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Review

Excited-state equilibration: a process leading to long-lived metal-to-ligand charge transfer luminescence in supramolecular systems

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Contents

Abstract

A recently developed strategy to prolong the luminescence lifetime of metal polypyridine complexes is discussed, and various resulting supramolecular systems are presented. The intervening mechanism demands that certain thermodynamic and kinetic parameters are satisfied, notably rapid and reversible electronic energy transfer between lowest-lying isoenergetic triplet excited states located on an inorganic moiety, e.g., a triplet metal-to-ligand charge transfer state (^{3}MLCT), and localised on a separate organic chromophore, such as a triplet $^3\pi$–π^* state, although the involvement of other states is also considered. Originally implemented with a pyrenyl-appended Ru(II) polypyridine complex, the generality of this approach has been demonstrated through the judicious combination of different metal complexes having ^{3}MLCT states in conjunction with various matched organic chromophores and thus presents a new tool to instil made-to-order properties in supramolecular systems. Multichromophoric species and systems invoking second-sphere interactions are also considered.

Keywords: Metal polypyridine complexes; Excited-state equilibration; Energy transfer; Luminescence lifetimes; Supramolecular photochemistry/photophysics

1. Introduction

Ruthenium(II) polypyridine complexes, most notably $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine), and to a lesser extent analogous osmium(II), rhenium(I), iridium(III) and copper

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(I) complexes have been subject to an intense research effort due to a combination of their desirable absorption, photophysical and redox properties [1]. As well as being of interest for reasons of fundamental research, these increasingly well-understood species have been introduced into numerous supramolecular systems [2] rivalled only by porphyrin and metalloporphyrin species as the choice for active components for photoinduced electron/energy transfer processes [3].

In addition to quantum yields and wavelength of luminescence, one fundamental property of these photoactive compounds concerns their luminescence lifetimes. A greater control over this parameter can lend a greater flexibility and scope to the applications, which could be realised with these species. For example, species with long-luminescence lifetimes can find use as sensors whose luminescence can be measured after the residual background fluorescence has decayed, either directly as oxygen sensors (due to energy transfer to ground-state diatomic oxygen) or after coupling with an appropriate receptor to give a more general strategy towards signalling the presence of a plethora of guest-species [4]. Also their better adaptation to participate as photosensitizers in bimolecular processes and to promote processes such as energy transfer in supramolecular systems has been identified [5].

Excited-state lifetimes of metal polypyridine complexes, which typically invoke the lowest lying triplet metal-to-ligand charge transfer (^{3}MLCT) state, are to a large extent governed by the non-radiative deactivation processes [6]. Besides population of thermally accessible ligand field states, these energy loss-channels include vibrational deactivation to the ground state in accordance with the “energy gap” law developed by Meyer for metal–polypyridine complexes, where the lower the energy of the excited state, E_{00} (and hence smaller the number of vibrational quanta required to effect the deexcitation), the faster the rate of the overall process [7]. This appears to be an unfortunate scenario, as red-emitters are interesting, for example in biological applications where these species can be effectively interrogated due to the penetration of red-light into tissue, and as low-lying energy traps in multichromophore arrays, reminiscent of the protein-embedded natural photosynthetic apparatus [8].

A second property governing the rate of non-radiative decay concerns the degree of excited state distortion compared to the ground state, in the weak coupling limit [9]. A resulting rule of thumb (which, as the energy gap law, has its foundation in Franck–Condon factors for non-radiative transitions between quantum states) is that systems with small variations in excited state versus ground state geometries (as MLCT emitters exhibiting a high degree of electronic delocalisation in the acceptor ligand of the MLCT state) will exhibit longer excited state lifetimes compared with systems with larger excited-state distortion [9,10].

Thus, approaches to designing long-lifetime species according the above cited rules typically involves changing the inherent properties of these systems such as energies of lowest-lying ^{3}MLCT levels and/or the ligands involved.

In a 1992 article by Ford and Rodgers, a new strategy was reported [11]. This new strategy was based on coupling a Ru(II) polypyridine emitter with an organic chromophore having its lowest-lying and long-lived triplet state close in energy to the triplet (emitting) MLCT state of the metal-based chromophore. In the presence of suitable kinetic and thermodynamic parameters, the triplet state of the organic chromophore could act as an excited-state storage element, leading to a prolongation of the MLCT emission, a case related to the “delayed fluorescence” of some organic species.

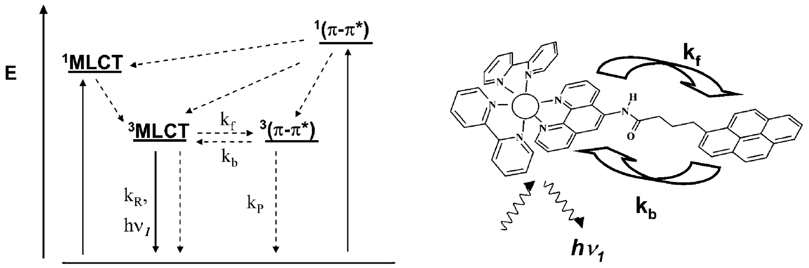
This article reviews systems reported to date where a metal unit based on polypyridine complexes and an aryl hydrocarbon are covalently linked. These systems present quasi-isoenergetic ^{3}MLCT and ($^3\pi$–π^*) triplet states, the latter being non-emitting and localised on the appended hydrocarbon chromophores, allowing for increased luminescence lifetimes of the metal-based unit, as a consequence of excited-state equilibration. The linker (or spacer) between the chromophores has the role of keeping the subunits separated enough to let them maintain most of their own individual properties, such as intrinsic decay rate constants. While the focus is on the aforementioned mechanism and its utility in molecular design, other kinetic schemes using similar components are also presented, less comprehensively. Reversible interchromophore triplet–triplet energy transfer processes in all-organic systems [12a] will not be considered here, nor will recent application to bimolecular processes in a solid-state matrix [12b] or lanthanide-based systems appended with organic chromophores [12c]. Other aspects, in particular those related to compounds with large delocalized ligands, have been reported in a review article [13] published during the preparation of the present paper and are only marginally discussed here.

2. Delayed luminescence from modular systems

The focus of this section is directed towards metal polypyridine complexes appended with a remote organic chromophore. As the two active components are separated by an insulating spacer, they retain their individual properties, yet efficient intercomponent transfer of absorbed light energy can take place. This situation allows to define such multicomponent species as supermolecules, featuring photophysical properties which are different than simply the sum of the properties of the individual modules. Section 2.3 illustrates means to further control the luminescence lifetime and the role of degeneracy of states in multichromophoric systems.

2.1. Prerequisites for excited-state equilibration

The conditions necessary to establish an excited-state equilibrium after light absorption can conveniently be described in reference to the prototypical example of this type of systems [11]. The energetic and kinetic parameters called



Equilibrium constant between excited-triplet:

$K_{eq} = k_f/k_b = [\alpha]/[1-\alpha]$

k_f = rate constant for forward energy transfer (from metal-based to hydrocarbon chromophores)

k_b = rate constant for back energy transfer process

$[\alpha]$ = no. of $^3(\pi\text{-}\pi^*)$ hydrocarbon -based triplets

$[1-\alpha]$ = no. of ^{3}MLCT triplets.

Rate of reaching equilibrium $= k_f + k_b$

Deactivation rate of equilibrium mixture $= (1-\alpha)\,k_R + (\alpha)\,k_p$

k_R and k_p are the intrinsic deactivation rates for ^{3}MLCT and $^3(\pi\text{-}\pi^*)$ triplets, respectively.

Fig. 1. Jablonski diagram showing the pertinent energy levels and kinetic parameters giving rise to prolonged luminescence lifetime in bichromophoric mixed organic-inorganic systems, along with a kinetic description for $[\mathrm{Ru(bpy)_2}(\mathbf{1})]^{2+}$. In the scheme, k_{R} represents the summation of k_{r} and k_{nr}, the radiative and non-radiative intrinsic decay rate constants of the ^{3}MLCT state.

upon in this strategy are outlined in Fig. 1, with molecule $[\mathrm{Ru(bpy)_2}(\mathbf{1})]^{2+}$ (for the structural formulas of the ligands, see Figs. 2 and 3). The discrete chromophores in this species are only weakly coupled, as indicated by the electronic absorption spectrum, which is a summation of the individual organic and inorganic chromophore contributions. Importantly, the energy difference between the two lowest lying excited states located at the inorganic moiety (^{3}MLCT) and the pyrene, a non-emissive $^3(\pi\text{–}\pi^*)$, is within a few kcal mol^{-1}, such that one state is thermally accessible from the other at ambient temperature and energy transfer processes between these two triplets can occur. It is important to note that the intrinsic deactivation rate to the ground state of MLCT triplet, k_{R} (typically around $10^6\,\mathrm{s}^{-1}$ [14]) for a $\mathrm{Ru(bpy)_3}^{2+}$-type chromophore is much greater than that of $^3(\pi\text{–}\pi^*)$ triplet, k_{P} (typically around $10^3\,\mathrm{s}^{-1}$ or slower) for an aryl hydrocarbon chromophore. In $[\mathrm{Ru(bpy)_2}(\mathbf{1})]^{2+}$, downhill forward energy transfer (i.e., energy transfer from the ^{3}MLCT to the pyrene-centred $^3\pi\text{–}\pi^*$ states) was determined to occur at a rate around $1.3\times10^8\,\mathrm{s}^{-1}$, while the slightly uphill back energy transfer ($\Delta E = -595\,\mathrm{cm}^{-1}$) occurs with a rate 18-times lower. Note that from herein, as ΔE we indicate the difference in energy between the ^{3}MLCT and the aromatic $^3\pi\text{–}\pi^*$ levels. As a consequence, positive ΔE indicates down-hill, exergonic processes and negative ΔE indicates up-hill processes. These results clearly indicate that the energy transfer rates for the forward and back processes greatly exceed (2–3 orders of magnitude) the intrinsic decay pathways of the two chromophores ($k_{\mathrm{f}} \gg k_{\mathrm{R}}$ and $k_{\mathrm{b}} \gg k_{\mathrm{P}}$) so that an excited-state equilibration is established. In this regime, the role of the pyrene chromophore is to repopulate the depleted ^{3}MLCT state, and as such can be considered as an energy "reservoir" or an excited-state storage element. As a result of the excited-state equilibrium, a long luminescence lifetime ($\tau = 11\,\mu\mathrm{s}$) can be measured for the ^{3}MLCT luminescence ($\tau < 1\,\mu\mathrm{s}$ for the model complex, missing the pyrene subunit). The approach to equilibrium following absorption of light proceeds with a rate which is a sum of rate constants for forward and back energy transfer. After equilibration, the two participants will decay with a common rate which is a linear combination of the rate parameters k_{R} and k_{P} leading to a common lifetime (Fig. 1). The fraction of molecules with excitation energy located on one moiety (e.g., "$\mathrm{Ru(bpy)_3}$") rather than the other (e.g., pyrene) at equilibrium can be described by K_{eq}. This value is governed by the relative rates of forward (k_{f}) and back energy transfer (k_{b}). As the energy gap between the two states increases, the k_{b} value diminishes until back energy transfer becomes negligible, and an excited-state equilibrium is no longer possible.

The work of Ford and Rodgers [11] is the first direct observation of an equilibrium being reached via an intramolecular triplet–triplet energy transfer reaction between a metal-based and an organic chromophoric unit.

Finally, it should be recalled that prolongation of luminescence lifetime via the excited-state equilibration approach here described can have a price, which is an eventual decrease in the overall luminescence quantum yield, when the intrinsic decay of the organic chromophore (the k_{P} rate constant in Fig. 1) is not fully negligible compared to the intrinsic decay of the emissive metal-based chromophore and the equilibration rate constants. At best, the overall luminescence quantum yield of the equilibrated systems can in fact approach (but not surpass) the quantum yield of the parent MLCT chromophore not containing the pendant organic reservoir species. Most

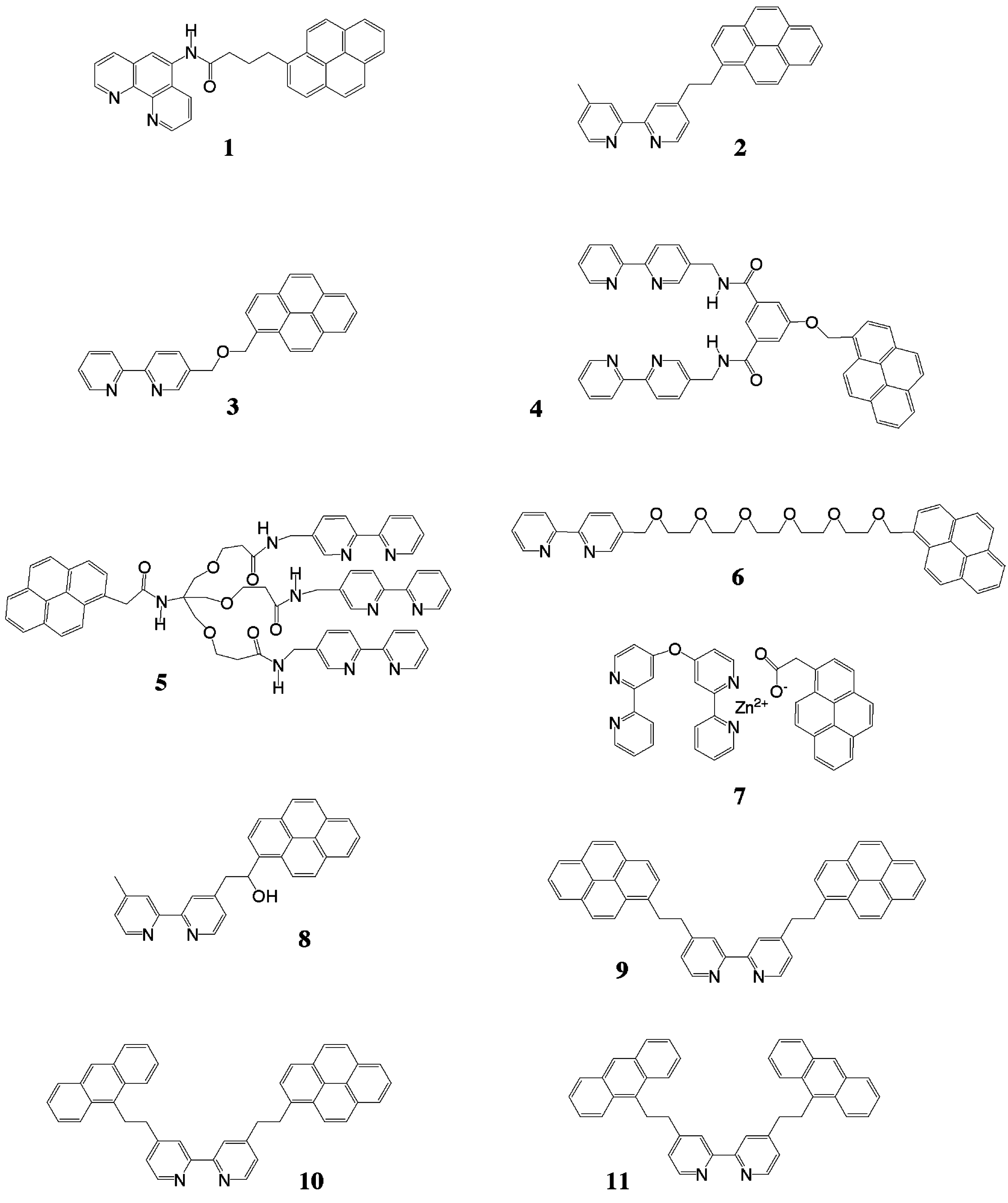


Fig. 2. Structural formulae of ligands containing a bidentate unit and a remote pyrene chromophore.

commonly, anyway, this price is however quite small, since k_p is orders of magnitudes lower than the other rate constants in Fig. 1, in all the examples studied. It should also be taken into account that in the kinetic scheme reported in Fig. 1, within which all the compounds reported in this review article can be essentially discussed, the intrinsic decay of the organic chromophore is considered to be dominated by radiationless processes.

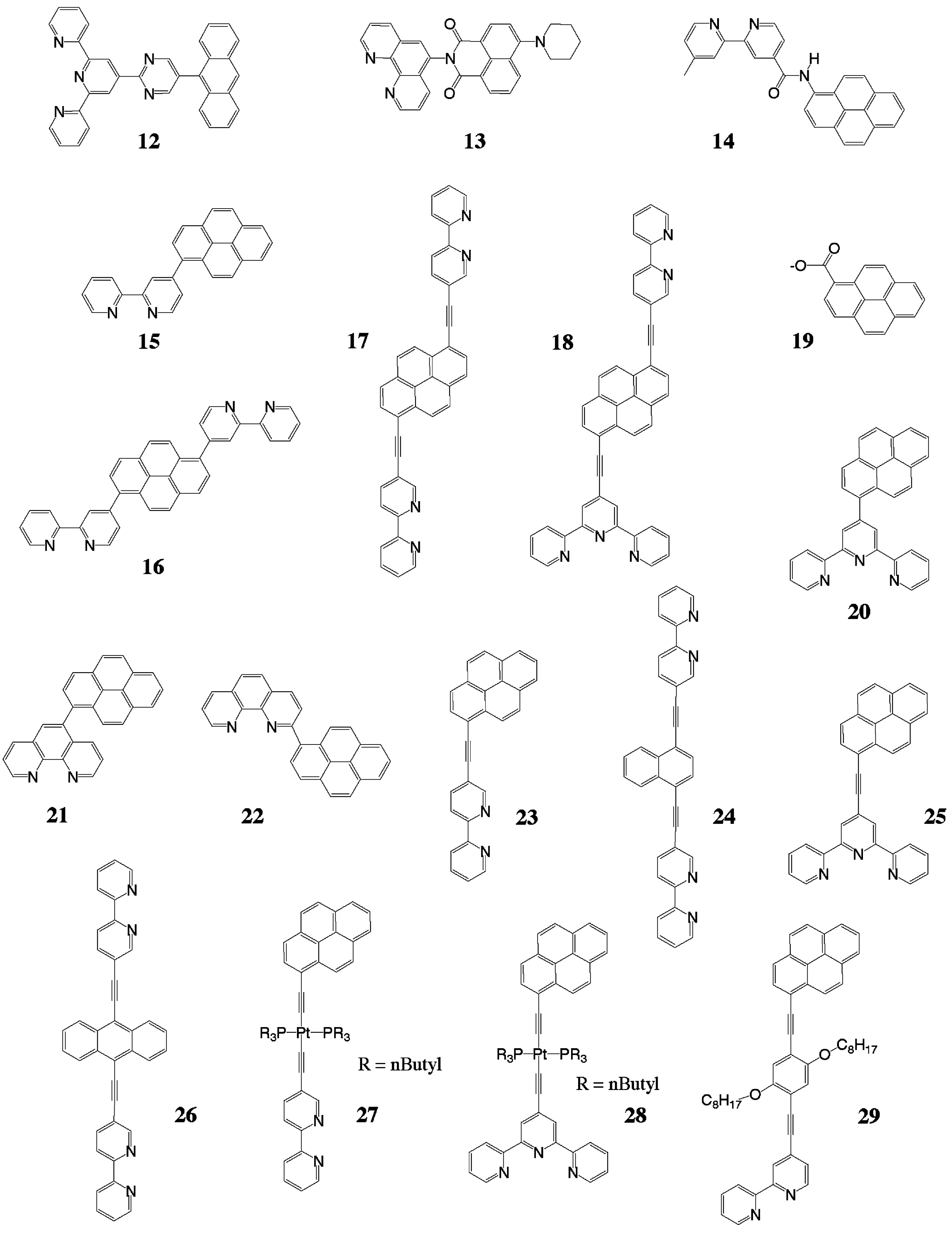


Fig. 3. Structural formulae of ligands containing a bi/terpyridine unit and an organic chromophore, separated by a single C—C bond or ethynylene linkages.

2.2. Metal polypyridine complexes with a remote organic chromophore

Following the elucidation of the mechanism described above [11], several other systems involving the pyrenyl chromophore tethered to a ruthenium(II) polypyridine complex have been reported. This is perhaps not surprising due to the predominance of the $[Ru(bpy)_3]^{2+}$ chromophore, which can be selectively excited in the presence of an organic chromophore absorbing at higher energy, leading to (after intersystem crossing) population of the ^{3}MLCT state. This fact, arising from the typically larger splitting between singlet and triplet states of organic molecules compared to transition metal polypyridine complexes, along with distinctive transient absorption signatures of each component makes these systems particularly amenable to study. Relevant photophysical data for the supramolecular complexes discussed in Sections 2 and 3 are regrouped in Table 1.

Wilson and co-workers [15,16] highlighted the importance of matching the pertinent triplet energies in the system of choice by comparing the properties of $[Ru(bpy)_2(\mathbf{2})]^{2+}$ with related complexes where pyrene is replaced with a homologous naphthalene or anthracene chromophore. For the pyrene-containing species where the Ru-based ^{3}MLCT and the lowest pyrene triplet (energy level $E = 16.4 \times 10^3\ cm^{-1}$) are almost isoenergetic, a ^{3}MLCT emission lifetime of 5.23 μs was measured and a transient absorption with signature at 415 nm, characteristic of a $T_1 \rightarrow T_n$ transition in pyrene, was observed reflecting an equilibrium distribution where excitation energy resides predominantly (80–90%) on the ^{3}pyrene component. In contrast, no excited-state equilibration was observed in either of the other two cases because the energy level of the organic triplet is too high (naphthalene case, $E = 21.3 \times 10^3\ cm^{-1}$) or low (anthracene case, $E = 14.5 \times 10^3\ cm^{-1}$) with respect to the MLCT triplet.

An important aspect of their work concerned the applicability of their findings towards hydrogen production from hydronium ions using a photoredox system comprising a $Ru(bpy)_3{}^{2+}$ linked to an aromatic unit and methyl viologen [17,18]. Considering the parent $Ru(bpy)_3{}^{2+}$ and methylviologen (MV^{2+}) components, a limitation in this latter system is the relatively low escape efficiency of the $\{Ru(bpy)_3{}^{3+}/MV^+\}$ ion pair from its solvent cage, due to a competition with unwanted back electron transfer [19]. In contrast, the intervening of triplet excited states involving aromatic organic species increases the efficiency of the cage escape. Actually, while for the naphthalene-appended Ru(II) species, where the lowest energy triplet state is MLCT in character, the cage escape is less than 10% efficient, for the anthracene-appended Ru(II) species, whose lowest excited state is an aromatic triplet state, the cage escape process is >70% efficient in methanol and acetonitrile. Interestingly, for the pyrene-containing species the efficiency of MV^+ production reflects the partitioning (K_{eq} value) of the excitation energy between the two states at the equilibrium [20,21].

Species $[Ru(bpy)_2(\mathbf{3})]^{2+}$, reported by Fages, is reminiscent of $[Ru(bpy)_2(\mathbf{1})]^{2+}$ in that it bears a flexible tether between active units, exhibited a lifetime of 10.5 μs in acetonitrile. Dinuclear $\{[(bpy)_2Ru]_2(\mathbf{4})\}^{2+}$, also equipped with a reasonably flexible linkage showed a lifetime of over 8 μs [22]. Complex $[Ru(\mathbf{5})]^{2+}$ having a hemicage chelating unit gives similar photophysical response to $[Ru(bpy)_2(\mathbf{2})]^{2+}$ [23]. In this case, the authors attempted to exploit the increased stability of a hemicage complex to excited-state ligand dissociation, as originally demonstrated in a report emanating from a Bologna–Fribourg–Bonn collaboration [24,25], with the equilibration effect to give longer-lived species, but ascribe the experimental results to a lack of conformational rigidity of the coordination sphere of the complex derived from this particular ligand [23].

The distance dependence between the active components on the excited-state equilibration process was recently investigated by Barigelletti and co-workers using flexible poly(ethylene glycol) chains of different lengths to bridge the organic and inorganic units [26]. While with molecule $[Ru(bpy)_2(\mathbf{6})]^{2+}$ the centre-to-centre distance (d_{cc}) can be up to 21 Å in an extended conformation, the apparent separation changes resulting from chain folding varies according to a Gaussian distribution with an average distance of 12 Å, compared with 13.6 Å for the shorter linker $[Ru(bpy)_2(\mathbf{3})]^{2+}$. For both species a long luminescence lifetime, of ∼9 μs, practically independent on the poly(ethylene glycol) chain, was measured. High rates constants for forward triplet–triplet energy transfer processes ($k_f = 4 \times 10^8\ s^{-1}$ and $2 \times 10^8\ s^{-1}$ for $[Ru(bpy)_2(\mathbf{3})]^{2+}$ and $[Ru(bpy)_2(\mathbf{6})]^{2+}$, respectively) were observed. These results are attributed by the authors to the folding properties of the linking chains. A natural extension of this work may be the study of the photophysical properties of a series of $[Ru(bpy)_3]^{2+}$ and pyrene-decorated systems with fixed d_{cc} values, utilising rigid spacers.

Prodi and Juris reported a nice variation on these systems where a zinc cation directs the assembly of discrete photoactive components using the free chelating site of $[Ru(bpy)_2(bpy\text{-}O\text{-}bpy)]^{2+}$ along with the deprotonated caboxylic acid group of 1-pyrene acetic acid. Supermolecule $[Ru(bpy)_2(\mathbf{7})]^{2+}$ was formed with greater than 95% yield [27]. In the assembly, the MLCT emission in air-equilibrated acetonitrile had a lifetime of 380 ns, somewhat longer than the 149 ns value recorded for the parent molecule. The authors suggest this type of system may have a role in a combinatorial chemistry context, using a library of carboxylate group bearing species.

2.3. Tuning excited-state lifetimes

2.3.1. Multichromophore approach

The important roles of the relative rates of forward and back energy transfer processes and relative energies of the low-lying triplet excited states in governing lifetimes of the MLCT emission, in relevant bichromophoric species, were outlined above. Another methodology to affect the resulting

Table 1

Photophysical data reported for complexes with ligands **1**–**29** showing long-lived luminescence in room temperature fluid solution and for selected parent compounds

Species	$\lambda_{em\,max}$ (nm)	τ_{em}[a] (μs)	Φ_r	α[b,c]	$1-\alpha$[b,c]	K_{eq}[b,c]	k_f (s^{-1})	k_b (s^{-1})	ΔE[d] (cm^{-1})	References
$[Ru(bpy)_3]^{2+}$	608	0.9	0.09	–	–	–	–	–	–	[26]
$[Ru(dmb)_3]^{2+}$	616	0.87	0.06	–	–	–	–	–	–	[29]
$[Ru(dmb)(CN)_4]^{2-}$	640[e]	30×10^{-3}[e]	–	–	–	–	–	–	–	[40]
$[Os(dmb)_3]^{2+}$	745	35×10^{-3}	4×10^{-3}	–	–	–	–	–	–	[30]
$[Ru(bpy)_2\mathbf{1}]^{2+}$	600[e]	7.2×10^{-3}, 11.2	–	0.95	0.05	18	1.3×10^{8}	7×10^{6}	600	[11]
$[Ru(bpy)_2\mathbf{2}]^{2+}$	610[e]	$<10 \times 10^{-3}$, 5.23	0.044	0.85	0.15	5.7	–	–	–	[15]
$[Ru(dmb)_2\mathbf{2}]^{2+}$	614	2.47	0.06	0.71 (0.78)	0.29 (0.22)	2.5 (3.5)	–	–	–	[29,30]
$[Ru(dmb)(\mathbf{2})_2]^{2+}$	614	6.65	0.06	0.89 (0.88)	0.11 (0.12)	8.1 (7.1)	–	–	–	[29,30]
$[Ru(\mathbf{2})_3]^{2+}$	614	7.92	0.06	0.91 (0.91)	0.09 (0.09)	10.1 (10.6)	–	–	–	[29,30]
$[Ru(\mathbf{2})_2\mathbf{9}]^{2+}$	612	10.99	0.06	0.93 (0.93)	0.07 (0.07)	13.3 (14.2)	–	–	–	[29,30]
$[Ru(CN)_4(\mathbf{2})]^{2-}$	640[e]	1.2×10^{-3}, 0.26[e] (0.25)[c]	–	0.88	0.12	7.3	5×10^{9}	–	410	[40]
$[Ru(bpy)_2(\mathbf{3})]^{2+}$	608	2.9×10^{-3}, 8.8	0.096	–	–	11	3×10^{8}	–	480	[26]
$[Ru(bpy)_2(\mathbf{4})]^{2+}$	610	8	–	–	–	–	–	–	–	[22]
$[Ru(bpy)_2(\mathbf{5})]^{2+}$	606	2.1	0.04	–	–	–	–	–	–	[23]
$[Ru(bpy)_2(\mathbf{6})]^{2+}$	608	5.9×10^{-3}, 10	0.117	–	–	11	2×10^{8}	–	480	[26]
$[Ru(bpy)_2(\mathbf{7})]^{2+}$	624	12×10^{-3}, 0.380[f]	–	–	–	–	6.1×10^{7}	–	200	[27]
$[Ru(bpy)_2(\mathbf{8})]^{2+}$	621	2.96	0.065	0.64	0.36	1.8	–	–	–	[28]
$[Ru(\mathbf{8})_3]^{2+}$	617	9.0	0.064	0.87	0.13	6.7	–	–	–	[28]
$[Ru(CN)_4(\mathbf{9})]^{2-}$	640[d]	0.6×10^{-3}, 0.46 (0.50)[c]	–	0.94	0.06	15.7	–	–	410	[40]
$[Ru(dmb)_2\mathbf{9}]^{2+}$	614	6.95	0.06	0.90 (0.88)	0.10 (0.12)	9.0 (7.1)	–	–	–	[29,30]
$[Ru(dmb)(\mathbf{9})_2]^{2+}$	610	11.30	0.06	0.94 (0.93)	0.06 (0.07)	15.7 (14.2)	–	–	–	[29,30]
$[Ru(\mathbf{2})(\mathbf{9})_2]^{2+}$	610	14.96	0.06	0.95 (0.95)	0.05 (0.05)	19.0 (17.7)	–	–	–	[29,30]
$[Ru(\mathbf{9})_3]^{2+}$	608	18.10	0.06	0.96 (0.96)	0.04 (0.05)	24.0 (21.3)	–	–	–	[29,30]
$[Os(\mathbf{10})_3]^{2+}$	732	61×10^{-3} (58×10^{-3})[c]	0.006	0.09	0.91	0.10	–	–	−700	[30]
$[Os(\mathbf{11})_3]^{2+}$	728	65.3×10^{-3} (65×10^{-3})[c]	0.006	0.17	0.83	0.20	–	–	−700	[30]
$[Ru(trpy)(\mathbf{12})]^{2+}$	680	5.5×10^{-3}, 0.40	1.3×10^{-4}	–	–	–	–	–	840	[37]
$[Ru(\mathbf{12})_2]^{2+}$	675	5.8×10^{-3}, 1.80	1.8×10^{-4}	–	–	–	–	–	960	[37]
$[Ru(bpy)_2(\mathbf{13})]^{2+}$	606	27.6	0.033	–	–	–	–	–	750	[41]
$[Ru(\mathbf{13})_3]^{2+}$	595	60.8	0.013	–	–	–	–	–	900	[41]
$[Ru(bpy)_2(\mathbf{14})]^{2+}$	630	0.98	0.071	–	–	–	2.6×10^{5}	–	350	[42]
$[Ru(bpy)_2(\mathbf{15})]^{2+}$	640	1.30, 57.4	0.10	–	–	<0.4	$<2 \times 10^{4}$	–	−200	[45]
$\{[Ru(bpy)_2](\mathbf{16})\}^{2+}$	670	1.8, 100[g]	8.6×10^{-3}	–	–	–	–	–	–	[46]
$\{[Ru(bpy)_2]_2(\mathbf{17})\}^{4+}$	640, 680[g]	165[g]	7×10^{-3}	–	–	–	–	–	–	[50]
$[Ru(bpy)_2(\mathbf{18})]^{2+}$	640, 680[g]	140[g]	6.3×10^{-3}	–	–	–	–	–	–	[50]
$[Ru(bpy)_2(\mathbf{18})Ru(trpy)]^{4+}$	640, 680[g]	48[g]	4.5×10^{-3}	–	–	–	–	–	–	[50]
$[(bpy)Re(CO)_3(\mathbf{19})]^{2+}$	–	0.428	–	–	–	–	–	–	–	[51]
$[Pt(\mathbf{20})Cl]^{+}$	640sh, 685[h]	64[g]	1×10^{-3}, 34×10^{-3}	–	–	–	–	–	–	[54,55]
$[Ru(bpy)_2(\mathbf{21})]^{2+}$	606	23.7	0.071	0.935	0.065	14.5	2.8×10^{10}	(1.9×10^{9})[c]	780	[56,57]
$[Ru(\mathbf{21})_3]^{2+}$	597	148	0.064	0.989	0.011	86.7	2.4×10^{11}	(2.8×10^{9})[c]	1030	[56,57]
$[Ru(bpy)_2(\mathbf{22})]^{2+}$	610	4×10^{-3}	9×10^{-4}	–	–	<29	10^{8}	–	700	[45]
$[Ru(bpy)_2(\mathbf{23})]^{2+}$	670	42	0.026	0.98	0.02	49	1.4×10^{11}	2×10^{9}	930	[60,61]
$[Ru(bpy)_2(\mathbf{24})]^{2+}$	656	8.6	0.035	–	–	4.5	1.1×10^{10}	2.5×10^{9}	305	[62]
$[Ru(trpy)(\mathbf{25})]^{2+}$	698	0.580	5×10^{-3}	0.13	0.87	0.15	–	–	−390	[60]
$[Os(bpy)_2(\mathbf{26})]^{2+}$	800	0.415	1.2×10^{-3}	0.975	0.025	40	2.9×10^{10}	7.3×10^{8}	750	[62,63]
$[Ru(bpy)_2(\mathbf{27})]^{2+}$	620	3.2×10^{-3}, 17	0.022	0.970	0.03	32	3×10^{8}	9.4×10^{6}	710	[61]
$[Ru(bpy)_2(\mathbf{29})]^{2+}$	652, 680	3, 20	–	–	–	–	2×10^{5}	3.3×10^{4}	920	[69]

[a] Degassed acetonitrile solvent unless otherwise stated. When two lifetimes are reported, the shorter one is assigned to equilibration time (see original references).

[b] Calculated from experimental parameters.

[c] Values in parentheses from equilibria modelling.

[d] Energy difference between the ^{3}MLCT and the aromatic $^3\pi$–π^* levels.

[e] In methanol.

[f] Aerated solution.

[g] ILCT origin.

[h] In dichloromethane.

equilibration distribution, and hence lifetime is to introduce a degeneracy factor, i.e., multiple organic chromophores. This enhances the probability of energy residing on the organic part, increases K_{eq}, and hence the observed luminescence lifetime. Questions then arise regarding the resulting lifetime values and equilibrium energy distribution patterns as a function of number of chromophores.

Castellano initially investigated the multichromophore effect with molecules $[Ru(bpy)_2(\mathbf{8})]^{2+}$ and $[Ru(\mathbf{8})_3]^{2+}$, bearing one and three pyrenyl-chromophores, respectively [28]. While a lifetime of 2.96 μs was recorded for $[Ru(bpy)_2\mathbf{8}]^{2+}$, an even longer lifetime of 9.0 μs was measured for $[Ru(\mathbf{8})_3]^{2+}$ in degassed acetonitrile. These results are indicative of excited-state equilibrium and the origin of the difference between the dyad and tetrad clearly resides in the number of chromophores. In the monopyrene species 64% of the population of excited molecules was estimated to have energy localised on the pyrene ($K_{eq} = 1.8$), while a measured 3.7-fold increase in K_{eq} in the tetrad results (87% population of pyrene triplet). Due to the fact that the back energy transfer reaction involves one ^{3}MLCT state, the rate constant for back triplet energy transfer is not expected to change between the dyad and tetrad, so the increase of K_{eq} is due to an increase of k_f as the number of triplet acceptors increases. A more detailed discussion could be made on the basis of statistical thermodynamics.

With two species being insufficient to demonstrate a trend, a more systematic investigation of the role of number of chromophores on the luminescence lifetime was undertaken in a Messina–Bologna collaboration [29]. Using different combinations of ligands bearing none (4,4′-dimethyl-2,2′-bipyridine; dmb), one (**2**) or two pyrenes (**9**), nine complexes were prepared representing the full series of possible permutations with three different bidentate ligands on a single Ru(II) metal centre (with the exception of the tris-heteroleptic complex $[Ru(dmb)(\mathbf{2})(\mathbf{9})]^{2+}$). Lifetime values ranged from 0.8 μs for $[Ru(dmb)_3]^{2+}$ with no appended pyrene units to 18.1 μs for the heptad (with a K_{eq} value around 24) with six appended pyrene units in degassed acetonitrile at room temperature. The linear relationship observed, describing the increased luminescence lifetime as a function of the number of appended chromophores, is shown in Fig. 4a, along with energy distribution at equilibrium, shown in Fig. 4b and c. It can be seen that on average 2.7 μs was added to the lifetime with each additional appended chromophore. Arrangement of chromophores around the metal core and ligand-connectivity were shown to have a minimal effect on the observed lifetime in two different examples of species bearing either two ($[Ru(dmb)_2(\mathbf{9})]^{2+}$ cf. $[Ru(dmb)(\mathbf{2}_2)]^{2+}$) or four pyrenes ($[Ru(dmb)(\mathbf{9})_2]^{2+}$ cf. $[Ru(\mathbf{2})_2(\mathbf{9})]^{2+}$). This trend appears to be unrelenting and no deviation from linearity is observed, even upon incorporation of six organic chromophores with quasi-isoenergetic states.

Recently the multichromophore approach was applied to osmium(II) polypyridine complexes, which are particularly prone to non-radiative deexcitation due partly to their low-lying ^{3}MLCT states [30]. These represent interesting candidates, in addition to their Ru(II) analogues, owing to their long wavelength absorption (due to formally spin-forbidden MLCT transitions) and emission spectra which mean that these chromophores can be addressed with a high degree of selectivity.

While the excited state lifetime of parent $[Os(dmb)_3]^{2+}$ is only 35 ns in deaerated acetonitrile, this is extended to 61 ns in $[Os(\mathbf{10})_3]^{2+}$, a three anthracene (and three pyrene) containing species. Further prolongation of the luminescence lifetime ($\tau = 65$ ns) is observed with the six anthracene-containing complex $[Os(\mathbf{11})_3]^{2+}$. In the former case, pyrene units are not directly involved in the equilibration process, but rather serve as light-harvesting units, transferring absorbed energy with high efficiency to the active components.

The discernible, but modest emission lifetime enhancement in the aforementioned complexes can be ascribed to imperfections in the energy match of ^{3}MLCT and $^3(\pi–\pi^*)$ states. Indeed the anthracene triplet state is located higher in energy ($\Delta E_{(MLCT-\pi-\pi^*)} = -700\ cm^{-1}$) than its ^{3}MLCT partner. On this basis, 9% of excited $[Os(\mathbf{10})_3]^{2+}$ molecules would be anticipated to have electronic excitation energy localized on the anthracene, while this value is increased to 17% in $[Os(\mathbf{11})_3]^{2+}$. The corresponding calculated lifetimes ($\tau = 58$ and 65 ns, respectively, obtained by considering statistical thermodynamics including degeneracy of states [30]) correspond to those measured, as reported above.

Thus far, metal polypyridine complexes have been considered which encompass bidentate ligands. Complexes derived from tridendate (e.g., 2,2′:6′,2″-terpyridine; trpy) ligands offer the possibility to construct different supramolecular architectures than those possible with their bidentate cousins (for example, linear arrays as wires for vectorial energy or electron transfer, etc.) and are devoid of stereochemical implications ($[Ru(bpy)_3]^{2+}$ exists as Δ and Λ isomers). However, due to thermally-accessible low-lying metal centred (MC) states, in $[Ru(trpy)_2]^{2+}$ the luminescence is typically weak and short-lived [31,32]. Methods to overcome this obstacle rely on increasing the energy gap between MLCT states and MC states (using cyclometalating ligands [5,33] or electron withdrawing and/or donor substituents [34]) to minimise the effect of this thermally-activated loss channel. Alternatively, modification of Franck–Condon factors for non-radiative decay can be called upon, using ligands with extended π* orbitals to increase delocalisation in the acceptor ligand of the MLCT state [35].

Combining the latter approach, using pyrimidine-substituted terpyridine ligands [36], with the excited-state equilibration process (using an anthracene energy-storage unit), the generation of Ru(II) terpyridine complexes with long-lived luminescence lifetimes was anticipated [37]. Indeed, with the anthracene-based triplet lying close to the ^{3}MLCT ($\Delta E_{(MLCT-\pi-\pi^*)} = 840\ cm^{-1}$ and $960\ cm^{-1}$ for $[Ru(trpy)(\mathbf{12})]^{2+}$ and $[Ru(\mathbf{12})_2]^{2+}$, respectively) this appears to be the case. The different values for homo- and heteroleptic complexes are related to differences in the energy of the

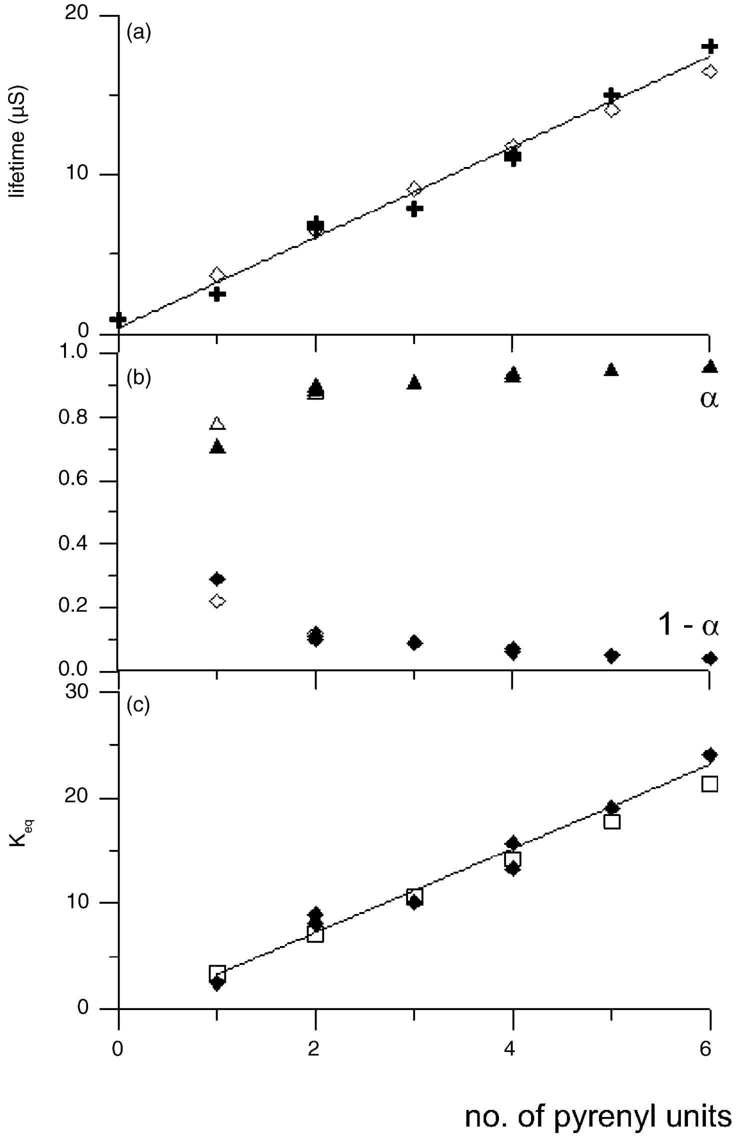


Fig. 4. Luminescence lifetime (a), fraction of pyrene-based (α) and "Ru(bpy)$_3$"-based (1 − α) triplets at equilibrium (b) and equilibrium constant (c) as a function of number of pyrene units appended to a "Ru(bpy)$_3$" core. Solid points represent experimentally determined values, unfilled points are obtained via equilibrium modelling [reference [29]].

MLCT states, as discussed in the original reference. For one anthracene-containing dyad $[Ru(trpy)(\mathbf{12})]^{2+}$(for structural formula of **12**, see Fig. 3), a lifetime of 0.40 µs was measured in degassed acetonitrile, which compares favourably with the value 15 ns obtained for the parent species. In the triad, a value of 1.8 µs was obtained (compared with $\tau = 21$ ns for the non-anthracenic parent) which may additionally be partly due to a modification of the energy gap between ^{3}MLCT and $^3\pi$–π^* states, and $[Ru(\mathbf{12})_2]^{2+}$ could be the longest-lived room-temperature MLCT emission reported to date for a ruthenium polypyridine complex based on tridentate ligands. Although no saturated hydrocarbon spacer can be discerned in **12**, and as such these species may equally be considered in Section 3, steric hindrance may be anticipated to push the adjacent π-systems towards orthogonality, introducing a sort of "virtual", insulating spacer.

2.3.2. Solvent effects on luminescence lifetime

In the systems discussed so far, the relative energies of pertinent low energies triplet excited states are synthetically established and indeed are intricately linked to the equilibrium distribution (described by $\Delta G^\circ = -RT \ln K_{eq}$). In this manner, a large synthetic effort is typically required to obtain systematic variations in the driving force of the energy transfer process. An alternative design strategy calls upon supramolecular systems with a tunable driving force for electronic energy transfer. For example, by taking advantage of second-sphere donor–acceptor (SSDA) interactions [38,39], the energies of the excited states of the metal complex component can be modified in a predictable way while that of the organic component remains unchanged. Mixed cyano-polypyridine complexes of Ru(II) are typical examples in which the SSDA interactions between the cyanides

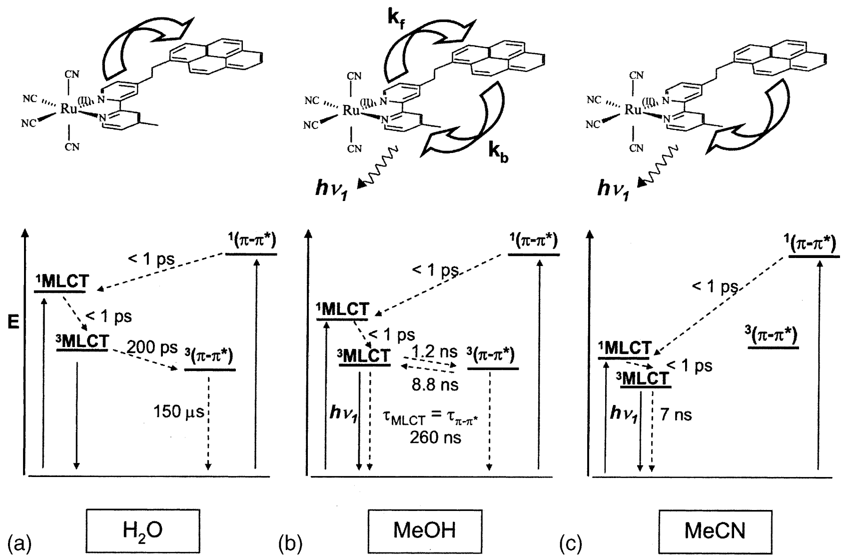


Fig. 5. Second-sphere interactions leading to solvent-modulated lifetime with $[Ru(\mathbf{2})CN_4]^{2-}$ in water (a), methanol (b) and acetonitrile (c). Top: thermodynamically allowed excited-state energy transfer processes and observed radiative deexcitation. Bottom: energy level diagrams and photophysical processes in water (a), methanol (b) and acetonitrile (c). Acceptor numbers of the solvents are: water, 58.4; methanol, 41.3; acetonitrile, 19.3.

and the solvent produce a pronounced solvatochromic behaviour, both in absorption and emission. The larger the acceptor character of the solvent (denoted by the Gutmann acceptor number) the higher the oxidation potential of the metal centre and the higher the energy of the MLCT excited states.

The overall scheme for the supramolecular species $[Ru(\mathbf{2})(CN)_4]^{2-}$ is shown in Fig. 5 [40]. Figure caption also includes acceptor numbers of the solvents employed. The tuning of ^{3}MLCT energy levels obtained through SSDA interactions with the solvent causes drastic changes in the relative energy order position of the triplets of the two chromophores and hence the intercomponent energy transfer in these supramolecular systems.

In water, see Fig. 5a, the MLCT emission of the Ru-based chromophore is completely quenched and rapid (200 ps) irreversible triplet energy transfer to the lower lying pyrene units (ΔE = ca. 1900 cm^{-1}) is detected in ultrafast spectroscopy. In acetonitrile, Fig. 5c, where the triplet order is reversed the MLCT emission is unaffected by the presence of the appended pyrene groups implying the absence of intercomponent triplet energy transfer (ΔE = ca. −1100 cm^{-1}). In methanol, see Fig. 5b, where the triplets are very close in energy with the pyrene triplet expected to be only slightly lower in energy (ΔE = ca. 400 cm^{-1}), the triplet energy transfer leads to an equilibrium between excited chromophores, with considerable prolongation of the MLCT lifetime.

Considering both $[Ru(\mathbf{2})(CN)_4]^{2-}$ and $[Ru(\mathbf{9})(CN)_4]^{2-}$ in methanol, from a biexponential fit of luminescence decays the values of the time of reaching equilibrium (short component) and the lifetime of equilibrium mixture (long component) were obtained. The values are 1.2 ns and 260 ns, respectively, for the complex bearing one pyrenyl group and 0.6 ns and 460 ns, respectively, for the species with two pyrenyl groups. These data are mirrored in transient absorption measurements. Thus, both systems present greatly extended lifetimes compared to the model complex $[Ru(bpy)(CN)_4]^{2-}$ (τ = 30 ns in methanol). A statistical factor due to a second pyrenyl group explains why the lifetime of the short component is halved in $[Ru(\mathbf{9})(CN)_4]^{2-}$ with respect to $[Ru(\mathbf{2})(CN)_4]^{2-}$.

The results described above highlight that the coupling of organic chromophores and appropriate MLCT emitters can allow to switch the direction of energy transfer by changing solvents, provided that the organic unit has a triplet energy within the tunability range of the MLCT state.

Castellano described interesting long-lifetime complexes comprising phenanthroline ligands bearing the 4-piperidinyl-1,8-naphthalimide (PNI) chromophore, presenting perhaps the first observation of triplet excited-state equilibrium in a Ru(II) complex without incorporating pyrene [41]. Complexes $[Ru(bpy)_2(\mathbf{13})]^{2+}$ and $[Ru(\mathbf{13})_3]^{2+}$ display at room temperature ^{3}MLCT emission with lifetimes extremely enhanced with respect to the parent complex missing the PNI unit. This enhancement is a result of an excited-state equilibrium between the higher energy ^{3}MLCT and the slightly lower energy intraligand triplet present on the pendant naphthalimide chromophore. The lifetimes that range from 16 µs in acetone to 115 µs in DMSO depend strongly both upon solvent and the number of PNI chromophores present. The lifetime of $[Ru(\mathbf{13})_3]^{2+}$ is 2–3 times that of $[Ru(bpy)_2(\mathbf{13})]^{2+}$ in the solvents investigated and followed the trend DMSO > EtOH > CH_2Cl_2 > MeOH > MeCN > Me_2CO for $[Ru(bpy)_2\mathbf{13}]^{2+}$, while the relative positions of CH_2Cl_2 and MeOH are inverted for $[Ru(\mathbf{13})_3]^{2+}$. In these cases no trend could be conveniently demonstrated linking the observed luminescence lifetime and several of the more common solvent parameters.

The effect of different solvents (acetonitrile, dichloromethane and methanol) on the luminescence of [Ru(bpy)$_2$(**14**)]$^{2+}$ (ligand shown in Fig. 2) was recently reported by Gehlen and co-workers [42]. A very long-lived component of 46 μs (although this constitutes less than 4% of the total luminescence emission) was recorded in acetonitrile along with a shorter component of 0.98 μs. The small difference in the shorter component luminescence lifetime and quantum yield between [Ru(bpy)$_2$(**14**)]$^{2+}$ and the model compound suggest intercomponent energy transfer is almost inefficient. In dichloromethane, the emission lifetime values were 0.64 μs and 2.3 μs, while in polar protic methanol, a monoexponential lifetime (0.9 μs) was measured. Slow rates of energy transfer (up to $2.9 \times 10^5\ s^{-1}$ in dichloromethane) were observed. The weak electronic coupling of the amide bridge along with the small difference in triplet energy between Ru-based and pyrene units were proposed to account for the slow energy transfer rate and the lack of equilibrium regime. The authors selected the amide linkage for their series of model compounds, due to the role of peptides in mediating long-range interactions in natural systems [43].

3. Non-modular systems showing long-lived luminescence

In this section, an overview of some species with long ^{3}MLCT luminescence lifetimes are presented which use similar building blocks presented previously, but do not contain a discernible spacer. As such, the chromophores may show a higher degree of coupling with one another. Some of these systems do not show evidence for excited-state equilibration as the dominant mechanism for the lifetime enhancement. Rather, an intervening (new) excited state can be identified. Predictability in the resulting MLCT luminescence lifetime in supramolecular systems of these latter types is in a some way more difficult to achieve. Information on kinetic schemes which can be useful in these latter cases can be found in references [13] and [44]. As mentioned in Section 1, the cases reported in this section are illustrated as examples of slightly different approaches to obtain prolonged CT emission from a metal-based species, but the section does not pretend to be exhaustive.

Schmehl, Piotrowiak, Thummel and co-workers reported ligand **15** which is based on a pyrene directly substituted on its 1-position with a 2,2′-bipyridine unit [45]. More recently the homologous ligand **16**, bearing bpy moieties in the 1- and 6-positions of pyrene was described by Schmehl, Fages and co-workers [46]. Concerning complex [Ru(bpy)$_2$(**15**)]$^{2+}$, the ^{3}MLCT state was found to be around 200 cm^{-1} lower in energy than the ^{3}(π–π*)-state of the appended pyrene. A remarkably long-lived luminescence of over 50 μs, originating from a ^{3}MLCT involving the substituted bpy, was measured in deaerated acetonitrile. Analysis of biexponential luminescence decays clearly shows that the energy transfer is slower than relaxation of the ^{3}MLCT state but more rapid than decay of the ^{3}(π–π*)-state (i.e., with referring to Fig. 1, $k_R > k_f > k_P$) so that the kinetic conditions for an excited-state equilibrium (k_f, $k_b > k_R \gg k_P$) are not reached. Thus, despite the similarity of the building blocks, the directly linked species displays profoundly different photophysical properties than the related tethered species. The reasons for this different behavior are not completely clear.

[Ru(bpy)$_2$(**15**)]$^{2+}$ was later incorporated into a pressure-sensitive paint formulation. A long-lived emission ($\tau = 50$ μs) was similarly recorded when introduced into an acrylic copolymer matrix. Slight temperature dependence (in the range 298–328 K) and high oxygen sensitivity of emission in these formulations make these good candidates for the development of new oxygen sensitive paints relevant in aircraft manufacture [47].

The binuclear complex {[(bpy)$_2$Ru]$_2$(**16**)}$^{4+}$ presents an emissive state with a long-lifetime of 130 μs in O$_2$-free DMSO, which the authors ascribe to the deexcitation of a triplet intraligand charge transfer (^{3}ILCT) state or a ^{3}ILCT state with mixed parentage [46]. The nature of the ^{3}ILCT state is thought to be derived from pyrene (π) to bpy (π*) charge transfer, with evidence to this effect coming from ground- and excited-state absorption spectra, electrochemical and luminescence (room temperature and 77 K) data. The authors suggest that with this type of system it would be possible to make complexes having both MLCT and ILCT transitions in the visible, with one of the triplet CT states as the active state for photoredox reactions. For examples of systems where ILCT states are thermally coupled with MLCT states see also references [48] and [49].

Lowest-lying triplet intra-ligand CT states are again invoked to account for the photophysical properties of Harriman and Ziessel's slightly emissive [Ru(bpy)$_2$(**17**)]$^{2+}$, [{(bpy)$_2$Ru}$_2$(**17**)]$^{4+}$ and [(bpy)$_2$Ru(**18**)Ru(trpy)]$^{4+}$ [50]. After grafting a second ethynylated group onto the central pyrene unit, this becomes more easily oxidized, and an ILCT is stabilised. This state becomes the lowest energy triplet state and displays a long-lived but weak emission at room temperature.

Wolcan and Féliz held a ligand-to-ligand charge-transfer (LLCT) and a MLCT state to be responsible for the dual emission of the complex containing ligand **19**, that is [(bpy)Re(CO)$_3$OCOR], where R = pyrene-1-carboxylate (naphthalene-2-carboxylate and anthracene-9-carboxylate were also studied) [51]. The remarkable result is the lack of the energy transfer quenching of the emitting states by the triplet of pyrene. This is attributed to an insulating effect introduced by the intermediary carboxylate group, in accordance with authors' previous findings [52,53]. The apparent disagreement with the previously mentioned results reported in reference [27] is not discussed.

In a 2000 paper, McMillin and co-workers reported the complex [Pt(**20**)Cl]$^+$, the polypyridine ligand being a terpyridine where the central pyridine ring is connected to a pyrene through a single C–C bond [54,55]. This complex exhibits a luminescence extremely long-lived (a lifetime of

64 μs in deoxygenated dichloromethane was recorded) with respect the unsubstituted complex $[Pt(trpy)Cl]^+$. The origin of this long-lived emission is from an aryl-to-trpy intraligand charge transfer (ILCT) state. Changing the pyrene for another substituent allows significant modification of photophysical properties of the luminescent excited state in terms of emission quantum yield, lifetime and energy.

Castellano reported systems based on ligand **21** [56,57]. The properties of complex $[Ru(bpy)_2(\mathbf{21})]^{2+}$ based on this 1,10-phenanthroline ligand substituted in the 5-position with a pyrene contrast dramatically to those measured by Simon et al. [45] for the corresponding complex containing the 2-substituted 1,10-phenanthroline $[Ru(bpy)_2(\mathbf{22})]^{2+}$. The complex with the 5-substituted phenanthroline exhibits at room temperature a long-lived ^{3}MLCT emission (τ about 24 μs) while the 2-substituted one exhibits a weak luminescence with a lifetime (4 ns) much shorter than the parent unsubstituted complex $[Ru(bpy)_2(phen)]^{2+}$, having a lifetime of about 0.8 μs in the same conditions. The reason of this behavior is due to the different position of pyrene in the two ligands. According to the authors, for $[Ru(bpy)_2(\mathbf{22})]^{2+}$ a weakening of the ligand field is induced by steric restraints that impose an orientation of pyrenyl group nearly perpendicular to the phenanthroline [45,58] and consequently thermally accessible low-energy ^{3}MC states become responsible for the fast deactivation of MLCT triplet. For the homoleptic complex $[Ru(\mathbf{21})_3]^{2+}$, lifetime increases to 148 μs in degassed acetonitrile. Despite many similarities with the aforementioned non-equilibrating complexes, the authors presented evidence typically ascribed to an excited-state equilibration process (outlined in previous sections). Energy gaps of 780 cm^{-1} and 1030 cm^{-1} between the lowest-lying relevant triplet states (i.e., ^{3}MLCT and $^3\pi$–π^*) and K_{eq} values of 14.5 and 86.7 were measured for $[Ru(bpy)_2(\mathbf{21})]^{2+}$ and $[Ru(\mathbf{21})_3]^{2+}$, respectively. The substantial increase in lifetime in going from $[Ru(bpy)_2(\mathbf{21})]^{2+}$ to $[Ru(\mathbf{21})_3]^{2+}$ is attributed by the authors to a combined result of increasing the number of pyrenyl units and a larger energy gap which substantially favours "pyrene"-like triplets in the equilibrium mixture. These Ru(II) complexes were also found to efficiently sensitize the production of molecular singlet oxygen [57].

Harriman and Ziessel reported a series of interesting ligands where a polypyridine chelating agent and a polyaromatic chromophore are bridged by an ethynylene bridging unit and the corresponding complexes [50,59–63]. The key features of these species is the structural rigidity imparted by the connector, along with increased rates of forward and back triplet energy transfer that ensure an equilibrium regime [64].

Perhaps the least complex of these attractive molecules is ligand **23**. The resulting complex $[Ru(bpy)_2(\mathbf{23})]^{2+}$ shows a triplet MLCT lifetime of 42 μs, which is greatly prolonged with respect to $[Ru(bpy)_3]^{2+}$ [60,61]. In this case the proportion of the lower lying pyrene-like triplets populated in the equilibrium mixture was estimated to be 98%, and relaxation to the equilibrium distribution takes place in some picoseconds indicating high rates of forward and back energy transfer reactions. Similarly, when pyrene is replaced with a bpy-terminated ethynylated naphthalene, i.e., $[Ru(bpy)_2(\mathbf{24})]^{2+}$, evidence is observed for reversible energy transfer and a 8.6 μs lifetime of ^{3}MLCT emission was measured [62]. The corresponding dinuclear compound $\{[(bpy)_2Ru]_2(\mathbf{24})\}^{4+}$ in the same report gave a luminescence lifetime of 6.7 μs. K_{eq} values of 4.5 and 3.0 were calculated, respectively. It should be noted that the naphthalene subunit in **24** cannot be seen as "isolated". In this case, as the organic chromophore at least the delocalized ethynyl–naphthalene–ethynyl moiety (whose $^3\pi$–π^* lowest-lying excited state is significantly lower than that of the "isolated" naphthalene) has to be considered.

For the terpyridine-based analogue, $[Ru(trpy)(\mathbf{25})]^{2+}$ [60], the energy ordering of the relevant triplets is reversed. The triplet pyrene lies around 390 cm^{-1} higher than the ^{3}MLCT state, but remains thermally accessible at room temperature in acetonitrile. A greatly enhanced lifetime of 580 ns results, along with an increased quantum yield (5×10^{-3}) compared to related non-pyrene containing mononuclear ethynylated terpy compounds [65] or the parent $[Ru(trpy)_2]^{2+}$ [66,67]. The authors suggest that this enhancement is too dramatic to result solely from an excited-state equilibration process where a small K_{eq} value of 0.15 with a concomitant 13% triplet pyrene population is present and believe another unelucidated factor may be responsible [61]. Most likely the stabilization of the MLCT level in $[Ru(trpy)(\mathbf{25})]^{2+}$ compared to model compounds, due to the presence in **25** of the aromatic hydrocarbon substituent, inducing an increased energy gap between the luminescent level and the deactivating, upper-lying ^{3}MC state, can have an important role.

In complex $[Os(bpy)_2(\mathbf{26})]^{2+}$, the combined effects of an ethynylene substituent and reversible energy transfer to an appended anthracene unit provide access to luminescent osmium(II) tris-bpy derivatives of prolonged long triplet lifetime ($\tau = 415$ ns, degassed acetonitrile, cf. $\tau = 60$ ns for $[Os(bpy)_3]^{2+}$), while pushing the luminescence further to the red [62,63]. This bathochromic shift results from increased delocalisation and an electron-attracting effect of the ethynylene unit. Double substitution of the anthracene chromophore at the 9- and 10-positions appears to be a requisite in this system to match the energy of the ($^3\pi$–π^*) and ^{3}MLCT states ($\Delta E_{(MLCT-\pi-\pi^*)} = 750\ cm^{-1}$, with the $^3\pi$–π^* state being lower in energy). Selective excitation of the osmium polypyridine chromophore with a sub-ps laser pulse at 600 nm leads to the reaching of the excited-state equilibrium with a rate of $3 \times 10^{10}\ s^{-1}$. Assuming a K_{eq} value of 40, remarkably high forward and back rate constants ($k_f = 2.9 \times 10^{10}\ s^{-1}$ and $k_b = 7.3 \times 10^8\ s^{-1}$), for energy transfer from Os-based to anthracene-like triplet are estimated. These very high values are ascribed to the high electronic conductivity of the alkyne connector [67]. Interestingly, it appears that the ethynylene group stabilises the anthracene-containing module against irreversible, unwanted endoperoxide formation with molecular oxygen which is known to degrade the parent chromophore in presence of light [17,18,68]. It should be stressed that in the case under discussion (as well as in other cases discussed in this section), the increase of excited-state lifetime is clearly due to two concomitant effects: delocalization of the acceptor ligand of the MLCT state and equilibration. To evaluate how much of the global effect can be attributed to each factor is difficult in the absence of additional information. Disentanglement of the effects can be obtained if species featuring an (almost) identical delocalization effect are available, without containing the organic chromophore responsible for the equilibration, but this is not always possible or easily accessible from a synthetic viewpoint.

The triad $[Ru(bpy)_2(\mathbf{27})]^{2+}$ containing a central Pt bis (σ-acetylide) unit in addition to the pyrene and $[Ru(bpy)_3]^{2+}$ moieties was also synthesized (for the trpy analogue see ligand **28**) [61]. Similarly to the ethynylene bridged dyad, $[Ru(bpy)_2(\mathbf{23})]^{2+}$, the triad was demonstrated to give a prolonged luminescence lifetime (17 μs) in acetonitrile due to reversible energy transfer. Although the energy differences between the relevant triplets of the two terminal chromophores are very similar for the two systems (710 cm^{-1} and 930 cm^{-1} for the triad and dyad, respectively) the rate constants for forward and back energy transfer are 2–3 orders of magnitude lower ($k_f = 3 \times 10^8\ s^{-1}$; $k_b = 9.4 \times 10^6\ s^{-1}$) for the system containing the central Pt unit. According to the authors [61], these results indicate that the central Pt bis(σ-acetylide) unit is a much inferior electronic conductor than a simple ethynylene group.

Most recently, De Cola and co-workers [69] reported a long luminescent species using a nice elaboration on the above systems with ligand **29**, where the bridge is a fragment of an oligo(phenylene ethynylene). In this case, the pyrene triplet is located around 900 cm^{-1} below the ^{3}MLCT state and, unusually, room temperature phosphorescence is observed along with the ^{3}MLCT-based emission. Unlike Harriman and Ziessel's ethynylated systems, the reported rates of forward and back energy transfer between closest lying states are slow: $2 \times 10^5\ s^{-1}$ and $3.3 \times 10^4\ s^{-1}$, respectively. These low values suggest that the electronic communication between the two chromophoric units is very weak and equilibration is hardly reached. The reasons for this unexpected behavior are not clear.

4. Summary

In carefully designed supramolecular systems comprising an organic chromophore linked to a metal polypyridine complex, prolongation of luminescence lifetime can be achieved when lowest lying ^{3}MLCT and $^3(\pi\text{–}\pi^*)$ states are quasi-isoenergetic. In this condition, equilibration between states can indeed lead to ^{3}MLCT emission with prolonged lifetimes, where the triplet state of the organic moiety plays the role of excited-state energy "reservoir" or storage element, provided that some kinetic parameters are fitted, in particular depending largely on the rates of intercomponent energy transfer and the intrinsic decay rates of the components. Tuning lifetime has been achieved using the multichromophore and/or solvent effects. Applications envisaged for these types of systems range from hydrogen-production using solar energy to oxygen sensors. Moreover, it should be considered that in multicomponent chromophore-spacer-quencher supramolecular systems, excited-state lifetime of the chromophore can be a limiting factor for the efficiency of long-range photoinduced electron and energy transfer processes: approaches leading to prolonged excited-state lifetimes of the photo-active subunit can indeed allow electron transfer or electronic energy transfer across longer distances and/or more efficiently.

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