0.0039	79
							703 u	1.1	
$[(bpy)_2Ru(\mathbf{FAF})Os^{III}(bpy)_2]^{5+}$	AN				0.240 a				79
Os_2									
$[(bpy)_2Os(\mathbf{FAF})Os(bpy)_2]^{4+}$	AN	≈655 f	≈4700 f	720 u	41 a				79
	BuCN						710 u	1.1	79
$[(bpy)_2Os(\mathbf{FAF})Os^{III}(bpy)_2]^{5+}$	AN				2.4 a				79

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru_2					
$[(bpy)_2Ru(\mathbf{FAF})Ru(bpy)_2]^{4+}$	AN	SCE	+1.265 [2] (Ru)	−1.285 [2]	79
RuOs					
$[(bpy)_2Ru(\mathbf{FAF})Os(bpy)_2]^{4+}$	AN	SCE	+0.800 [1] (Os), +1.260 [1] (Ru)	−1.275 [2]	79
Os_2					
$[(bpy)_2Os(\mathbf{FAF})Os(bpy)_2]^{4+}$	AN	SCE	+0.800 [2] (Os)	−1.245 [2]	79

Table 9.42

dpop



A. Photophysical Data

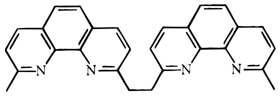
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru_2									
$[(bpy)_2Ru($**dpop**$)Ru(bpy)_2]^{4+}$	AN	775 sh	≈5000 f	>950					254

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru_2					
$[(bpy)_2Ru($**dpop**$)Ru(bpy)_2]^{4+}$	AN	SCE	+1.49 [1] (Ru), +1.66 [1] (Ru)	−0.18 [1] (BL), −0.90 [1] (BL)	254

Table 9.43

9Mephen-S2_2-phen9Me



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Cu_2									
$[Cu($**9Mephen-S2_2-phen9Me**$)_2Cu]^{2+}$	CH_2Cl_2	445	10900	663 u	16 d	1.0×10^{-4} d	672 u	1.89	248
	Et/Met†						692 c	1.6	255

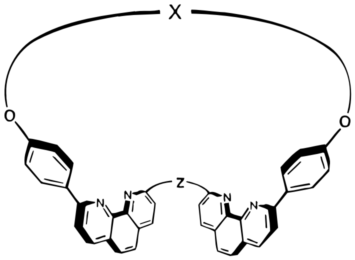
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Cu_2					
$[Cu($**9Mephen-S2_2-phen9Me**$)_2Cu]^{2+}$	acetone	SSCE	+0.65 [2] (Cu)		255
	AN	SCE	+0.85 [2] (Cu)	−1.55 i	249
	AN	SSCE	+0.64 [2] (Cu)		255
	CH_2Cl_2	SSCE	+0.92 [2] (Cu)		255
	DMF	SSCE	+0.55 [2] (Cu)		255
	DMSO	SSCE	+0.76 [2] (Cu)		255
	MeOH	SSCE	+0.61 [2] (Cu)		255
	nitrobenzene	SSCE	+0.77 [2] (Cu)		255
	nitromethane	SSCE	+0.80 [2] (Cu)		255
	PC	SSCE	+0.65 [2] (Cu)		255

† Absorption data in several solvents are given in the original paper.

Table 9.44

m-43: X = $CH_2(CH_2OCH_2)_5CH_2$; Z = $(CH_2)_4$
m-45: X = $CH_2(CH_2OCH_2)_5CH_2$; Z = $(CH_2)_6$



A. Photophysical Data

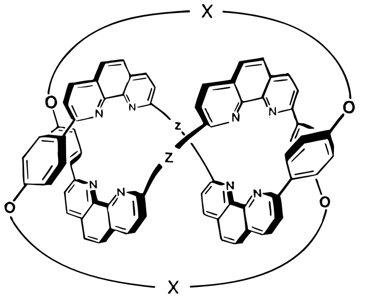
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Cu_2									
$[Cu_2($**m-43**$)_2]^{2+}$	CH_2Cl_2	442	6200	745 c	170 d	5.3×10^{-4} d	730 c		256
	CH_2Cl_2/MeOH							2.3	256
$[Cu_2($**m-45**$)_2]^{2+}$	CH_2Cl_2	437	6200	745 c	171 d	5.5×10^{-4} d	740 c		256
	CH_2Cl_2/MeOH							2.7	256

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Cu_2					
$[Cu_2($**m-43**$)_2]^{2+}$	AN	SCE	+0.55 i (Cu)		256

Table 9.45

Knot-k-80: $X = CH_2(CH_2OCH_2)_4CH_2$; $Z = (CH_2)_4$
Knot-k-82: $X = CH_2(CH_2OCH_2)_5CH_2$; $Z = (CH_2)_2$
Knot-k-84: $X = CH_2(CH_2OCH_2)_4CH_2$; $Z = (CH_2)_6$
Knot-k-86: $X = CH_2(CH_2OCH_2)_5CH_2$; $Z = (CH_2)_4$
Knot-k-90: $X = CH_2(CH_2OCH_2)_5CH_2$; $Z = (CH_2)_6$



A. Photophysical Data

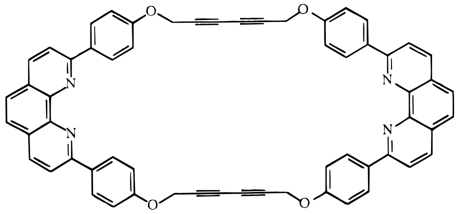
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Cu_2									
$[Cu_2($**Knot-k-80**$)]^{2+}$	CH_2Cl_2	437	6200	750 c	150 d	3.7×10^{-4} d	755 c		256
	CH_2Cl_2/MeOH							2.6	256
$[Cu($**Knot-k-82**$)]^{2+}$	CH_2Cl_2	440	6200	750 c	149 d	3.7×10^{-4} d	770 c		256
	CH_2Cl_2/MeOH							1.2	256
$[Cu_2($**Knot-k-84**$)]^{2+}$	CH_2Cl_2	431	6200	742 c	208 d	7.2×10^{-4} d	750 c		256
	CH_2Cl_2/MeOH							0.9	256
$[Cu_2($**Knot-k-86**$)]^{2+}$	CH_2Cl_2	439	6200	750 c	154 d	4.1×10^{-4} d	750 c		256
	CH_2Cl_2/MeOH							0.9	256
$[Cu_2($**Knot-k-90**$)]^{2+}$	CH_2Cl_2	434	6200	742 c	174 d	5.5×10^{-4} d	755 c		256
	CH_2Cl_2/MeOH							1.2	256

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Cu_2					
$[Cu_2($**Knot-k-84**$)]^{2+}$	AN	SCE	+0.75 [2] (Cu)		256
$[Cu_2($**Knot-k-86**$)]^{2+}$	AN	SCE	+0.61 [2] (Cu)		256

Table 9.46

caten



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Cu_2									
[(cyclo-phen)Cu(**caten**)Cu(cyclo-phen)]$^{2+}$	CH_2Cl_2	≈580sh f		735 c	168 d	5.9×10^{-4} d	750 c	1.4	257
CuZn									
[(cyclo-phen)Cu(**caten**)Zn(cyclo-phen)]$^{3+}$	CH_2Cl_2	≈580sh f		457 c†	0.090 d†	0.0068 d†	730 c	1.7	257
				725 c§	163 d§				
CuAg									
[(cyclo-phen)Cu(**caten**)Ag(cyclo-phen)]$^{2+}$	CH_2Cl_2	≈580sh f		735 c	162 d	6.1×10^{-4} d	735 c	1.8	257
Ag_2									
[(cyclo-phen)Ag(**caten**)Ag(cyclo-phen)]$^{2+}$	CH_2Cl_2						502 c	17000	257

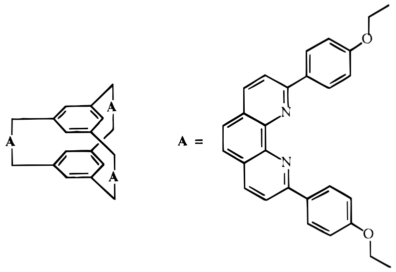
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Cu_2					
[(cyclo-phen)Cu(**caten**)Cu(cyclo-phen)]$^{2+}$	AN	SCE	+0.67 [1] (Cu)		258
CuAg					
[(cyclo-phen)Cu(**caten**)Ag(cyclo-phen)]$^{2+}$	CH_2Cl_2	SCE	+0.668 [1] (Cu)	−0.480 [1] (Ag)	258

† Excitation at 355 nm. § Excitation at 500 nm.

Table 9.47

cage-phen$_3$

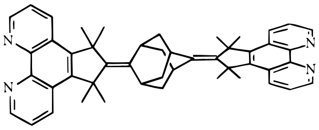


A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Cu$_3$									
$[\{Cu(dtol\text{-}phen)\}_3$(**cage-phen$_3$**)$]^{3+}$	CH_2Cl_2	437		730 c	170 d	7.0×10^{-4} d			259
$[\{Cu(2,9\text{-}Me_2\text{-}phen)\}_3$(**cage-phen$_3$**)$]^{3+}$	CH_2Cl_2	443		760 c	50 d	0.8×10^{-4} d			259

Table 9.48

PAP



A. Photophysical Data

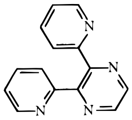
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
$[(bpy)_2Ru($**PAP**$)Ru(bpy)_2]^{4+}$	AN	450	28000	610 u	145 a				80
	BuCN						583 u	5.5	80
RuOs									
$[(bpy)_2Ru($**PAP**$)Os(bpy)_2]^{4+}$	AN	449	28000	609 u 712 u	21 a 41 a				80
	BuCN						581 u 705 u	0.041 1.2	80
Os$_2$									
$[(bpy)_2Os($**PAP**$)Os(bpy)_2]^{4+}$	AN	480	27800	717 u	41 a				80
	BuCN						709 u	1.0	80

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
$[(bpy)_2Ru($**PAP**$)Ru(bpy)_2]^{4+}$	AN	SCE	+1.235 [2] (Ru)	−1.380 [2] (bpy)	80
RuOs					
$[(bpy)_2Ru($**PAP**$)Os(bpy)_2]^{4+}$	AN	SCE	+0.795 [1] (Os), +1.240 [1] (Ru)	−1.345 [2] (bpy)	80
Os$_2$					
$[(bpy)_2Os($**PAP**$)Os(bpy)_2]^{4+}$	AN	SCE	+0.800 [2] (Os)	−1.305 [2] (bpy)	80

Table 9.49

2,3-dpp



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
FeRu									
$[(CN)_4Fe($**2,3-dpp**$)Ru(phen)_2]$	AN	476		700 u	≈90 a				260
$[(CN)_4Fe($**2,3-dpp**$)Ru(phen)_2]^{+}$	AN	498		680 u	95 a				260
Cu$_2$									
$[(PPh_3)_2Cu($**2,3-dpp**$)Cu(PPh_3)_2]^{2+}$	$CH_2Cl_2^{\ddagger}$	418	5655	650 u					261
	Et/Met						652 u		261

Table 9.49 (Continued)

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[Cl$_2$(CO)$_2$Ru(**2,3-dpp**)Ru(CO)$_2$Cl$_2$]	AN	410	4500						262
	BuCN						555 u	146	262
[(bpy)$_2$Ru(**2,3-dpp**)Ru(bpy)$_2$]$^{4+}$	AN	523	22500	756 u	134 a				263
	AN	527	24200	802 c	102 a, 125 d	0.003 d			264
	AN	526	24700	802 u	125				265
	AN	526	24800	790 c	140 d	0.025 d	702 c	2.38	200
	CH$_2$Cl$_2$	519	24000	770 c	154 d	0.065 d			200
	EtOH	522	23400	753 u	84 d				200
	EtOH					0.0030 d			266
	EtOH	525	21700	800 c	80 d	0.0012 d			267
	Et/Met						709 c	2.00	264
	H$_2$O	525	21000	755 u	54 d				266
	H$_2$O			755 u	53	0.0070 a			268
	H$_2$O	530	27500	800 c	55 d	0.012 d			200
	MeOH	525	25300	797 c	100 d				200
[(bpy)$_2$Ru(**2,3-dpp**)Ru(biq)$_2$]$^{4+}$	AN	543	22400	799 c	75 d				264
	DMF	548	22800	760 c	175 d				269
	Et/Met						710 u	3.17	269
	Et/Met						723 c	1.55	264
[(bpy)$_2$Ru(**2,3-dpp**)Ru(phen)$_2$]$^{4+}$	AN	523	27400	752 u	113 a				263
[(dcbpyH$_2$)$_2$Ru(**2,3-dpp**)Ru(dcbpyH$_2$)$_2$]$^{4+}$	AN		745 c						200
	H$_2$O (pH = 0)	518	16600						200
	MeOH	530		763 c	123 d		699 c	2.32	200
[(dcbpy)$_2$Ru(**2,3-dpp**)Ru(dcbpy)$_2$]$^{4-}$	H$_2$O (pH = 7)	530	20800	778 c	87 d				200
[(biq)$_2$Ru(**2,3-dpp**)Ru(biq)$_2$]$^{4+}$	AN	537	15600	789 c	65 d				264
	DMF	538	21200	746 c	232 d				269
	Et/Met						714 u	2.24	269
	Et/Met						720 c	1.73	264
[(phen)$_2$Ru(**2,3-dpp**)Ru(phen)$_2$]$^{4+}$	AN	525	23400	746 u	153 a				263
	AN	526	22200	746 u	153 d				200
RuRh									
[(bpy)$_2$Ru(**2,3-dpp**)RhH$_2$(PPh$_3$)$_2$]$^{3+}$	acetone	488	13000	776	106	0.0092			203
[(bpy)$_2$Ru(**2,3-dpp**)Rh(bpy)$_2$]$^{5+}$	AN	514		778 c	37				270
	CH$_2$Cl$_2$	508		738 c	48				270
	Et/Met						632 c	1.71	270
	THF	528		786 c					270
RuPd									
[(bpy)$_2$Ru(**2,3-dpp**)PdCl$_2$]$^{2+}$	AN	501	14080	700 c	370				271
	Et/Met						700 c	4.0	271
RuRe									
[(bpy)$_2$Ru(**2,3-dpp**)ReCl(CO)$_3$]$^{2+}$	CH$_2$Cl$_2$	512	9570	770 c					272
	EtOH						697 u	1.96	272
RuOs									
[(bpy)$_2$Ru(**2,3-dpp**)Os(bpy)$_2$]$^{4+}$	AN	542	28500						273
	DMF	534	21500	†					274
RuPt									
[(bpy)$_2$Ru(**2,3-dpp**)PtMe$_2$]$^{2+}$	acetone	524	12010	735 c	330				271
[(bpy)$_2$Ru(**2,3-dpp**)PtCl$_2$]$^{2+}$	acetone			800 c					271
	AN	509	15240	800 c	450				271
	Et/Met						752 c	2.2	271
Re$_2$									
[Cl(CO)$_3$Re(**2,3-dpp**)Re(CO)$_3$Cl]	AN	454	8400						221
	CH$_2$Cl$_2$	486	6320	790 c	$\leq$20				272
	EtOH						690 u	0.28	272
Os$_2$									
[(bpy)$_2$Os(**2,3-dpp**)Os(bpy)$_2$]$^{4+}$	AN	555	21800						275
	AN	552	25200						276
	DMF	550	24000	†					274
	Et/Met						928 c§		142
Ru$_3$									
[(bpy)Ru{(**2,3-dpp**)Ru(bpy)$_2$}$_2$]$^{6+}$	AN	545	23500	766 u	75 a				277
	AN			804 c	80 d	0.001 d			264
	Et/Met						712 u	1.78	277
	Et/Met						721 c		264
[(bpy)Ru{(**2,3-dpp**)Ru(biq)$_2$}$_2$]$^{6+}$	AN	546	28700	742 u	142 a				277
	AN			773 c					264
	Et/Met						702 u	2.18	277
	Et/Met						713 c		264
RuOs$_2$									
[(bpy)Ru{(**2,3-dpp**)Os(bpy)$_2$}$_2$]$^{6+}$	AN	559	36300						142
	Et/Met						896 c§		142

Table 9.49 (Continued)

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_4$									
[Ru{(**2,3-dpp**)Ru(bpy)$_2$}$_3$]$^{8+}$	AN	534	49600	772	89				138
	AN	545	46000	811 c	50 a, 60 d	0.001 d			264
	Et/Met						727 c	1.38	264
[(biq)$_2$Ru(**2,3-dpp**)Ru{(**2,3-dpp**)-Ru(bpy)$_2$}$_2$]$^{8+}$	AN			768 u	110 a				140
	Et/Met						720 u	1.5	140
[Ru{(**2,3-dpp**)Ru(biq)$_2$}$_3$]$^{8+}$	AN	610	41500	795 c	130 a, 190 d	0.001 d			264
	Et/Met						725 c	1.86	264
[Ru{(**2,3-dpp**)Ru(phen)$_2$}$_3$]$^{8+}$	AN	539	51400	760	87				138
[Ru{(**2,3-dpp**)Ru(tpy)Cl}$_3$]$^{5+}$	AN	564	23800	758	84				138
[Ru{(**2,3-dpp**)Ru(2,3-dpp)$_2$}$_3$]$^{8+}$	AN	461	38200	722 c	300 d	1×10^{-4} d			102
	Et/Met						698 c	3.6	102
[Ru{(**2,3-dpp**)Ru(2,3-Medpp)$_2$}$_3$]$^{14+}$	AN	505 sh	38000	714 c	600 d	6.5×10^{-3} d			102
	Et/Met						698 c	4.3	102
Ru$_3$Os									
[{(bpy)$_2$Ru(**2,3-dpp**)}$_3$Os]$^{8+}$	AN	549	40000	875 c	18 d				137
	Et/Met						802 c	0.41	137
[{(2,3-Medpp)$_2$Ru(**2,3-dpp**)}$_3$Os]$^{14+}$	AN	526		812 u	445 a				278
RuRh$_3$									
[Ru{(**2,3-dpp**)Rh(ppy)$_2$}$_3$]$^{5+}$	CH$_2$Cl$_2$	471	15400	681 c	330 d	0.018 d	645 c	1.05 3.40	144
RuIr$_3$									
[Ru{(**2,3-dpp**)Ir(ppy)$_2$}$_3$]$^{5+}$	CH$_2$Cl$_2$	499	31500	812 c	2.2 d	1.5×10^{-4} d	726 c	0.57 1.71	144
OsRh$_3$									
[Os{(**2,3-dpp**)Rh(ppy)$_2$}$_3$]$^{5+}$	CH$_2$Cl$_2$	515	23300	821 c	55 d	0.0058 d	789 c	0.62	144
OsIr$_3$									
[Os{(**2,3-dpp**)Ir(ppy)$_2$}$_3$]$^{5+}$	CH$_2$Cl$_2$	534	25400	825 c	5.2 d	4.5×10^{-4} d	810 c	0.43	144
Ru$_6$									
[{(bpy)$_2$Ru(**2,3-dpp**)}$_2$Ru(**2,3-dpp**)-Ru{(**2,3-dpp**)Ru(bpy)$_2$}$_2$]$^{12+}$	AN	540	59000	770 u	53 a				279
	Et/Met						716 u	1.33	279
[{(biq)$_2$Ru(**2,3-dpp**)}$_2$Ru(**2,3-dpp**)-Ru{(**2,3-dpp**)Ru(biq)$_2$}$_2$]$^{12+}$	AN	571	60200	760 u	80 a				141
	Et/Met						716 u	1.5	141
Ru$_2$Os$_4$									
[{(bpy)$_2$Os(**2,3-dpp**)}$_2$Ru(**2,3-dpp**)-Ru{(**2,3-dpp**)Os(bpy)$_2$}$_2$]$^{12+}$	AN	560	81500						141
	Et/Met						912 c§		142
Ru$_7$									
[Ru{(**2,3-dpp**)Ru(bpy)(**2,3-dpp**)-Ru(bpy)$_2$}$_3$]$^{14+}$	AN	547	76200	808	80 d	0.0009 d			280
	Et/Met						725	2.0	280
Ru$_{10}$									
[Ru{(**2,3-dpp**)Ru[(**2,3-dpp**)-Ru(bpy)$_2$]$_2$}$_3$]$^{20+}$	AN	541	125000	809 c	55 d	0.001 d			281
	Et/Met						732 c	1.3	281
[Ru{(**2,3-dpp**)Ru[(**2,3-dpp**)-Ru(biq)$_2$]$_2$}$_3$]$^{20+}$	AN	555	109500	789 c	130 d	0.006 d			96
	Et/Met						722 c	1.65	96
[Ru{(**2,3-dpp**)Ru[(**2,3-dpp**)-Ru(2,3-dpp)$_2$]$_2$}$_3$]$^{20+}$	AN	500 sh	30000	750 c	too weak	$<3 \times 10^{-5}$ d			102
	Et/Met						too weak	too weak	102
[Ru{(**2,3-dpp**)Ru[(**2,3-dpp**)-Ru(2,3-Medpp)$_2$]$_2$}$_3$]$^{32+}$	AN	550 sh	40000	668 c	600 d	3.9×10^{-4} d			102
	Et/Met						649 c	5.1	102
Ru$_9$Os									
[Os{(**2,3-dpp**)Ru[(**2,3-dpp**)-Ru(bpy)$_2$]$_2$}$_3$]$^{20+}$	AN	550	117000	808 c 860 c	65 d	5×10^{-4} d			96
	Et/Met						720 c	1.33	96
[Os{(**2,3-dpp**)Ru[(**2,3-dpp**)-Ru(biq)$_2$]$_2$}$_3$]$^{20+}$	AN	556	117500	789 c 860 c	125 d	3×10^{-4} d			96
	Et/Met						722 c	1.71	96
Ru$_4$Os$_6$									
[Ru{(**2,3-dpp**)Ru[(**2,3-dpp**)-Os(bpy)$_2$]$_2$}$_3$]$^{20+}$	AN	560	132500						96
	Et/Met						892 c		142
Ru$_3$Os$_7$									
[Os{(**2,3-dpp**)Ru[(**2,3-dpp**)-Os(bpy)$_2$]$_2$}$_3$]$^{20+}$	AN	563	140500						96
	Et/Met						900 c		142
Ru$_{13}$									
[Ru{(**2,3-dpp**)Ru(bpy)(**2,3-dpp**)-Ru[(**2,3-dpp**)Ru(bpy)$_2$]$_2$}$_3$]$^{26+}$	AN	544	133000	800 c	62 d				282
	Et/Met						722 c	1.46	282
Ru$_{22}$									
[Ru{(**2,3-dpp**)[Ru[(**2,3-dpp**)-Ru{(**2,3-dpp**)Ru(bpy)$_2$}$_2$]$_2$}$_3$]$^{44+}$	AN	542	202000	786 c	45 d	3.0×10^{-4} d			101,102
	Et/Met						730 c	1.4	101, 102

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
FeRu					
[(CN)$_4$Fe(**2,3-dpp**)Ru(phen)$_2$]	H$_2$O	SCE	+0.54 [1] (Fe)		260
Cu$_2$					
[(PPh$_3$)$_2$Cu(**2,3-dpp**)Cu(PPh$_3$)$_2$]$^{2+}$	CH$_2$Cl$_2$	SCE	+1.25 i	−1.01 (BL)	261

Table 9.49 (Continued)

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[Cl$_2$(CO)$_2$Ru(**2,3-dpp**)Ru(CO)$_2$Cl$_2$]	AN	SCE	+2.00 i [2]	−0.620 (BL)	262
[(bpy)$_2$Ru(**2,3-dpp**)Ru(bpy)$_2$]$^{4+}$	AN	NHE	+1.57 [1] (Ru), +1.76 [1] (Ru)		266
	AN	SCE	+1.33 [1] (Ru), +1.52 [1] (Ru)	−0.71, −1.18, −1.55	268
	AN	SCE	+1.44 [1] (Ru), +1.65 [1] (Ru)	−0.64, −1.13, −1.4	263
	AN	Ag/AgCl	+1.50 [1] (Ru), +1.72 [1] (Ru)		267
	AN	SCE	+1.38 [1] (Ru), +1.55 [1] (Ru)	−0.67 [1] (BL), −1.17 [1] (BL), −1.57 [2] (bpy), −1.89 [2] (bpy)	264
	AN	Ag/AgCl¶	+1.43 [1] (Ru), +1.61 [1] (Ru)	−0.61 [1] (BL), −1.09 [1] (BL)	283
	AN	Fc/Fc$^+$	+0.99 [1] (Ru), +1.16 [1] (Ru)	−1.05 (BL), −1.55 (BL), −1.95 (bpy)	265
	AN	SCE	+1.41 [1] (Ru), +1.61 [1] (Ru)	−0.69 [1] (BL)	284
	DMF	SCE		−1.19 [1] (BL), ≈−1.4 (bpy), ≈−1.5 (bpy), −1.73 (bpy), −1.86 (bpy)	284
	DMF	Ag/AgCl		−0.60 [1] (BL), −1.04 [1] (BL), −1.37 [1] (bpy), −1.47 [1] (bpy), −1.64, −1.77	267
[(bpy)$_2$Ru(**2,3-dpp**)Ru(biq)$_2$]$^{4+}$	AN	SCE	+1.36 [1] (Ru), +1.48 [1] (Ru)	−0.68 [1] (BL), −1.18 [1], −1.57 [2], −1.81 [2]	264
	DMF	SCE		−0.75 (biq), −0.93 (biq), −1.10 (BL)	269
[(bpy)$_2$Ru(**2,3-dpp**)Ru(phen)$_2$]$^{4+}$	AN	SCE	+1.41 [1] (Ru), +1.61 [1] (Ru)	−0.6 i, −1.15 i, −1.4 i	263
[(biq)$_2$Ru(**2,3-dpp**)Ru(biq)$_2$]$^{4+}$	AN	SCE	+1.57 [2] (Ru)	−0.45 [1] (BL), −0.81 [2] (biq), −0.95 [1] (BL), −1.19 [2] (biq)	264
	DMF	SCE		−0.71 (biq), −0.87 (biq), −1.07 (BL)	269
[(phen)$_2$Ru(**2,3-dpp**)Ru(phen)$_2$]$^{4+}$	AN	SCE	+1.44 [1] (Ru), +1.65 [1] (Ru)	−0.64 [1] (BL), −1.13 (BL), −1.38	138
RuRh					
[(bpy)$_2$Ru(**2,3-dpp**)RhH$_2$(PPh$_3$)$_2$]$^{3+}$	AN	SCE	+1.56 i (Rh), +1.70 [1] (Ru)	−0.66 [1] (BL), −1.28, −1.51, −1.73	203
RuRe					
[(bpy)$_2$Ru(**2,3-dpp**)Re(CO)$_3$Cl]$^{2+}$	CH$_2$Cl$_2$	SCE	>+1.34 i (Re)	−0.66 (BL), −1.20 (BL)	272
RuOs					
[(bpy)$_2$Ru(**2,3-dpp**)Os(bpy)$_2$]$^{4+}$	AN	Ag/AgCl¶	+1.01 [1] (Os), +1.56 [1] (Ru)		273
	DMF	SCE	+0.90 (Os), >+1.60 (Ru)	−0.73 (BL), −1.13 (BL), −1.45 (bpy), −1.55 (bpy), −1.73 (bpy), −1.89 (bpy)	274
	DMF	Ag/AgCl¶		−0.62 [1] (BL), −1.03 [1] (BL), −1.34 [1] (bpy), −1.41 [1] (bpy), −1.61 [1] (bpy), −1.74 [1] (bpy)	273
RuPt					
[(bpy)$_2$Ru(**2,3-dpp**)PtMe$_2$]$^{2+}$	acetone	SCE	+0.66 i, +1.12 i, +1.63 (Ru)	−0.84, −1.39, −1.31, −1.83	271
[(bpy)$_2$Ru(**2,3-dpp**)PtCl$_2$]$^{2+}$	AN	SCE	+1.47 i, +1.57 (Ru)	−0.54, −1.11, −1.49	271
Re$_2$					
[Cl(CO)$_3$Re(**2,3-dpp**)Re(CO)$_3$Cl]	CH$_2$Cl$_2$	SCE	>+1.4 i (Re)	−0.69 (BL), −0.97 (BL)	272
	DMF	SSCE		−0.46 [1] (BL), −1.11 i (Re)	221
Os$_2$					
[(bpy)$_2$Os(**2,3-dpp**)Os(bpy)$_2$]$^{4+}$	AN	SCE	+0.90 [1] (Os), +1.20 [1] (Os)	−0.68 [1] (BL), −1.10 [1] (BL), −1.38 [2] (bpy), −1.62 [2] (bpy)	275
	AN	Ag/AgCl¶	+0.91 [1] (Os), +1.22 [1] (Os)	−0.68 [1] (BL), −1.06 [1] (BL)	276
	DMF	Ag/AgCl¶		−0.61 [1] (BL), −1.00 [1] (BL), −1.28 [1] (bpy), −1.38 [1] (bpy), −1.58 [1] (bpy), −1.76 [1] (bpy)	276
	DMF	SCE	+0.83 [1] (Os), +1.12 [1] (Os)	−0.72 (BL), −1.10 (BL), −1.39 (bpy), −1.50 (bpy), −1.69 (bpy), −1.89 (bpy)	274
Ru$_3$					
[(bpy)Ru{(**2,3-dpp**)Ru(bpy)$_2$}$_2$]$^{6+}$	AN	SCE	+1.48 [2] (Ru$_p$)$^\nabla$	−0.71 two overlapping waves	277
	AN	SCE	+1.48 [2] (Ru$_p$)$^\nabla$	−0.55 [1] (BL), −0.75 [1] (BL), −1.17 [1] (BL), −1.47 [2] (bpy + BL), −1.75 [2] (bpy)	264
[(bpy)Ru{(**2,3-dpp**)Ru(biq)$_2$}$_2$]$^{6+}$	AN	SCE	+1.62 [2] (Ru$_p$)$^\nabla$	−0.63 two overlapping waves	277
	AN	SCE	+1.60 [2] (Ru$_p$)$^\nabla$	−0.47 [2] (BL), −0.87 [2] (biq), −1.17 [2] (BL), −1.50 [1] (bpy), −1.79 [2] (biq)	264
Ru$_4$					
[Ru{(**2,3-dpp**)Ru(bpy)$_2$}$_3$]$^{8+}$	AN	SCE	+1.50 [>2.5] (Ru$_p$)$^\nabla$	−0.56 [1] (BL), −0.74 [1] (BL), −0.89 [1] (BL), −1.12 [1] (BL), −1.24 [1] (BL), −1.37 [1] (BL), −1.51, −1.65	138

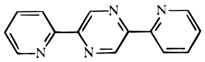
Table 9.49 (Continued)

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_4$					
[Ru{(**2,3-dpp**)Ru(bpy)$_2$}$_3$]$^{8+}$	AN	SCE	+1.50 [3] (Ru$_p$)[▽]	−0.56 [1] (BL), −0.63 [1] (BL), −0.70 [1] (BL), −1.20 [1], −1.33 [1], −1.48 [1]	264
	AN	SCE	+1.53 [3] (Ru$_p$)[▽]	−0.62 [1] (BL), −0.77 [1] (BL), −1.23 [1] (BL)	102
[Ru{(**2,3-dpp**)Ru(biq)$_2$}$_3$]$^{8+}$	AN	SCE	+1.58 [3] (Ru$_p$)[▽]	−0.6 [3] (BL), −0.87 [3] (biq), −1.15 [3] (BL)	264
[Ru{(**2,3-dpp**)Ru(phen)$_2$}$_3$]$^{8+}$	AN	SCE	+1.43 [>2.5] (Ru$_p$)[▽]	−0.5 series of broad, unresolved waves	138
[Ru{(**2,3-dpp**)Ru(tpy)Cl}$_3$]$^{5+}$	AN	SCE	+1.06 [>2.5] (Ru$_p$)[▽]	−0.60 [1] (BL), −0.72 [1] (BL), −0.84 [1] (BL)	138
[Ru{(**2,3-dpp**)Ru(2,3-Medpp)$_2$}$_3$]$^{14+}$	AN	SCE	+1.82 [1] (Ru$_i$)[▽]	−0.79 [6] (2,3-Medpp$^+$); −0.98 [3] (BL)	102
Ru$_3$Os					
[{(bpy)$_2$Ru(**2,3-dpp**)}$_3$Os]$^{8+}$	AN	SCE	+1.25 [1] (Os), +1.55 [3] (Ru)	−0.55 [1] (BL), −0.65 [1] (BL), −0.77 [1] (BL)	137
RuRh$_3$					
[Ru{(**2,3-dpp**)Rh(ppy)$_2$}$_3$]$^{5+}$	CH_2Cl_2	SCE	+1.25 i [∼1] (Ru)	−0.48 [1] (BL), −0.60 [1] (BL), −0.70 [1] (BL), −1.19 [1] (BL), −1.37 [1] (BL), ≈−1.60	144
RuIr$_3$					
[Ru{(**2,3-dpp**)Ir(ppy)$_2$}$_3$]$^{5+}$	CH_2Cl_2	SCE	+1.40 i [>3] (Ru + Ir)	−0.44 [1] (BL), −0.55 [1] (BL), −0.65 [1] (BL), −1.12 [1] (BL), −1.29 [1] (BL), ≈−1.53	144
OsRh$_3$					
[Os{(**2,3-dpp**)Rh(ppy)$_2$}$_3$]$^{5+}$	CH_2Cl_2	SCE	+0.75 i [1] (Os), +1.50 i [>1] (Rh)	−0.35 i [1] (BL), −0.54 i [1] (BL), −0.82 i [1] (BL)	144
OsIr$_3$					
[Os{(**2,3-dpp**)Ir(ppy)$_2$}$_3$]$^{5+}$	CH_2Cl_2	SCE	+1.00 [1] (Os), +1.40 i [3] (Ir)	−0.32 [1] (BL), −0.49 [1] (BL), −0.67 [1] (BL), −1.11 [1] (BL), −1.29 [1] (BL), ≈−1.44, −1.60	144
Ru$_6$					
[{(bpy)$_2$Ru(**2,3-dpp**)}$_2$Ru(**2,3-dpp**)-Ru{(**2,3-dpp**)Ru(bpy)$_2$}$_2$]$^{12+}$	AN	SCE	+1.44 [4] (Ru$_p$)[▽]	−0.55 overlapping waves	141,279
[{(biq)$_2$Ru(**2,3-dpp**)}$_2$Ru(**2,3-dpp**)-Ru{(**2,3-dpp**)Ru(biq)$_2$}$_2$]$^{12+}$	AN	SCE	∼+1.8 [4] (Ru$_p$)[▽]		141
Ru$_2$Os$_4$					
[{(bpy)$_2$Os(**2,3-dpp**)}$_2$Ru(**2,3-dpp**)-Ru{(**2,3-dpp**)Os(bpy)$_2$}$_2$]$^{12+}$	AN	SCE	+1.06 [4] (Os)		141
Ru$_7$					
[Ru{(**2,3-dpp**)Ru(bpy)(**2,3-dpp**)-Ru(bpy)$_2$}$_3$]$^{14+}$	AN	SCE	+1.38 [3] (Ru$_p$)[▽]	−0.58 [3] (BL)	280
Ru$_{10}$					
[Ru{(**2,3-dpp**)Ru[(**2,3-dpp**)-Ru(bpy)$_2$]$_2$}$_3$]$^{20+}$	AN	SCE	+1.43 [6] (Ru$_p$)[▽]		281
	AN	SCE	+1.53 [6] (Ru$_p$)[▽]	−0.73 [6] (BL$_o$), −1.22 [3] (BL$_i$)[‖]	102
[Ru{(**2,3-dpp**)Ru[(**2,3-dpp**)-Ru(biq)$_2$]$_2$}$_3$]$^{20+}$	AN	SCE	+1.62 [6] (Ru$_p$)[▽]		96
[Ru{(**2,3-dpp**)Ru[(**2,3-dpp**)-Ru(2,3-dpp)$_2$]$_2$}$_3$]$^{20+}$	AN	SCE	∼+1.69 [∼6] adsorption	adsorption	102
[Ru{(**2,3-dpp**)Ru[(**2,3-dpp**)-Ru(2,3-Medpp)$_2$]$_2$}$_3$]$^{32+}$	AN	SCE	+1.83 [3] (Ru$_i$)[▽]	−0.75 [12] (2,3-Medpp$^+$), −0.95 [3] (BL$_i$)[‖]	102
Ru$_9$Os					
[Os{(**2,3-dpp**)Ru[(**2,3-dpp**)-Ru(bpy)$_2$]$_2$}$_3$]$^{20+}$	AN	SCE	+1.17 [1] (Os), +1.50 [6] (Ru$_p$)[▽]		96
[Os{(**2,3-dpp**)Ru[(**2,3-dpp**)-Ru(biq)$_2$]$_2$}$_3$]$^{20+}$	AN	SCE	+1.24 [1] (Os), +1.59 [6] (Ru$_p$)[▽]		96
Ru$_4$Os$_6$					
[Ru{(**2,3-dpp**)Ru[(**2,3-dpp**)-Os(bpy)$_2$]$_2$}$_3$]$^{20+}$	AN	SCE	+1.00 [6] (Os$_p$)[▽]		96
Ru$_3$Os$_7$					
[Os{(**2,3-dpp**)Ru[(**2,3-dpp**)-Os(bpy)$_2$]$_2$}$_3$]$^{20+}$	AN	SCE	+1.05 [6] (Os$_p$); +1.39 [1] (Os$_c$)[▽]		96
Ru$_{13}$					
[Ru{(**2,3-dpp**)Ru(bpy)(**2,3-dpp**)-Ru[(**2,3-dpp**)Ru(bpy)$_2$]$_2$}$_3$]$^{26+}$	AN	SCE	+1.50 [9] (Ru$_p$)[▽]		282
Ru$_{22}$					
[Ru{(**2,3-dpp**)[Ru[(**2,3-dpp**)-Ru{(**2,3-dpp**)Ru(bpy)$_2$}$_2$]$_2$}$_3$]$^{44+}$	AN	SCE	+1.52 [12] (Ru$_p$)[▽]	overlapping waves	101,102

[‡] Absorption data in other solvents are given in the original paper. [†] No emission <850 nm. [§] At 90 K. [¶] This electrode is 0.268 V vs NHE. [▽] M$_c$, M$_i$, M$_p$ stand for central, intermediate, and peripheral metal, respectively. [‖] BL$_i$ and BL$_o$ stand for inner and outer bridging ligand, respectively.

Table 9.50

2,5-dpp



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[Cl$_2$(CO)$_2$Ru(**2,5-dpp**)Ru(CO)$_2$Cl$_2$]	AN	448	4600						262
	BuCN						539 u	80	262
[(bpy)$_2$Ru(**2,5-dpp**)Ru(bpy)$_2$]$^{4+}$	AN	584	19000	near IR					201
	AN	585	15900	824 c	155 a				264
	Et/Met						771 c	0.94	264
[(bpy)$_2$Ru(**2,5-dpp**)Ru(biq)$_2$]$^{4+}$	AN	595	13700	830 c	190 a				264
	Et/Met						792 c	1.00	264
[(biq)$_2$Ru(**2,5-dpp**)Ru(biq)$_2$]$^{4+}$	AN	609	11500	820 c	170 a				264
	Et/Met						722 c	1.82	264
RuOs									
[(bpy)$_2$Ru(**2,5-dpp**)Os(bpy)$_2$]$^{4+}$	AN	601	19200						142
	Et/Met						968 c§		142
[(bpy)$_2$Ru(**2,5-dpp**)Os(biq)$_2$]$^{4+}$	AN	620	17900						142
	Et/Met						900 c§		142
Os$_2$									
[(bpy)$_2$Os(**2,5-dpp**)Os(bpy)$_2$]$^{4+}$	AN	616	27000						275
	Et/Met						984 c§		142
Ru$_3$									
[(bpy)Ru{(**2,5-dpp**)Ru(bpy)$_2$}$_2$]$^{6+}$	AN	592	28100	814 u	64 a				277
	AN			831 c					264
	Et/Met						755 u	0.98	277
	Et/Met						767 c		264
[(bpy)Ru{(**2,5-dpp**)Ru(biq)$_2$}$_2$]$^{6+}$	AN	591	22900	774 u	120 a				277
	AN			805 c	190 d	0.006 d			264
	Et/Met						734 u	1.28	277
	Et/Met						739 c		264
RuOs$_2$									
[(bpy)Ru{(**2,5-dpp**)Os(bpy)$_2$}$_2$]$^{6+}$	AN	606	33800						142
	Et/Met						980 c§		142
RuOs$_3$									
[Ru{(**2,5-dpp**)Os(bpy)$_2$}$_3$]$^{8+}$	AN	618	24600						142
	Et/Met						960 c§		142
Ru$_6$									
[{(bpy)$_2$Ru(**2,5-dpp**)}$_2$Ru(**2,5-dpp**)-Ru{(**2,5-dpp**)Ru(bpy)$_2$}$_2$]$^{12+}$	AN	582	52000	810 u	40 a				279
	Et/Met						756 u	0.83	279

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[Cl$_2$(CO)$_2$Ru(**2,5-dpp**)Ru(CO)$_2$Cl$_2$]	AN	SCE	+1.92 i [2]	−0.380 (BL)	262
[(bpy)$_2$Ru(**2,5-dpp**)Ru(bpy)$_2$]$^{4+}$	AN	SCE	+1.39 [1] (Ru), +1.58 [1] (Ru)	−0.55 [1] (BL), −1.09 [1] (BL), −1.30 [>1] (bpy)	201
	AN	SCE	+1.37 [1] (Ru), +1.54 [1] (Ru)	−0.53 [1] (BL), −1.08 [1] (BL), −1.50 [2] (bpy), −1.81 [2] (bpy)	264
[(bpy)$_2$Ru(**2,5-dpp**)Ru(biq)$_2$]$^{4+}$	AN	SCE	+1.43 [2] (Ru)	−0.47 [1] (BL), overlapping waves	264
[(biq)$_2$Ru(**2,5-dpp**)Ru(biq)$_2$]$^{4+}$	AN	SCE	+1.48 [2] (Ru)	−0.45 [1] (BL), −0.82 [2] (biq), −0.99 [1] (BL), −1.26 [2] (biq)	264
Os$_2$					
[(bpy)$_2$Os(**2,5-dpp**)Os(bpy)$_2$]$^{4+}$	AN	SCE	+0.92 [1] (Os), +1.22 [1] (Os)	−0.56 [1] (BL), −1.00 [1] (BL), −1.46 [2] (bpy), −1.71 [2] (bpy)	275
Ru$_3$					
[(bpy)Ru{(**2,5-dpp**)Ru(bpy)$_2$}$_2$]$^{6+}$	AN	SCE	+1.45 [2] (Ru$_p$)†	−0.66 two overlapping waves	277
	AN	SCE	+1.45 [2] (Ru$_p$)†	−0.48 [1] (BL), −0.60 [1] (BL), −1.10 [1] (BL), −1.30 [1] (BL), −1.52 [1] (bpy)	264
[(bpy)Ru{(**2,5-dpp**)Ru(biq)$_2$}$_2$]$^{6+}$	AN	SCE	+1.60 [2] (Ru$_p$)†	−0.55 two overlapping waves	277
	AN	SCE	+1.57 [2] (Ru$_p$)†	−0.47 [2] (BL), −0.89 [2] (biq), −1.21 [2] (BL), −1.53 [1] (bpy), −1.78 [1] (biq)	264
RuOs$_3$					
[Ru{(**2,5-dpp**)Os(bpy)$_2$}$_3$]$^{8+}$	AN	SCE	+0.92, +1.10, +1.37	−0.64, −0.80, −0.92, −1.22, −1.38	285
Ru$_6$					
[{(bpy)$_2$Ru(**2,5-dpp**)}$_2$Ru(**2,5-dpp**)-Ru{(**2,5-dpp**)Ru(bpy)$_2$}$_2$]$^{12+}$	AN	SCE	+1.38 [3] (Ru$_p$)†	−0.50 overlapping waves	141,279

§ At 90 K. † Ru$_p$ stands for peripheral Ru.

Table 9.51

2,3-dpp and 2,5-dpp

A. Photophysical Data

compound	solvent	abs (nm)	ϵ ($M^{-1}\ cm^{-1}$)	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru_4									
[(bpy)$_2$Ru(**2,5-dpp**)Ru{(**2,3-dpp**)-Ru(bpy)$_2$}$_2$]$^{8+}$	AN	552	41700	812 u	44 a				139
	Et/Met						752 u	0.90	139
Ru_6									
[{(bpy)$_2$Ru(**2,3-dpp**)}$_2$Ru(**2,5-dpp**)-Ru{(**2,3-dpp**)Ru(bpy)$_2$}$_2$]$^{12+}$	AN	540	62200	768 u	55 a				279
	Et/Met						716 u	1.30	279
[{(bpy)$_2$Ru(**2,5-dpp**)}$_2$Ru(**2,3-dpp**)-Ru{(**2,5-dpp**)Ru(bpy)$_2$}$_2$]$^{12+}$	AN	577	54100	812 u	44 a				279
	Et/Met						764 u	0.83	279
[{(bpy)$_2$Ru(**2,5-dpp**)}$_2$Ru(**2,3-dpp**)-Ru{(**2,3-dpp**)Ru(biq)$_2$}$_2$]$^{12+}$	AN	588	39000	790 u	41 a				141
	Et/Met						750 u	1.27	141
Ru_4Os_2									
[{(bpy)$_2$Ru(**2,5-dpp**)}$_2$Ru(**2,3-dpp**)-Ru{(**2,3-dpp**)Os(bpy)$_2$}$_2$]$^{12+}$	AN	576	50300	802 u	39 a				141
	Et/Met						752 u	0.82	141

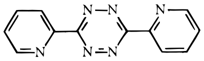
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru_6					
[{(bpy)$_2$Ru(**2,3-dpp**)}$_2$Ru(**2,5-dpp**)-Ru{(**2,3-dpp**)Ru(bpy)$_2$}$_2$]$^{12+}$	AN	SCE	+1.41 [4] (Ru_p)†	−0.50 overlapping waves	141,279
[{(bpy)$_2$Ru(**2,5-dpp**)}$_2$Ru(**2,3-dpp**)-Ru{(**2,5-dpp**)Ru(bpy)$_2$}$_2$]$^{12+}$	AN	SCE	+1.36 [4] (Ru_p)†	−0.50 overlapping waves	141,279
[{(bpy)$_2$Ru(**2,5-dpp**)}$_2$Ru(**2,3-dpp**)-Ru{(**2,3-dpp**)Ru(biq)$_2$}$_2$]$^{12+}$	AN	SCE	+1.50 [2] (Ru-bpy), +1.66 [2] (Ru-biq)		141
Ru_4Os_2					
[{(bpy)$_2$Ru(**2,5-dpp**)}$_2$Ru(**2,3-dpp**)-Ru{(**2,3-dpp**)Os(bpy)$_2$}$_2$]$^{12+}$	AN	SCE	+1.05 [2] (Os), +1.45 [2] (Ru_p)†		141

† Ru_p stands for peripheral Ru.

Table 9.52

BPTZ



A. Photophysical Data

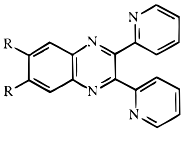
compound	solvent	abs (nm)	ϵ ($M^{-1}\ cm^{-1}$)	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru_2									
[(bpy)$_2$Ru(**BPTZ**)Ru(bpy)$_2$]$^{4+}$	AN	685	16600	near IR					201
	DMF	683	12100						286

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru_2					
[(bpy)$_2$Ru(**BPTZ**)Ru(bpy)$_2$]$^{4+}$	AN	SCE	+1.52 [1] (Ru), +2.02 [1] (Ru)	−0.03 [1] (BL), −1.25 i (BL), −1.55 [>1] (bpy)	201
	DMF	SCE	+1.58 [1] (Ru), +2.10 [1] (Ru)	0.00, −0.92, −1.52, −1.78	286

Table 9.53

dpq, R = H
Me_2dpq, R = CH_3
Cl_2dpq, R = Cl



A. Photophysical Data

compound	solvent	abs (nm)	ϵ ($M^{-1}\ cm^{-1}$)	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Cu_2									
[(PPh_3)$_2$Cu(**dpq**)Cu(PPh_3)$_2$]$^{2+}$	CH_2Cl_2‡	476	3815	708 u					261
	Et/Met						710 u		261
[(PPh_3)$_2$Cu(**Me_2dpq**)Cu(PPh_3)$_2$]$^{2+}$	CH_2Cl_2‡	477	4550	692 u					261
	Et/Met						686 u		261
[(PPh_3)$_2$Cu(**Cl_2dpq**)Cu(PPh_3)$_2$]$^{2+}$	CH_2Cl_2‡	482	2900	726 u					261
	Et/Met						720 u		261
Ru_2									
[(bpy)$_2$Ru(**dpq**)Ru(bpy)$_2$]$^{4+}$	AN	605	9800						115
	AN	603	18200	822 u	<20 a				263

Table 9.53 (Continued)

compound	solvent	abs (nm)	ϵ ($M^{-1}\,cm^{-1}$)	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru_2									
$[(bpy)_2Ru(\mathbf{dpq})Ru(phen)_2]^{4+}$	AN	603	25400	820 u	<20 a				263
$[(phen)_2Ru(\mathbf{dpq})Ru(phen)_2]^{4+}$	AN	601	22000	810 u	20 a				263
$[(bpy)_2Ru(\mathbf{Me_2dpq})Ru(bpy)_2]^{4+}$	AN	593	≈20000 f	808 u					283
$[(bpy)_2Ru(\mathbf{Cl_2dpq})Ru(bpy)_2]^{4+}$	AN	635	≈22000 f	860 u					283
RuRe									
$[(bpy)_2Ru(\mathbf{dpq})Re(CO)_3Cl]^{2+}$	CH_2Cl_2	580	8820	†					272
Re_2									
$[Cl(CO)_3Re(\mathbf{dpq})Re(CO)_3Cl]$	CH_2Cl_2	528	4860	†					272
ReOs									
$[Cl(CO)_3Re(\mathbf{dpq})Os(bpy)_2]^{2+}$	CH_2Cl_2	596	12120	†					272

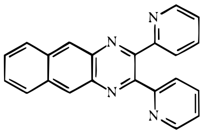
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Cu_2					
$[(PPh_3)_2Cu(\mathbf{dpq})Cu(PPh_3)_2]^{2+}$	CH_2Cl_2	SCE	+1.32 i	−0.67 (BL)	261
$[(PPh_3)_2Cu(\mathbf{Me_2dpq})Cu(PPh_3)_2]^{2+}$	CH_2Cl_2	SCE	+1.51 i	−0.82 (BL)	261
$[(PPh_3)_2Cu(\mathbf{Cl_2dpq})Cu(PPh_3)_2]^{2+}$	CH_2Cl_2	SCE	+1.63 i	−0.53 (BL), −1.43 (BL)	261
Ru_2					
$[(bpy)_2Ru(\mathbf{dpq})Ru(bpy)_2]^{4+}$	AN	SSCE	+1.47 [1] (Ru), +1.62 [1] (Ru)	−0.37 [0.96] (BL), −1.10 [1] (BL)	115
	AN	SCE	+1.48 [1] (Ru), +1.64 [1] (Ru)	−0.40, −1.09, −1.4	263
	AN	SCE	+1.50 [1] (Ru), +1.68 [1] (Ru)	−0.37 [1] (BL), −1.15 [1] (BL), ≈−1.4 [1] (bpy), ≈−1.5 [1] (bpy), −1.70 [1] (bpy), −1.82 [1] (bpy)	284
	AN	Ag/AgCl§	+1.52 [1] (Ru), +1.67 [1] (Ru)	−0.32 [1] (BL), −1.10 [1] (BL)	283
$[(bpy)_2Ru(\mathbf{dpq})Ru(phen)_2]^{4+}$	AN	SCE	+1.51 [1] (Ru), +1.69 [1] (Ru)	−0.36, −1.08, −1.41	263
$[(bpy)_2Ru(\mathbf{Me_2dpq})Ru(bpy)_2]^{4+}$	AN	Ag/AgCl§	+1.48 [1] (Ru), +1.65 [1] (Ru)	−0.41 [1] (BL), −1.15 [1] (BL)	283
$[(bpy)_2Ru(\mathbf{Cl_2dpq})Ru(bpy)_2]^{4+}$	AN	Ag/AgCl§	+1.53 [1] (Ru), +1.72 [1] (Ru)	−0.20 [1] (BL), −0.89 [1] (BL)	283
RuRe					
$[(bpy)_2Ru(\mathbf{dpq})Re(CO)_3Cl]^{2+}$	CH_2Cl_2	SCE	>+1.36 i (Re)	−0.30 (BL), −0.91 (BL)	272
Re_2					
$[Cl(CO)_3Re(\mathbf{dpq})Re(CO)_3Cl]$	CH_2Cl_2	SCE	>+1.30 i (Re)	−0.33 (BL), −1.13 (BL)	272
ReOs					
$[Cl(CO)_3Re(\mathbf{dpq})Os(bpy)_2]^{2+}$	CH_2Cl_2	SCE	+1.17 (Os)	−0.30 (BL), −0.88 (BL)	272

[‡] Absorption data in other solvents are given in the original paper. [†] No emission ($\Phi_{RT} < 10^{-4}$) below 850 nm. [§] This electrode is +0.268 V vs NHE.

Table 9.54

dpbq



A. Photophysical Data

compound	solvent	abs (nm)	ϵ ($M^{-1}\,cm^{-1}$)	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Cu_2									
$[(PPh_3)_2Cu(\mathbf{dpbq})Cu(PPh_3)_2]^{2+}$	CH_2Cl_2‡	538 sh	4285	770 u					261
	Et/Met						740 u		261

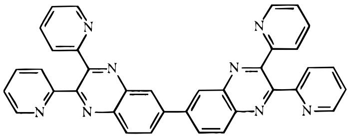
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Cu_2					
$[(PPh_3)_2Cu(\mathbf{dpbq})Cu(PPh_3)_2]^{2+}$	CH_2Cl_2	SCE	+1.65 i	−0.52 (BL), −1.31 (BL)	261

[‡] Absorption data in other solvents are given in the original paper.

Table 9.55

dpq-dpq



A. Photophysical Data

compound	solvent	abs (nm)	ϵ ($M^{-1}\,cm^{-1}$)	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru_2									
$[(bpy)_2Ru(\mathbf{dpq{\cdot}dpq})Ru(bpy)_2]^{4+}$	AN	528	16300	≈780 u, f	≤60	6×10^{-6}			287

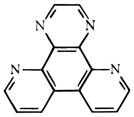
Table 9.55 (Continued)

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru_2					
$[(bpy)_2Ru(\mathbf{dpq{\cdot}dpq})Ru(bpy)_2]^{4+}$	AN	SSCE	+1.42 [2] (Ru)	−0.67 [1] (BL), −0.80 [1] (BL), −1.41 (bpy)	287

Table 9.56

ppz



A. Photophysical Data

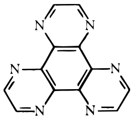
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru_2									
$[(bpy)_2Ru(\mathbf{ppz})Ru(bpy)_2]^{4+}$	H_2O	573	16000	820 u	≤50 d	0.0157 a			268

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru_2					
$[(bpy)_2Ru(\mathbf{ppz})Ru(bpy)_2]^{4+}$	AN	SCE	+1.35 [1] (Ru), +1.55 [1] (Ru)	−0.67 [1], −1.34 [1], −1.57 [1]	268

Table 9.57

HAT



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru_2									
$[(bpy)_2Ru(\mathbf{HAT})Ru(bpy)_2]^{4+}$	AN			>800 u	550 a				288
	Et/Met						727 u	2.7	288
	H_2O	572	15000	825 u	148 a				289
	H_2O	572	15000	>800 u	160 a				288
Ru_2									
$[(bpy)_2Ru(\mathbf{HAT})Ru(HAT)_2]^{4+}$	AN			>800 u	232 a†				288
	Et/Met						725 u	2.8†	288
	H_2O	564	19000	>800 u	54 a†				288
$[(bpy)_2Ru(\mathbf{HAT})Ru(tap)_2]^{4+}$	AN			>800 u	182 a†				288
	Et/Met							3.5†	288
	H_2O	570	18000	>800 u	57 a†				288
$[(phen)_2Ru(\mathbf{HAT})Ru(phen)_2]^{4+}$	AN			>800 u	830 a				288
	Et/Met						738 u	4.2	288
	H_2O	564	20000	>800 u	260 a				288
	H_2O	≈570 f		800 u	260 d				290
Ru_3									
$[\{(bpy)_2Ru\}_2(\mathbf{HAT})Ru(bpy)_2]^{6+}$	AN			>800 u	106 a				288
	Et/Met						771 u	1.4	288
	H_2O	580	38000	880 u	40 a				288,289
$[\{(bpy)_2Ru\}_2(\mathbf{HAT})Ru(HAT)_2]^{6+}$	AN			>800	158 a				288
	Et/Met						743 u	2†	288
	H_2O	576	34000	>800 u	62 a				288
$[\{(bpy)_2Ru\}_2(\mathbf{HAT})Ru(tap)_2]^{6+}$	AN			>800 u	70 a				288
	Et/Met						771 u	1.9†	288
	H_2O	566	32000	>800 u	60 a				288
$[\{(phen)_2Ru\}_2(\mathbf{HAT})Ru(phen)_2]^{6+}$	AN			>800 u	193 a				288
	Et/Met						771 u	1.7	288
	H_2O	576	43000	>800 u	52 a				288
$RuRe_2$									
$[(bpy)_2Ru(\mathbf{HAT})\{Re(CO)_3Cl\}_2]^{2+}$	AN	529	22000	670					204
	Et/Met						604		204

Table 9.57 (Continued)

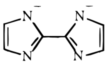
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[(bpy)$_2$Ru(**HAT**)Ru(bpy)$_2$]$^{4+}$	AN	SCE	+1.53 [1] (Ru), +1.78 [1] (Ru)	−0.49 [1] (BL), −1.06 [1] (BL)[§]	288,289
[(bpy)$_2$Ru(**HAT**)Ru(HAT)$_2$]$^{4+}$	AN	SCE	+1.68 [1] (Ru-bpy)	−0.37 [1] (BL), −0.77 [1] (BL), −0.95 [1]	288
[(bpy)$_2$Ru(**HAT**)Ru(tap)$_2$]$^{4+}$	AN	SCE	+1.57 [1] (Ru-bpy), +2.18 [1] (Ru-tap)	−0.38 [1] (BL), −0.85 [1] (BL), −1.03 [1]	288
[(phen)$_2$Ru(**HAT**)Ru(phen)$_2$]$^{4+}$	AN	SCE	+1.52 [1] (Ru), +1.78 [1] (Ru)	−0.49 [1] (BL), −1.07 [1] (BL)[§]	288
	AN	SCE		−0.49 [1] (BL), −1.06 [1]	290
	H_2O (pH = 5.9)	SCE		−0.64 [1] (BL)	290
Ru$_3$					
[{(bpy)$_2$Ru}$_2$(**HAT**)Ru(bpy)$_2$]$^{6+}$	AN	SCE	+1.61 [1] (Ru), +1.87 [1] (Ru), +2.12 [1] (Ru)	−0.25 [1] (BL), −0.58 [1] (BL), −1.07 [1]	288,289
[{(bpy)$_2$Ru}$_2$(**HAT**)Ru(tap)$_2$]$^{6+}$	AN	SCE	+1.66 [1] (Ru-bpy), +1.93 [1] (Ru-bpy)	−0.23 [1] (BL), −0.55 [1] (BL), −0.66 [1]	288
[{(phen)$_2$Ru}$_2$(**HAT**)Ru(phen)$_2$]$^{6+}$	AN	SCE	+1.61 [1] (Ru), +1.88 [1] (Ru), +2.16 [1] (Ru)	−0.30 [1] (BL), −0.64 [1] (BL), −1.12 [1]	288
RuRe$_2$					
[(bpy)$_2$Ru(**HAT**){Re(CO)$_3$Cl}$_2$]$^{2+}$	AN	SSCE	+1.48 [1] (Ru), +1.74 i (Re)	−0.07 (BL), −0.44 (BL), −0.97 (BL), −1.20 (BL), −1.45, −1.58 i (Re), −1.82	204

[†] The decay is not a pure single exponential. [§] Overlapping waves follow at more negative potential.

Table 9.58

BiIm^{2-}



A. Photophysical Data

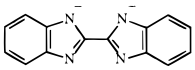
compound	solvent	abs (nm)	ε (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[(bpy)$_2$Ru(**BiIm**)Ru(bpy)$_2$]$^{2+}$	AN	498	21000	738 c	37 d	4.7 × 10^{-4} d			291
	Et/Met						680 u		291

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[(bpy)$_2$Ru(**BiIm**)Ru(bpy)$_2$]$^{2+}$	AN	SSCE	+0.75 [1] (Ru), +1.09 [1] (Ru)	−1.54 [>1] (bpy), −1.84 [>1] (bpy)	291

Table 9.59

BiBzIm^{2-}



A. Photophysical Data

compound	solvent	abs (nm)	ε (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[(bpy)$_2$Ru(**BiBzIm**)Ru(bpy)$_2$]$^{2+}$	AN	512	20000	733 c	60 d	2.0 × 10^{-4} d			291
	Et/Met						610 u 675 u		291
Ru$_3$									
[(bpy)Ru{(**BiBzIm**)Ru(bpy)$_2$}$_2$]$^{2+}$	AN	513	23000	734 c	58 d	2.2 × 10^{-4} d			291
	Et/Met						675 u		291

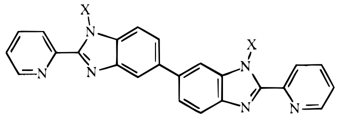
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[(bpy)$_2$Ru(**BiBzIm**)Ru(bpy)$_2$]$^{2+}$	AN	SCE	+0.74 [1] (Ru), +1.04 [1] (Ru)		292
	AN	SSCE		−1.49 (bpy), −1.78 (bpy)	291
Ru$_3$					
[(bpy)Ru{(**BiBzIm**)Ru(bpy)$_2$}$_2$]$^{2+}$	AN	SSCE	+0.32 [1] (Ru), +0.96 [2] (Ru)	−1.53 [2] (bpy), −1.83 [2] (bpy)	291

Table 9.60

bpbimH$_2$, X = H;

dmbpbim, X = CH$_3$



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[(bpy)$_2$Ru(**bpbimH$_2$**)Ru(bpy)$_2$]$^{4+}$	AN	459	27000		560 d				293,294
	BuCN			629 c			611 c		293,295
	Et/Met						611 u	2.77	293
[(bpy)$_2$Ru(**bpbimH$_2$**)Ru(4DCE-bpy)$_2$]$^{4+}$	BuCN			678			649		295
[(dmbpy)$_2$Ru(**bpbimH$_2$**)Ru(dmbpy)$_2$]$^{4+}$	AN				480 d				293
	Et/Met						611 u	2.22	293
[(dmbpy)$_2$Ru(**bpbimH$_2$**)Ru(phen)$_2$]$^{4+}$	AN	458	31300		480 d				293,294
	Et/Met						627 u		293
RuRh									
[(bpy)$_2$Ru(**bpbimH$_2$**)Rh(bpy)$_2$]$^{5+}$	AN	≈460 f	≈12300 f		<10 d				296
	nitrile						603 u		296
[(bpy)$_2$Ru(**bpbimH**)Rh(bpy)$_2$]$^{4+}$	AN			≈657 f					294
	nitrile						606 u		296
[(dmbpy)$_2$Ru(**bpbimH$_2$**)Rh(phen)$_2$]$^{5+}$	nitrile						614 u		296
[(bpy)$_2$Ru(**dmbpbim**)Rh(bpy)$_2$]$^{5+}$	nitrile						609 u		296

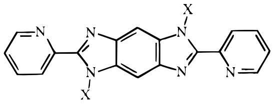
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[(bpy)$_2$Ru(**bpbimH$_2$**)Ru(bpy)$_2$]$^{4+}$	AN	Fc/Fc$^+$	+0.777 (Ru)	−1.780 i [1] (BL), −1.875 [1] (bpy), −2.145 [1] (bpy)	293
	AN	Ag/AgCl	+0.94 [2] (Ru)		297
	AN/H$_2$O	Ag/AgCl	+0.94 [1] (Ru), +0.98 [1] (Ru)		298
[(dmbpy)$_2$Ru(**bpbimH$_2$**)Ru(dmbpy)$_2$]$^{4+}$	AN	Fc/Fc$^+$	+0.680 (Ru)		293
[(dmbpy)$_2$Ru(**bpbimH$_2$**)Ru(phen)$_2$]$^{4+}$	AN/H$_2$O	Ag/AgCl	+0.86 [1] (Ru-dmbpy), +0.97 [1] (Ru-phen)		298
RuRh					
[(bpy)$_2$Ru(**bpbimH$_2$**)Rh(bpy)$_2$]$^{5+}$	AN	Fc/Fc$^+$	+0.774 [1] (Ru)	−1.147 [1] (Rh)	296
[(bpy)$_2$Ru(**bpbimH**)Rh(bpy)$_2$]$^{4+}$	AN	Fc/Fc$^+$	+0.680 [1] (Ru)	irreproducible	296
[(dmbpy)$_2$Ru(**bpbimH$_2$**)Rh(phen)$_2$]$^{5+}$	AN	Fc/Fc$^+$	+0.683 [1] (Ru)	−1.127 [1] (Rh)	296
[(bpy)$_2$Ru(**dmbpbim**)Rh(bpy)$_2$]$^{5+}$	AN	Fc/Fc$^+$	+0.756 [1] (Ru)	−1.200 [1] (Rh)	296

Table 9.61

dpimbH$_2$, X = H;

bptb, X = S



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[(bpy)$_2$Ru(**dpimbH$_2$**)Ru(bpy)$_2$]$^{4+}$	AN	461	24900	680 u	606				265
	Et/Met						637 u	2.70†	299
[(bpy)$_2$Ru(**dpimbH**)Ru(bpy)$_2$]$^{3+}$	AN				<35 d				299
	Et/Met						651 u	0.101§	299
[(bpy)$_2$Ru(**dpimb**)Ru(bpy)$_2$]$^{2+}$	Et/Met						678 u		299
[(bpy)$_2$Ru(**bptb**)Ru(bpy)$_2$]$^{4+}$	AN	516	14300	746 u	115				265
RuRh									
[(bpy)$_2$Ru(**dpimbH$_2$**)Rh(bpy)$_2$]$^{5+}$	AN	≈460 f	≈12200		<10 d				296
	nitrile						632 u		296
[(bpy)$_2$Ru(**dpimbH**)Rh(bpy)$_2$]$^{4+}$	nitrile						633 u		296

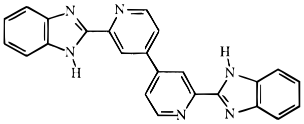
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[(bpy)$_2$Ru(**dpimbH$_2$**)Ru(bpy)$_2$]$^{4+}$	AN	Fc/Fc$^+$	+0.750 [1] (Ru), +0.830 [1] (Ru)		299
	AN	Fc/Fc$^+$		−1.79 i, −1.88 (bpy), −2.17 (bpy)	265
[(bpy)$_2$Ru(**bptb**)Ru(bpy)$_2$]$^{4+}$	AN	Fc/Fc$^+$	+0.96 [1] (Ru), +1.00 [1] (Ru)	−1.13 [1] (BL), −1.42 [1] (BL), −1.90 [2] (bpy)	265
RuRh					
[(bpy)$_2$Ru(**dpimbH$_2$**)Rh(bpy)$_2$]$^{5+}$	AN	Fc/Fc$^+$	+0.798 [1] (Ru)	−1.186 [1] (Rh)	296
[(bpy)$_2$Ru(**dpimbH**)Rh(bpy)$_2$]$^{4+}$	AN	Fc/Fc$^+$		−1.333 [1] (Rh)	296

† At 90 K. § At 171 K.

Table 9.62

bbbpyH$_2$



A. Photophysical Data

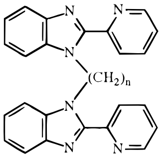
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
$[(bpy)_2Ru(\mathbf{bbbpyH_2})Ru(bpy)_2]^{4+}$	AN	498		719	202				294

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
$[(bpy)_2Ru(\mathbf{bbbpyH_2})Ru(bpy)_2]^{4+}$	AN/H$_2$O	Fc/Fc$^+$	+0.80 [2] (Ru)	−1.32 [1], −1.81 [1], −2.13 [1]	294

Table 9.63

pbim-S$_n$-pbim



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
$[(bpy)_2Ru(\mathbf{pbim\text{-}S_1\text{-}pbim})Ru(bpy)_2]^{4+}$	BuCN						628 c		295
$[(bpy)_2Ru(\mathbf{pbim\text{-}S_1\text{-}pbim})Ru(4DCE\text{-}bpy)_2]^{4+}$	BuCN			667 c			632 c		295
$[(bpy)_2Ru^{III}(\mathbf{pbim\text{-}S_1\text{-}pbim})Ru(4DCE\text{-}bpy)_2]^{5+}$	BuCN				0.0077				300
$[(bpy)_2Ru(\mathbf{pbim\text{-}S_2\text{-}pbim})Ru(4DCE\text{-}bpy)_2]^{4+}$	BuCN			667 c			643 c		295
$[(bpy)_2Ru^{III}(\mathbf{pbim\text{-}S_2\text{-}pbim})Ru(4DCE\text{-}bpy)_2]^{5+}$	BuCN				0.120				300
$[(bpy)_2Ru(\mathbf{pbim\text{-}S_3\text{-}pbim})Ru(4DCE\text{-}bpy)_2]^{4+}$	BuCN			674 c			646 c		295
$[(bpy)_2Ru(\mathbf{pbim\text{-}S_4\text{-}pbim})Ru(4DCE\text{-}bpy)_2]^{4+}$	BuCN			674 c			645 c		295
$[(bpy)_2Ru(\mathbf{pbim\text{-}S_5\text{-}pbim})Ru(4DCE\text{-}bpy)_2]^{4+}$	AN				500				300
	BuCN			678 c			651 c		295
$[(bpy)_2Ru^{III}(\mathbf{pbim\text{-}S_5\text{-}pbim})Ru(4DCE\text{-}bpy)_2]^{5+}$	BuCN				0.550†				300
$[(bpy)_2Ru(\mathbf{pbim\text{-}S_6\text{-}pbim})Ru(4DCE\text{-}bpy)_2]^{4+}$	BuCN						650 c		295
$[(bpy)_2Ru(\mathbf{pbim\text{-}S_{10}\text{-}pbim})Ru(4DCE\text{-}bpy)_2]^{4+}$	BuCN			678 c			651 c		295
RuRh									
$[(bpy)_2Ru(\mathbf{pbim\text{-}S_2\text{-}pbim})Rh(bpy)_2]^{5+}$	AN	≈458 f	≈14800 f		<10 d				296
	nitrile						609 u		296
$[(bpy)_2Ru(\mathbf{pbim\text{-}S_2\text{-}pbim})Rh(phen)_2]^{5+}$	nitrile						610 u		296

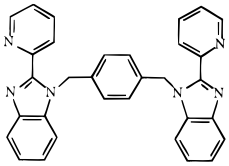
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
$[(bpy)_2Ru(\mathbf{pbim\text{-}S_2\text{-}pbim})Ru(bpy)_2]^{4+}$	AN	Fc/Fc$^+$	+0.830 (Ru)	−1.714 [1] (bpy), −1.918 [1] (bpy), −2.180 [1] (bpy)	293
	BuCN	Fc/Fc$^+$	+0.793 (Ru)		293
RuRh					
$[(bpy)_2Ru(\mathbf{pbim\text{-}S_2\text{-}pbim})Rh(bpy)_2]^{5+}$	AN	Fc/Fc$^+$	+0.825 [1] (Ru)	−1.175 [1] (Rh)	296
$[(bpy)_2Ru(\mathbf{pbim\text{-}S_2\text{-}pbim})Rh(phen)_2]^{5+}$	AN	Fc/Fc$^+$	+0.820 [1] (Ru)	−1.177 [1] (Rh)	296

† At 213 K.

Table 9.64

pbim-S$_B$-pbim

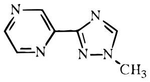


A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
$[(bpy)_2Ru(\mathbf{pbim\text{-}S_B\text{-}pbim})Ru(4DCE\text{-}bpy)_2]^{4+}$	BuCN			667 c			641 c		295

Table 9.65

mpzt



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru_2									
$[(bpy)_2Ru($**mpzt**$)Ru(bpy)_2Cl]^{3+}$	AN			no emission					301
	EtOH	530	19000						301
	MeOH						705 u		301

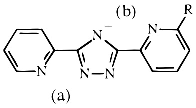
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru_2					
$[(bpy)_2Ru($**mpzt**$)Ru(bpy)_2Cl]^{3+}$	AN	SCE	+0.92, +1.41	−0.97, −1.51, −1.57, −1.76	301,302

Table 9.66

a-bpt-b⁻, R = H;

a-mbpt-b⁻, R = CH_3



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru_2									
$[(bpy)_2Ru($**a-bpt-b**$)Ru(bpy)_2]^{3+}$	AN	453	18500	648 c	100 d				303
	nitrile						608 c	3.6	303
	nitrile			648 c	100 d	2.1×10^{-3} a	608 c	3.6	304
					56 a				
$[(bpy)_2Ru($**a-bpt-b**$)Ru(phen)_2]^{3+}$	AN	440	23400	640	66 d				305
	EtOH						606		305
$[(phen)_2Ru($**a-bpt-b**$)Ru(bpy)_2]^{3+}$	AN	450	20400	636	51 d				305
	EtOH						603		305
Ru_2									
$[(phen)_2Ru($**a-bpt-b**$)Ru(phen)_2]^{3+}$	AN	421	35500	627	33 d				305
	EtOH						597		305
$[(bpy)_2Ru($**a-mbpt-b**$)Ru(bpy)_2]^{3+}$	AN			655 u	65 a				306
	EtOH	456	20200						306
	nitrile						610 u	3.8	306
RuRh									
$[(bpy)_2Ru($**a-bpt-b**$)Rh(ppy)_2]^{2+}$	EtOH	455	10000						307
	Et/Met			636	130 d		601	4.6	307
RuOs									
$[(bpy)_2Ru($**a-bpt-b**$)Os(bpy)_2]^{3+}$	AN	458	23000	751 c	30 d				303
	nitrile						726 c	0.67	303
$[(bpy)_2Ru($**b-bpt-a**$)Os(bpy)_2]^{3+}$	AN	452	22000	758 c	28 d				303
	nitrile						730 c	0.59	303
RuIr									
$[(bpy)_2Ru($**a-bpt-b**$)Ir(ppy)_2]^{2+}$	EtOH	465	12000						307
	Et/Met			635	130 d		600	4.7	307
Rh_2									
$[(ppy)_2Rh($**a-bpt-b**$)Rh(ppy)_2]^{+}$	EtOH	375	9000	no emission					307
	Et/Met						458	160	307
Os_2									
$[(bpy)_2Os($**a-bpt-b**$)Os(bpy)_2]^{3+}$	AN	600 sh		754 c	33 d				303
	AN	475	18000	762 u	33 d				308
	nitrile						742 c	0.34	303
	nitrile						765 u†	0.34	308
Ir_2									
$[(ppy)_2Ir($**a-bpt-b**$)Ir(ppy)_2]^{+}$	EtOH	420	1000						307
	Et/Met			484	70 d		473	4.8	307

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru_2					
$[(bpy)_2Ru($**a-bpt-b**$)Ru(bpy)_2]^{3+}$	AN	SCE	+1.04 [1] (Ru), +1.34 [1]	−1.40 [2] (bpy), −1.62 [1] (bpy), −1.67 [1], −2.22 [1], −2.33 i [1]	307
$[(bpy)_2Ru($**a-bpt-b**$)Ru(phen)_2]^{3+}$	AN	SCE	+1.07 [1], +1.38 [1]	−1.35 [1], −1.71 [1]	305
$[(phen)_2Ru($**a-bpt-b**$)Ru(bpy)_2]^{3+}$	AN	SCE	+1.06 [1], +1.37 [1]	−1.33, −1.71	305
$[(phen)_2Ru($**a-bpt-b**$)Ru(phen)_2]^{3+}$	AN	SCE	+1.04 [1], +1.34 [1]	−1.48, −1.71	305
$[(bpy)_2Ru($**a-mbpt-b**$)Ru(bpy)_2]^{3+}$	AN	SCE	+1.04 [1], +1.34 [1]	−1.37 [1] (bpy), −1.42 [1] (bpy), −1.62 [1] (bpy)	306

Table 9.66 (Continued)

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
RuRh					
[(bpy)$_2$Ru(**a-bpt-b**)Rh(ppy)$_2$]$^{2+}$	AN	SCE	+1.03 [1] (Ru), +1.39 [2]	−1.42 [1] (bpy), −1.65 [1] (bpy), −2.03 [1] (BL), −2.26 [1] (ppy), −2.49 i [1] (ppy)	307
RuOs					
[(bpy)$_2$Ru(**a-bpt-b**)Os(bpy)$_2$]$^{3+}$	AN	SCE	+0.73 [1] (Os), +1.20 [1] (Ru)	−1.33 [1] (bpy), −1.41 [1] (bpy)	309
[(bpy)$_2$Ru(**b-bpt-a**)Os(bpy)$_2$]$^{3+}$	AN	SCE	+0.65 [1] (Os), +1.30 [1] (Ru)	−1.36 [2] (bpy)	309
RuIr					
[(bpy)$_2$Ru(**a-bpt-b**)Ir(ppy)$_2$]$^{2+}$	AN	SCE	+1.05 [1] (Ru), +1.35 [1] (Ir)	−1.42 [1] (bpy), −1.66 [1] (bpy), −1.98 [1] (BL), −2.27 i [1] (ppy)	307
Rh$_2$					
[(ppy)$_2$Rh(**a-bpt-b**)Rh(ppy)$_2$]$^{+}$	AN	SCE	+1.36 i [1], +1.83 i [1]	−1.92 [1] (BL), −2.12 i [1] (ppy), −2.29 i [1] (ppy), −2.48 i [1] (ppy)	307
Os$_2$					
[(bpy)$_2$Os(**a-bpt-b**)Os(bpy)$_2$]$^{3+}$	AN	SCE	+0.64 [1], +0.85 [1]	−1.34 [2] (bpy), −1.58 [1] (bpy), −1.68 [1]	308
Ir$_2$					
[(ppy)$_2$Ir(**a-bpt-b**)Ir(ppy)$_2$]$^{+}$	AN	SCE	+1.13 i [1], +1.30 i [1]	−1.80 [1] (BL), −2.12 i (ppy), −2.29 i [1] (ppy), −2.44 i [1] (ppy)	307

† At 90 K.

Table 9.67

2,3-dpp and a-bpt-b$^-$

A. Photophysical Data

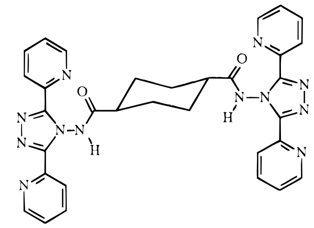
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_4$									
[(bpy)$_2$Ru(**a-bpt-b**)Ru{(**2,3-dpp**)Ru(bpy)$_2$}$_2$]$^{7+}$	AN	535		800 c	68 d	1 × 10^{-3} d			310
	Et/Met						600 c	4.0	310
							720 c	1.6	

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_4$					
[(bpy)$_2$Ru(**a-bpt-b**)Ru{(**2,3-dpp**)Ru(bpy)$_2$}$_2$]$^{7+}$	AN	SCE	+1.09 [1], +1.55 [2]	−0.64 [1], −0.89 [1], −1.49 [≈4], −1.75 [≈4]	310

Table 9.68

bpt-A10$_D$-bpt



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[(bpy)$_2$Ru(**bpt-A10$_D$-bpt**)Ru(bpy)$_2$]$^{4+}$	AN	446	25000	638 u	110 a				311
	Et/Met						585 u	4.37	311
RuOs									
[(bpy)$_2$Ru(**bpt-A10$_D$-bpt**)Os(bpy)$_2$]$^{4+}$	AN	450	22000	620 u	56 a				312
				724 u	34 a†				
	Et/Met						580 u	4.85	312
							715 u	0.90	
Os$_2$									
[(bpy)$_2$Os(**bpt-A10$_D$-bpt**)Os(bpy)$_2$]$^{4+}$	AN	477	15600	725 u	42 a				311
	Et/Met						716 u	0.95	311

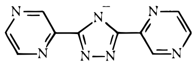
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[(bpy)$_2$Ru(**bpt-A10$_D$-bpt**)Ru(bpy)$_2$]$^{4+}$	AN	SCE	+1.33 [2] (Ru)	−1.30 [2] (bpy), −1.54 [2] (bpy)	311
RuOs					
[(bpy)$_2$Ru(**bpt-A10$_D$-bpt**)Os(bpy)$_2$]$^{4+}$	AN	SCE	+0.79 [1] (Os), +1.30 [1] (Ru)	−1.33 [2] (bpy), −1.51 [2] (bpy)	312
Os$_2$					
[(bpy)$_2$Os(**bpt-A10$_D$-bpt**)Os(bpy)$_2$]$^{4+}$	AN	SCE	+0.84 [2] (Os)	−1.27 [2] (bpy), −1.58 [2] (bpy)	311

† A longer-lived component is also present, but with intensity too low to measure lifetime.

Table 9.69

bpzt⁻



A. Photophysical Data

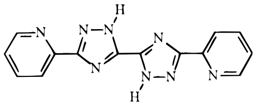
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
$[(\mathrm{bpy})_2\mathrm{Ru}(\mathbf{bpzt})\mathrm{Ru}(\mathrm{bpy})_2]^{3+}$	AN			670 u	106 a				306
	AN			671 u	200 d				313
	EtOH	449	26500						306
	Et/Met						617 u	7.03	313
	nitrile						610 u	5.0	306

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
$[(\mathrm{bpy})_2\mathrm{Ru}(\mathbf{bpzt})\mathrm{Ru}(\mathrm{bpy})_2]^{3+}$	AN	SCE	+1.16 [1], +1.46 [1]	−1.26 [1] (BL), −1.39, −1.55, −1.63	306

Table 9.70

bpbtH$_2$



A. Photophysical Data

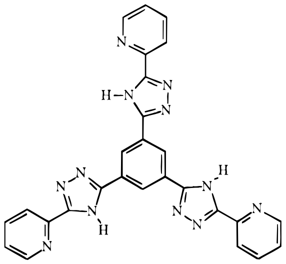
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
$[(\mathrm{bpy})_2\mathrm{Ru}(\mathbf{bpbtH_2})\mathrm{Ru}(\mathrm{bpy})_2]^{4+}$	AN	481	18000	711 c	118 d				314
	CH_2Cl_2			660 c	238 d				314
	EtOH			≈700 c	150 d				314
	H_2O (pH = 9)			686 c	94 d				314
Ru$_3$									
$[\{\mathrm{Ru}(\mathrm{bpy})_2\}_2(\mathbf{bpbt})\mathrm{Ru}(\mathrm{bpy})_2]^{4+}$	CH_2Cl_2			660 c	346 d				314
	EtOH			≈700 c	140 d				314
	AN	468	27000	711 c	82 d				314
	H_2O (pH = 0.5)			658 c	125 d				314
	H_2O (pH = 9)			675 c	93 d				314

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
$[(\mathrm{bpy})_2\mathrm{Ru}(\mathbf{bpbtH_2})\mathrm{Ru}(\mathrm{bpy})_2]^{4+}$	DMF	SCE	+0.85 [1], +1.01 [1]	−1.42 [2] (bpy), −1.67 [2] (bpy)	314
Ru$_3$					
$[\{\mathrm{Ru}(\mathrm{bpy})_2\}_2(\mathbf{bpbt})\mathrm{Ru}(\mathrm{bpy})_2]^{4+}$	DMF	SCE	+1.00 [1], +1.23 [1], +1.41 [1]	−1.35 [3] (bpy), −1.63 [3] (bpy)	314

Table 9.71

tpbH$_3$



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_3$									
$[\{(\mathrm{bpy})_2\mathrm{Ru}\}_2(\mathbf{tpb})\mathrm{Ru}(\mathrm{bpy})_2]^{3+}$	AN			683 u					301
	EtOH	475	27100						301
	MeOH						632 u		301
$[\{(\mathrm{bpy})_2\mathrm{Ru}\}_2(\mathbf{tpbH_3})\mathrm{Ru}(\mathrm{bpy})_2]^{6+}$	AN			620 u					301
	EtOH	441	32300						301
	MeOH						604 u		301

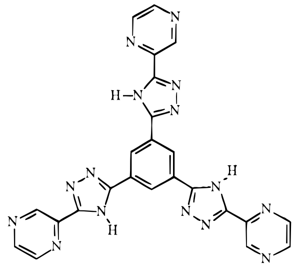
Table 9.71 (Continued)

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [*n*] (site)	E_{red}, V [*n*] (site)	ref(s)
Ru$_3$					
$[\{(bpy)_2Ru\}_2(\mathbf{tpb})Ru(bpy)_2]^{3+}$	AN	SCE	+0.86	−1.47 (bpy), −1.66, −1.82	301,302
$[\{(bpy)_2Ru\}_2(\mathbf{tpbH_3})Ru(bpy)_2]^{6+}$	AN	SCE	+1.18		301,302

Table 9.72

tpzbH$_3$



A. Photophysical Data

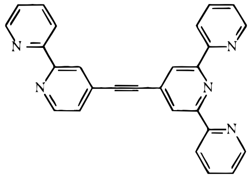
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_3$									
$[\{(bpy)_2Ru\}_2(\mathbf{tpzb})Ru(bpy)_2]^{3+}$	AN			677 u					301
	EtOH	460							301
	MeOH						650 u		301
$[\{(bpy)_2Ru\}_2(\mathbf{tpzbH_3})Ru(bpy)_2]^{6+}$	AN			675 u					301
	EtOH	445							301
	MeOH						645 u		301
Ru$_6$									
$[\{(bpy)_2Ru\}_3(\mathbf{tpzb})\{Ru(bpy)_2Cl\}_3]^{6+}$	AN			775 u					301
	EtOH	515	67200						301
	MeOH						685 u		301
$[\{(bpy)_2Ru\}_3(\mathbf{tpzbH_3})\{Ru(bpy)_2Cl\}_3]^{9+}$	AN			769 u					301
	EtOH	530	65000						301
	MeOH						695 u		301

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [*n*] (site)	E_{red}, V [*n*] (site)	ref(s)
Ru$_3$					
$[\{(bpy)_2Ru\}_2(\mathbf{tpzb})Ru(bpy)_2]^{3+}$	AN	SCE	+1.05	adsorption	301
Ru$_6$					
$[\{Ru(bpy)_2\}_3(\mathbf{tpzb})\{Ru(bpy)_2Cl\}_3]^{6+}$	AN	SCE	+0.94 ($Ru(bpy)_2Cl$), +1.16 ($Ru(bpy)_2$)	−1.14 [1] (BL), −1.50 (bpy), −1.71 (bpy)	301
$[\{Ru(bpy)_2\}_3(\mathbf{tpzbH_3})\{Ru(bpy)_2Cl\}_3]^{9+}$	AN	SCE	+0.97 ($Ru(bpy)_2Cl$), +1.35 ($Ru(bpy)_2$)	adsorption	301

Table 9.73

bpy-E4$_C$-tpy

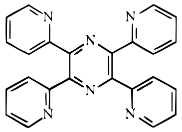


A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
FeRu$_2$									
$[\{(bpy)_2Ru(\mathbf{bpy\text{-}E4_C\text{-}tpy})\}_2Fe]^{6+}$	acetone	589	41900	620					207

Table 9.74

tpp



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[(tpy)Ru(**tpp**)Ru(tpy)]$^{4+}$	AN	650		826 u	100 a				260
RuIr									
[(tpy)Ru(**tpp**)IrCl$_3$]$^{2+}$	AN	≈660	≈2400 f	810 u	22 d				315

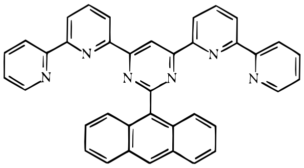
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[(tpy)Ru(**tpp**)Ru(tpy)]$^{4+}$	AN	SCE	+1.43 [1] (Ru), +1.72 [1] (Ru)	−0.34	260
	AN	SSCE	+1.40 [1] (Ru), +1.71 [1] (Ru)	−0.39 [1] (BL), −0.86 [1] (BL), −1.43 [2] (tpy), −1.86 [2] (BL)	316
RuIr					
[(tpy)Ru(**tpp**)IrCl$_3$]$^{2+}$	AN	Ag/AgCl§	+1.56 [1] (Ru), +1.92 [1] (Ir)		315
	DMF	Ag/AgCl§		−0.29 [1] (BL), −0.83 [1] (BL), −1.42 [1] (tpy)	315

§ This electrode is +0.268 V vs NHE.

Table 9.75

tpy-A-tpy



A. Photophysical Data

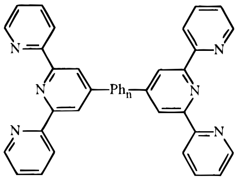
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[(tpy)Ru(**tpy-A-tpy**)Ru(tpy)]$^{4+}$	AN	≈620 f		845 c	60 d	5×10^{-4} d			317
	BuCN						775 c	1.6	317

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[(tpy)Ru(**tpy-A-tpy**)Ru(tpy)]$^{4+}$	AN	SCE	+1.41 [1] (Ru), +1.58 [1] (Ru)	−0.45 [1] (BL), −1.07 [1] (BL), −1.42 [1], −1.52 [1] (tpy), −1.58 [1] (tpy)	318

Table 9.76

tpy-tpy, n = 0
tpy-Ph-tpy, n = 1
tpy-Ph$_2$-tpy, n = 2



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em$_{RT}$ (nm)	τ_{RT} (ns)	Φ_{RT}	Em$_{77K}$ (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[(ttpy)Ru(**tpy-tpy**)Ru(ttpy)]$^{4+}$	AN	≈520 f	≈58000 f						319
	Et/Met						674 c	12.9	319
RuRh									
[(ttpy)Ru(**tpy-tpy**)Rh(ttpy)]$^{5+}$	AN	≈516 f	≈30200 f						319
	Et/Met						674 c	12.5	319

Table 9.76 (Continued)

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
[(ttpy)Ru(**tpy-Ph-tpy**)Rh(ttpy)]$^{5+}$	AN	≈497 f	≈35100 f						319
	Et/Met						636 c	13.0	319
[(ttpy)Ru(**tpy-Ph$_2$-tpy**)Rh(ttpy)]$^{5+}$	AN	≈493 f	≈39200 f						319
	Et/Met						629 c	13.2	319
RuOs									
[(ttpy)Ru(**tpy-tpy**)Os(ttpy)]$^{4+}$	AN	678	10500						97,320,321
	BuCN			800 u	110 d	0.13×10^{-2} †			97,320,321
[(ttpy)Ru(**tpy-Ph-tpy**)Os(ttpy)]$^{4+}$	AN	671	8500						97,320,321
	BuCN			746 u	190 d	1.5×10^{-2} †			97,320,321
[(ttpy)Ru(**tpy-Ph$_2$-tpy**)Os(ttpy)]$^{4+}$	AN	670	7700						97,320,321
	BuCN			738 u	200 d	1.3×10^{-2} †			97,320,321

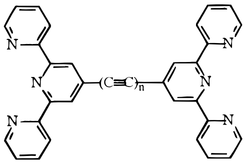
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru$_2$					
[(ttpy)Ru(**tpy-tpy**)Ru(ttpy)]$^{4+}$	AN	SCE	+1.31 [2] (Ru)		319
RuRh					
[(ttpy)Ru(**tpy-tpy**)Rh(ttpy)]$^{5+}$	AN	SCE	+1.31 [1] (Ru)	−0.54 i (Rh), −1.22 [1], −1.44 [1]	319
[(ttpy)Ru(**tpy-Ph-tpy**)Rh(ttpy)]$^{5+}$	AN	SCE	+1.29 [1] (Ru)	−0.56 i (Rh), −1.18 [1], −1.41 [1]	319
[(ttpy)Ru(**tpy-Ph$_2$-tpy**)Rh(ttpy)]$^{5+}$	AN	SCE	+1.27 [1] (Ru)	−0.56 i (Rh), −1.20 [1], −1.37 [1]	319
RuOs					
[(ttpy)Ru(**tpy-tpy**)Os(ttpy)]$^{4+}$	AN	SCE	+0.94 [1] (Os), +1.31 [1] (Ru)	−0.97 [1] (BL)	321
[(ttpy)Ru(**tpy-Ph-tpy**)Os(ttpy)]$^{4+}$	AN	SCE	+0.94 [1] (Os), +1.29 [1] (Ru)	−1.16 [1] (BL)	321
[(ttpy)Ru(**tpy-Ph$_2$tpy**)Os(ttpy)]$^{4+}$	AN	SCE	+0.94 [1] (Os), +1.28 [1] (Ru)	−1.18 [1] (BL)	321

† Excitation at 650 nm.

Table 9.77

tpy-E$_n$-tpy

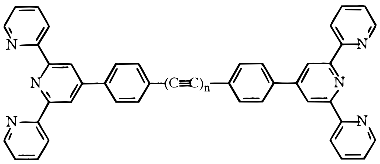


A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[(tpy)Ru(**tpy-E$_1$-tpy**)Ru(tpy)]$^{4+}$	AN	515	32800	722	565 d	1.4×10^{-3} d			322
[(tpy)Ru(**tpy-E$_2$-tpy**)Ru(tpy)]$^{4+}$	AN	512	39300	735	720 d	2.1×10^{-3} d			322
RuOs									
[(tpy)Ru(**tpy-E$_1$-tpy**)Os(tpy)]$^{4+}$	AN			746	0.014 d	$<1 \times 10^{-4}$ d			323
					225 d	0.016 d			
	EtOH						640	7.2×10^{-4}	323
							730	2.4	
[(tpy)Ru(**tpy-E$_2$-tpy**)Os(tpy)]$^{4+}$	AN			760	0.020 d	$<1 \times 10^{-4}$ d			323
					200 d	0.013 d			
	EtOH						650	1.07×10^{-3}	323
							745	2.2	

Table 9.78

tpy-Ph-E$_n$-Ph-tpy

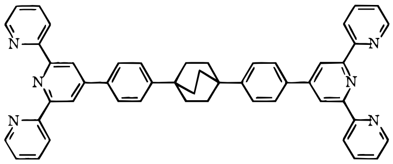


A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru$_2$									
[(tpy)Ru(**tpy-Ph-E$_1$-Ph-tpy**)Ru(tpy)]$^{4+}$	AN	488	48500	670	3.2 d	$<1 \times 10^{-4}$ d			322
[(tpy)Ru(**tpy-Ph-E$_2$-Ph-tpy**)Ru(tpy)]$^{4+}$	AN	490	62000	665	5.5 d	$<1 \times 10^{-4}$ d			322

Table 9.79

tpy-Ph-bco-Ph-tpy



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
RuOs									
[(ttpy)Ru(**tpy-Ph-bco-Ph-tpy**)Os(ttpy)]$^{4+}$	DMF/CH_2Cl_2	670	7600	640 u	1.1 a		634 u	0.22	324
				736 u	125 a		727 u	2.8§	
[(ttpy)Ru(**tpy-Ph-bco-Ph-tpy**)Os^{III}(ttpy)]$^{5+}$	DMF/CH_2Cl_2			640 u	1.1 a		632 u	10.5	324

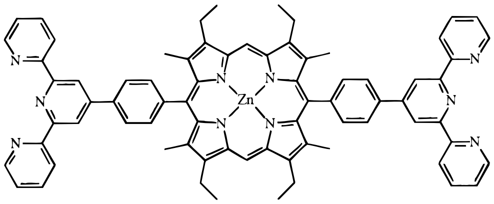
B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
RuOs					
[(ttpy)Ru(**tpy-Ph-bco-Ph-tpy**)Os(ttpy)]$^{4+}$	AN	SCE	+0.89 [1] (Os), +1.24 [1] (Ru)		324
	DMF	SCE		−1.17 [2] (ligands), −1.45 [2] (ligands)	324

[§] Double exponential decay.

Table 9.80

tpy-ZnP-tpy



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru_2									
[(ttpy)Ru(**tpy-ZnP-tpy**)Ru(ttpy)]$^{4+}$	AN	≈540 f		650 c	0.240 d				325

B. Electrochemical Data

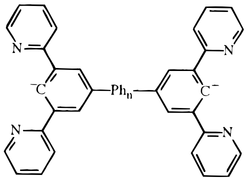
compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Ru_2					
[(ttpy)Ru(**tpy-ZnP-tpy**)Ru(ttpy)]$^{4+}$	AN	SCE	+0.66 [1] (porphyrin), +0.82 [1] (porphyrin)	−1.24 [1] (tpy), −1.47 [1] (tpy)	325

Table 9.81

(dpb-dpb)$^{-2}$, n = 0

(dpb-Ph-dpb)$^{-2}$, n = 1

(dpb-Ph_2-dpb)$^{-2}$, n = 2



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Ru_2									
[(ttpy)Ru(**dpb-dpb**)Ru(ttpy)]$^{2+}$	AN	547	29350						326
	BuCN			798 u	3.96 d	3.7×10^{-5} d	762 u	0.44	326
RuOs									
[(ttpy)Ru(**dpb-dpb**)Os(ttpy)]$^{2+}$	AN	770	2700						326
	BuCN			816 u	†	5.4×10^{-6} d	834 u	†	326
	BuCN			≈816 u	0.35 d		≈750 u	7.2×10^{-4}	327
				940 u	†		837 u	0.400	
[(ttpy)Ru(**dpb-Ph-dpb**)Os(ttpy)]$^{2+}$	AN	770	2900						327
	BuCN			800 u	3.5 d		750 u	0.042	327
				920 u	†		837 u	0.370	
[(ttpy)Ru(**dpb-Ph_2-dpb**)Os(ttpy)]$^{2+}$	AN	770	3000						327
	BuCN			792 u	4.9 d		750 u	0.178	327
				916 u	†		840 u	§	

Table 9.81 (Continued)

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Os_2									
[(ttpy)Os(**dpb-dpb**)Os(ttpy)]$^{2+}$	AN	770	4500						326
	BuCN			820 u	†	2.4 × 10^{-6} d	†	†	326

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [*n*] (site)	E_{red}, V [*n*] (site)	ref(s)
Ru_2					
[(ttpy)Ru(**dpb-dpb**)Ru(ttpy)]$^{2+}$	AN	SCE	+0.34 [1] (Ru), +0.50 [1] (Ru)	−1.55 [1] (ttpy)	326,328,329
RuOs					
[(ttpy)Ru(**dpb-dpb**)Os(ttpy)]$^{2+}$	AN	SCE	+0.29 [1] (Os), +0.51 [1] (Ru)	−1.48 (ttpy)	326
[(ttpy)Ru(**dpb-Ph-dpb**)Os(ttpy)]$^{2+}$	AN	SCE	+0.33 [1] (Os), +0.53 [1] (Ru)	−1.50 i (ttpy)	327
[(ttpy)Ru(**dpb-Ph_2-dpb**)Os(ttpy)]$^{2+}$	AN	SCE	+0.33 [1] (Os), +0.52 [1] (Ru)	−1.50 i (ttpy)	327
Os_2					
[(ttpy)Os(**dpb-dpb**)Os(ttpy)]$^{2+}$	AN	SCE	+0.22 [1] (Os), +0.34 [1] (Os)	−1.53 (ttpy)	326,328

† Too weak to be measured. § Hidden by the tail of the Ru-based emission.

Table 9.82

dppm $P(Ph)_2-CH_2-P(Ph)_2$

A. Photophysical Data

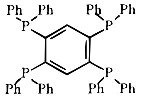
compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Pd_2									
[(CNN)Pd(**dppm**)Pd(CNN)]$^{2+}$	AN	457	4800	608 u	≤1.0 a				190
	BuCN						≈545 u	0.0022	190

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [*n*] (site)	E_{red}, V [*n*] (site)	ref(s)
Pd_2					
[(CNN)Pd(**dppm**)Pd(CNN)]$^{2+}$	CH_2Cl_2	SCE	+1.20 i	−1.30 i	190

Table 9.83

tppb



A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
NiOs									
[(dppb)Ni(**tppb**)Os$(bpy)_2$]$^{4+}$	AN	≈470 f		610	9 d	0.002 d			330
PdOs									
[(dppb)Pd(**tppb**)Os$(bpy)_2$]$^{4+}$	AN	≈470 f		605	12 d	0.002 d			330
Os_2									
[$(bpy)_2$Os(**tppb**)Os$(bpy)_2$]$^{4+}$	AN	≈470 f		603	400 d	0.063 d			330
OsPt									
[$(bpy)_2$Os(**tppb**)Pt(dppb)]$^{4+}$	AN	≈470 f		603	251 d	0.044 d			330

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [*n*] (site)	E_{red}, V [*n*] (site)	ref(s)
NiOs					
[(dppb)Ni(**tppb**)Os$(bpy)_2$]$^{4+}$	AN	SCE	+1.36 [1] (Os)	−0.18 [1] (Ni), −0.45 [1] (Ni), −1.30 [1] (bpy)	330
PdOs					
[(dppb)Pd(**tppb**)Os$(bpy)_2$]$^{4+}$	AN	SCE	+1.37 [1] (Os)	−0.60 [2] (Pd), −1.31 [1] (bpy)	330
Os_2					
[$(bpy)_2$Os(**tppb**)Os$(bpy)_2$]$^{4+}$	AN	SCE	+1.43 [2] (Os)	−1.27 [1] (bpy)	330
OsPt					
[$(bpy)_2$Os(**tppb**)Pt(dppb)]$^{4+}$	AN	SCE	+1.37 [1] (Os)	−0.76 [2] (Pt), −1.30 [1] (bpy)	330

Table 9.84

$S(C_2H_5)_2$

A. Photophysical Data

compound	solvent	abs (nm)	ϵ (M^{-1} cm^{-1})	Em_{RT} (nm)	τ_{RT} (ns)	Φ_{RT}	Em_{77K} (nm)	τ_{77K} (μs)	ref(s)
Pt_2									
[(bph)Pt{**$S(C_2H_5)_2$**}$_2$Pt(bph)]	CH_2Cl_2	340	23000	497 c	10500	0.0077			331
	CH_2Cl_2/EtOH						490 c	12.2	331

B. Electrochemical Data

compound	solvent	RE	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	ref(s)
Pt_2					
[(bph)Pt{**$S(C_2H_5)_2$**}$_2$Pt(bph)]	CH_2Cl_2	SSCE	+1.35 i [1] (Pt)		331

10. Abbreviations

$A5_B$-(bpy)$_3$	1,3,5-tris[[[(2,2′-bipyridyl-5-yl)carbonyl]benzylamino]methyl]benzene
$A5_B$-(5CE-bpy)$_3$	1,3,5-tris[[[[5-(ethoxycarbonyl)-2,2′-bipyridyl-5′-yl]carbonyl]benzylamino]methyl]benzene
$A5_C$-(bpy)$_3$	1,3,5-tris[4-[[(2,2′-bipyridyl-5-ylcarbonyl)benzylamino]methyl]phenyl]benzene
a-bpt-b$^-$	deprotonated 3,5-bis(pyridin-2-yl)-1,2,4-triazole
AN	acetonitrile
bbbpyH_2	2,2′-bis(2-benzimidazolyl)-4,4′-bipyridine
4-benzyl-py	4-benzylpyridine
BiBzIm^{2-}	deprotonated 2,2′-bibenzimidazole
BiIm^{2-}	deprotonated 2,2′-biimidazole
biq	2,2′-biquinoline
bpbimH_2	2,2′-bis(2-pyridyl)bibenzimidazole
bpbtH_2	5,5′-bis(2-pyridyl)-3,3′-bi(1,2,4-triazole)
bph	biphenyl dianion
bpy	2,2′-bipyridine
4,4′-bpy	4,4′-bipyridine
bpy-a-bpy	see Table 9.26
bpy-aa-bpy	see Table 9.27
bpy-$A5_A$-bpy	1,10-bis[[[(2,2′-bipyridinyl-5-yl)carbonyl]benzylamino]methyl]anthracene
bpy-bpy-bpy	see Table 9.30
bpy-$E4_C$	deprotonated 4-ethynyl-2,2′-bipyridine
bpy-$E4_C$-tpy	see Table 9.73
bpy-$E5_A$-bpy	1,4-bis[2-(2,2′-bipyridin-5-yl)ethenyl]bicyclo[2.2.2.]octane
bpy-$E5_B$-bpy	1,4-bis[2-(2,2′-bipyridin-5-yl)ethynyl]bicyclo[2.2.2.]octane
bpy$_a$-bpy$_b$	2,2′:3′,2″:6″,2‴-quaterpyridine
bpym	2,2′-bipyrimidine
bpt-$A10_D$-bpt	see Table 9.68
bptb	2,6-bis(2-pyridyl)-2,2′:6,2″-thiazolo[4,5-*d*]benzothiazole
BPTZ	3,6-bis(2-pyridyl)tetrazine
bpzt$^-$	deprotonated 3,5-bis(pyrazin-2-yl)-1,2,4-triazole
bsd	2,1,3-benzoselenadiazole
btd	2,1,3-benzothiadiazole
BTMFbpy	4,4′-bis(trifluoromethyl)-2,2′-bipyridine
BuCN	butyronitrile
bzq	benzo[*h*]quinoline
cage-phen$_3$	see Table 9.47
caten	see Table 9.46
Cl_2dpq	6,7-dichloro-2,3-bis(2-pyridyl)quinoxaline
CNN	C-deprotonated 2-acetylpyridine phenylhydrazone
Cp	cyclopentadienyl anion
cyclam	1,4,8,11-tetraazacyclotetradecane
cyclo-phen	see ref 257
dabpy	4,4′-diamino-2,2′-bipyridine
dcbpyH_2	4,4′-dicarboxy-2,2′-bipyridine
DCE	1,2-dichloroethane
4DCE-bpy	4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine
DCO-bpy	4,4′-bis(isopropoxycarbonyl)-2,2′-bipyridine
deabpy	4,4′-bis(diethylamino)-2,2′-bipyridine
dien	diethylenetriamine
dmbpbim	1,1′-dimethyl-2,2′-bis(2-pyridyl)-6,6′-bibenzimidazole
dmbpy	4,4′-dimethyl-2,2′-bipyridine
5,5′-dmbpy	5,5′-dimethyl-2,2′-bipyridine
5,5′-dmbpy-E6-5,5′-dmbpy	see Table 9.34
DMF	dimethylformamide
dmphen	4,7-dimethylphenanthroline
DMSO	dimethyl sulfoxide
(dpb-dpb)$^{2-}$	deprotonated 3,3′,5,5′-tetrapyridylbiphenyl
(dpb-Ph$_n$-dpb)$^{2-}$	see Table 9.81
dpbq	2,3-bis(2′-pyridyl)benzo[*g*]quinoxaline
dpimbH_2	2,6-bis(2′-pyridyl)benzdiimidazole
dpop	dipyrido(2,3-*a*:2′,3′-*h*)phenazine
2,3-dpp	2,3-bis(2-pyridyl)pyrazine
2,5-dpp	2,5-bis(2-pyridyl)pyrazine
dppb	1,2-bis(diphenylphosphino)benzene
dppe	1,2-bis(diphenylphosphino)-*cis*-ethene
dppm	bis(diphenylphosphino)methane
dpq	2,3-bis(2′-pyridyl)quinoxaline
dpq-dpq	2,2′,3,3′-tetra-2-pyridyl-6,6′-biquinoxaline
dpte	1,2-bis(diphenylthio)ethane
DPT$^-$	deprotonated 1,3-diphenyltriazene
dtol-phen	2,9-di-*p*-tolyl-1,10-phenanthroline
Et/Met	ethanol/methanol
EtOH	ethanol
FAF	2,6-bis(4,5-diazafluoren-9-ylidene)adamantane
Fc	ferrocene
hacod-bpy$_6$	1,4,7,10,13,16-hexakis[(2,2′-bipyridin-6-yl)methyl]-1,4,7,10,13,16-hexaazacyclooctodecane
HAT	1,4,5,8,9,12-hexaazatriphenylene
HMPA	hexamethylphosphoramide
knot-k-nn	see Table 9.45
m-nn	see Table 9.44
mbptH	3-(6-methylpyridin-2-yl)-5-(pyridin-2-yl)-1,2,4-triazole
Me_2-4,4′-bpy	3,3′-dimethyl-4,4′-bipyridine
4Mebpy-bd4-bpy4Me	1,4-bis(4-methyl-2,2′-bipyridin-4′-yl)buta-1,3-diene
4Mebpy-ch4-bpy4Me	1,4-bis(4-methyl-2,2′-bipyridin-4′-yl)-2-cyclohexene-5,6-dicarboxylic acid diethyl ester
4Mebpy-$E4_A$-bpy4Me	*trans*-1,2-bis(4′-methyl-2,2′-bipyrid-4-yl)ethene

4Mebpy-E4$_B$-bpy4Me	1,4-bis[2-(4′-methyl-2,2′-bipyrid-4-yl)ethenyl]benzene
4Mebpy-P4$_0$-bpy4Me	1,4-bis(4-methyl-2,2′-bipyridin-4′-yl)benzene
4Mebpy-P4$_n$-bpy4Me	see Table 9.22
4Mebpy-S4$_2$-Cp	see Table 9.16
4Mebpy-S4$_A$-bpy4Me	see Table 9.18
4Mebpy-S4$_B$-bpy4Me	see Table 9.18
4Mebpy-S4$_C$-bpy4Me	see Table 9.18
4Mebpy-S4$_D$-bpy4Me	1,12-bis(4-methyl-2,2′-bipyrid-4′-yl)-2,11-diazadodecane
4Mebpy-S4$_E$-bpy4Me	1,11-bis(4-methyl-2,2′-bipyrid-4′-yl)-6-methyl-2,6,10-triazaundecane
4Mebpy-S4$_n$-bpy4Me	see Table 9.17
6Mebpy-S6$_2$-bpy6Me	1,2-bis(6′-methyl-2,2′-bipyridin-6-yl)ethane
2,3-Medpp$^+$	2-[2-(1-methylpyridiniumyl)]-3-(2-pyridyl)pyrazine
Me$_2$dpq	6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline
Me$_4$bpy	4,4′,5,5′-tetramethyl-2,2′-bipyridine
1-MeIm	1-methylimidazole
(MeO)$_2$-bpy	4,4′-dimethoxy-2,2′-bipyridine
MeOH	methanol
2,9-Me$_2$-phen	2,9-dimethyl-1,10-phenanthroline
Me$_4$phen	3,4,7,8-tetramethyl-1,10-phenanthroline
9Mephen-S2$_2$-phen9Me	1,2-bis(9-methyl-1,10-phenanthrolin-2-yl)ethane
4-Mepy	4-methylpyridine
2Me-THF	2-methyltetrahydrofuran
mppy	3-methyl-2-phenylpyridine
mpzt	1-methyl-3-(pyrazin-2-yl)-1,2,4-triazole
N-bpy$_3$	see Table 9.37
NHE	normal hydrogen electrode
nitrile	propionitrile/butyronitrile
NMF	*N*-methylformamide
PAP	see Table 9.48
pbim-S$_B$-pbim	see Table 9.64
pbim-S$_n$-pbim	see Table 9.63
pbpy-Ph-E$_n$-Ph-pbpy	see Table 9.39
PBu$^n{}_3$	tri-*n*-butylphosphine
PC	propylene carbonate
phen	1,10-phenanthroline
PPh$_3$	triphenylphosphine
ppy	2-phenylpyridine anion
ppz	4′,7′-phenanthrolino-5′,6′:5,6-pyrazine
ptpy	2-(*p*-tolyl)pyridine
PTZ	phenothiazine
PTZ-py	10-(4-picolyl)phenothiazine
py	pyridine
py-crown-py	see Table 9.11
py-E4$_A$-py	*trans*-1,2-bis(4-pyridyl)ethylene
py-E4$_B$-py	1,4-bis(4-pyridyl-2-ethyl)benzene
py-NN-py	4,4′-azobispyridine
py-S4$_n$-py	see Table 9.7
pyz	pyrazine
QP	2,2′:6′,2″:6″,2‴-quaterpyridine
QP$_B$	2,2′:4′,4″:2″,2‴-quaterpyridine
SCE	saturated calomel electrode
SSCE	sodium saturated calomel electrode
tap	1,4,5,8-tetraazaphenanthrene
THF	tetrahydrofuran
tpbH$_3$	1,3,5-tris[5-(pyridin-2-yl)-1,2,4-triazol-3-yl]benzene
tpp	2,3,5,6-tetrakis(2′-pyridyl)pyrazine
tppb	1,2,4,5-tetrakis(diphenylphosphino)benzene
tpzbH$_3$	1,3,5-tris[5-(pyrazin-2-yl)-1,2,4-triazol-3-yl]benzene
tpy	2,2′,2″-terpyridine
tpy-E$_n$-tpy	see Table 9.77
tpy-Ph$_n$-tpy	see Table 9.76
tpy-Ph-bco-Ph-tpy	see Table 9.79
tpy-Ph-E$_n$-Ph-tpy	see Table 9.78
tpy-ZnP-tpy	[5,15-bis[4-(4′-phenyl-2,2′:6′,2″-terpyridyl)phenyl]-3,7,13,17-tetraethyl-2,8,12,18-tetramethylporphyrin]zinc(II)
tpy-tpy	see Table 9.76
tpy-A-tpy	see Table 9.75
ttpy	4′-(*p*-tolyl)-2,2′,6′,2″-terpyridine
ZnTPyP	*meso*-[5,10,15,20-tetrakis(pyridyl)porphyrin]zinc(II)

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