Luminescent polynuclear assemblies

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This *tutorial review* consists of five main sections. The first gives a general introduction and then a discussion about the need for luminescent assemblies. The next four sections present the various assemblies based on the metal ions used to assemble the final structures. Each of these sections gives a brief overview of the design principles, synthesis, and ground and excited-state properties of the ligands and complexes in question. The review concludes with some suggestions for future avenues of research.

1. Introduction

The harnessing of light energy by photoactive units has led to the pursuit of artificial light harvesting systems (LHS) that promise to resolve many of the world's energy needs.[1] Much of the inspiration for this research stems from natural LHS, which represent the pinnacle of complexity and function, and the lessons learned in elucidating their structure and function continue to be instrumental in the design of efficient devices. While several important issues need to be addressed in the development of functional artificial devices, perhaps the most significant is the assembly of many photoactive units by means conducive to energy and electron transfer. The reason for this stems from two considerations: the first is that the targeted function can involve the transfer of multiple electrons and so the absorption of multiple photons is required for every molecule produced;[2] the second is that energy transfer is never completely efficient, succumbing often to heat dissipation, and so a high input of light energy is required.[3]

In constructing its LHS, Nature uses many weak non-covalent interactions, however, constructing artificial LHS in a similar fashion may not be suitable to the photoactive units employed or the conditions of operation of an artificial device. Whereas covalent bonds give more durable, inert systems, low yields and laborious syntheses often precludes their use in artificial LHS. In between these two extremes lies dative bonding, with bond strengths ranging from weak to strong, which may allow for the self-assembly of multi-chromophoric structures while offering bond strengths suitable to afford robust systems. Recent examples of systems involving strong dative bonding have focused on utilizing iterative chemical transformations with compromised efficiency and demanding purification.[4] Although several limitations of this approach have been overcome,[5] synthesis of polynuclear assemblies with strong dative bonding remains tedious and structures of high nuclearity often possess a large degree of freedom which may preclude structural characterization and frustrate energy transfer processes. For example, multinuclear complexes composed of tris-bidentate ligand complexes of d^6-metal ions had previously been shown to transfer energy among the component parts depending on the choice of metal ion incorporated into the array.[6] One drawback of the $M(bpy)_3^{2+}$ motif, however, is that the Λ and Δ enantiomers of the monometallic unit will lead to diastereomeric complexes in its polynuclear assembly.[7] Although enantiopurification

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techniques have been developed to address this challenge,[8] the bis-tridentate ligand complexes can be used as achiral equivalents to $M(bpy)_3^{2+}$. For example, the $Ru(tpy)_2^{2+}$ motif (tpy = 2,2′:6′,2″-terpyridine) has been used. However, it has a short MLCT (metal-to-ligand charge-transfer) excited-state lifetime at room temperature (rt) due to thermal population of metal-centred (MC) states from the MLCT states, followed by ready non-radiative deactivation back to the ground state.[9] Its excited-state lifetime at rt can be prolonged by modifications to the ligands bound to the Ru(II) centre.[10] Several approaches were developed to increase the energy separation between the MC and MLCT states: by raising the energy of the MC state,[11] by lowering the energy of the MLCT state,[10b] and more recently, by a combination of these two approaches.[12]

The use of weaker dative bonding, along with various possible coordination geometries of the metal ions involved, is conducive to rapid synthesis of multinuclear photoactive arrays with pre-determined architectures. Apart from facilitating construction, incorporation of metal ions can also serve to greatly affect energy and electron transfer processes, and thus the photophysical properties of the final assemblies. In addition, control of the overall 3-D organization and morphology of the photoactive array has been found to dramatically affect energy migration,[13] which can be controlled to a great extent by metal ions. Such a wide range of modifications has served to provide ideal systems for study of electron and energy transfer processes and has permitted access to a wide range of potential applications. In this tutorial review we present recent achievements in the metal-directed self-assembly of photoactive systems classified according to the coordination geometry employed in their assembly.

2. Luminescent assemblies from metal ions with tetrahedral coordination geometry

Metal centers adopting a tetrahedral coordination motif are most frequently of d^{10} configurations, with the nature (*e.g.*, hapticity, bite angle, steric bulk) and flexibility of the ligand(s) leading to somewhat distorted geometries. Ag(I), Au(I), and Cu(I) complexes are the most prevalent metal ions in polymetallic assemblies, with Ag(I) and Au(I) being prone to metal–metal bonding interactions. Combined with non-specific coordination numbers, it is not surprising that these metals are often found in the context of luminescent clusters[14] and polymeric compounds.[15]

Ag(I) is regarded as a soft acid that favours coordination of soft bases, such as sulfur and phosphorus containing ligands. Such donors have typically been in the context of a simple chelating ligand.[16] While the assembly of polymeric structures and clusters still prevail, the appropriate design of ligands can lead to discrete structures normally exhibited by square planar and octahedral metal centers. For example, bis-bidentate N-heterocycles derived from imine formation, like those depicted in Fig. 1, are readily obtained by condensation of an appropriate diamine with 2-formyl pyridine.[17]

Equimolar amount of ligand **1** and $AgClO_4$ produced crystalline material comprising a zig-zag 1-D chain exhibiting intermolecular π–π stacking interactions. However, upon dissolution in acetonitrile, this polymer was observed to rearrange into a [2 × 2] grid structure **5**, as evidenced by a symmetric ^{1}H NMR spectrum and as confirmed by FAB-MS. However, when a methanol solution of $AgClO_4$ was layered over a solution of ligand **2** in nitrobenzene–toluene, a rectangular structure **3** was formed that showed no evidence of rearrangement in solution. These Ag(I) complexes do not possess significant MLCT bands in their absorption spectra, and so luminescence must derive from the ligand itself, although neither **1** nor **2** is luminescent in either the solid state or solution. Upon complexation, luminescence from ligand-centered π–π^* states is observed (τ = 1.2–12.7 ns), even at room temperature, due to an increase in ligand rigidity by complexation to the metal ions. This is a common theme with regard to d^{10} metal ions such as Ag(I) and Zn(II), however, the metal is not completely innocent in this regard, since decay profiles are clearly bi-exponential with both short-lived $^1\pi$–π^* and longer-lived $^3\pi$–π^* intraligand transitions, the latter

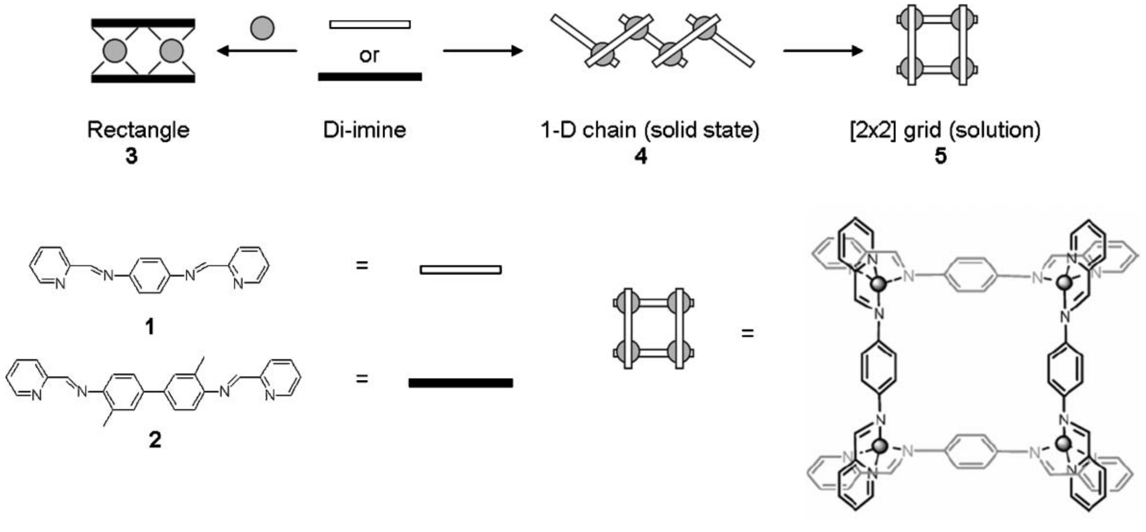


Fig. 1 Characteristic solution equilibria of Ag(I) complexes containing dinucleating ligands.

stemming from heavy-atom relaxation of spin-forbidden processes. This is clearly an interesting case considering that most Ag(I)-based systems display luminescence only in the solid state or at 77 K. Also, the inert nature and luminescence of the rectangle **3** indicates that this approach is certainly a step in the right direction towards viable applications.

In the pursuit of suitable photoactive units, much work has been devoted in the last twenty years to Cu(I) (bis)diimine complexes, where the diimine ligand is typically 1,10-phenanthroline (phen) or a derivative thereof.[18] Similar to Ru(II)-polypyridyl complexes, these complexes possess MLCT bands in the visible region. However, modification of the 1,10-phenanthroline ligand has much more dramatic effects on both the MLCT absorption profile and the excited-state lifetime and emission intensity. Considering that the parent complex $Cu(phen)_2^+$ is non-emissive in solution, homo- and heteroleptic analogues have been prepared which exhibit strong luminescence.[18] The strategies employed to prolong luminescence lifetimes have mirrored those employed with Ru(II) polypyridyls,[19] such as increasing ligand delocalization and lowering thermal accessibility of upper-lying deactivating states. The extent to which the emissive properties may be tuned bodes well for device applications, as does the fact that the excited state of such Cu(I) complexes leads to more powerful reductants than that of their $Ru(bpy)_3$ counterparts (-1.11 V for $Cu^*(phen)_2^+ \rightarrow Cu(phen)_2{}^{2+}$ *vs* -0.85 V for $Ru^*(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+}$). This has naturally led to such potential applications as electroluminescent devices[20] and photovoltaic devices.[21]

The incorporation of Cu(I) phenanthrolines into multi-component photoactive systems has, for the most part, been in the context of rotaxanes, catenanes, and dendritic systems.[18] With regard to these systems, fullerenes have been an attractive partner for Cu(I) phenanthrolines considering that it exhibits diagnostic singlet and triplet transient absorption spectra and is an excellent electron acceptor. Recently, fullerene helicates formed from bismethanofullerene (**A**) and methanofullerene (**B**) (Fig. 2) were found to be the sum of the spectra of their individual components, which suggests that no ground-state electronic interaction between the Cu(I)-phenanthroline and C_{60} moieties exists.[22]

Fluorescence from the bismethanofullerene was unaffected relative to a related model compound consisting of nearly the same ligand but without the bis-phenanthroline portion. This is in accord with other supramolecular assemblies containing such photoactive units. Considering the energies for the ^{3}MLCT of $Cu(I)(phen)_2$, the singlet emissive state of the bismethanofullerene, and the charge separated state ($Cu^+–F^-$) produced upon electron transfer, it was determined that excitation of either photoactive unit could lead to exergonic electron transfer. Although this driving force was found to be larger upon excitation of bismethanofullerene, the maintenance of the fullerene emission upon helicate formation points to electron transfer from the ^{3}MLCT of the Cu(I) core. Although this process is less thermodynamically favoured, the authors noted that it is likely that the occurrence of a MLCT prior to electron transfer serves to reduce kinetic activation barriers to electron transfer by a affecting the external and internal reorganization energy contributions.

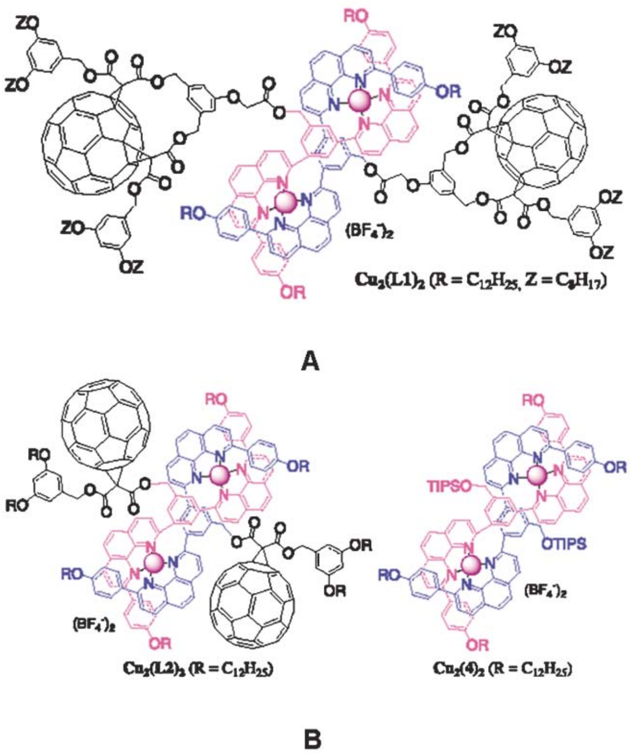


Fig. 2 Cu(I) helical fullerene structures: bismethanofullerene (**A**) and methanofullerene (**B**). (Reproduced with permission from ref. 22. Copyright 2006 Elsevier.)

3. Luminescent assemblies from metal ions with square planar coordination geometry

The role of square planar metal ions in producing many photoactive assemblies is primarily structural in nature. In this case, suitable photoactive units coordinated to the assembling metal ion can experience an increase in rigidity, which can in turn influence emission energy and intensity by enhancing ligand π-delocalization and minimizing excited-state structural perturbations. However, there exists a plethora of mononuclear square planar complexes which exhibit MLCT and, depending on the ligand, ILCT states from which emission may occur. It is therefore reasonable to develop polynuclear systems wherein these metals comprise the photoactive unit. Of these, Pt^{2+} complexes have received a great deal of attention,[23] while Pd^{2+} has received somewhat less,[24] and is due to the larger ligand field produced with Pt^{2+} compared to Pd^{2+} for any given ligand, making upper lying ^{3}MC states less thermally accessible from the emissive ^{3}MLCT or ^{3}ILCT states. In this way, efficient non-radiative decay from these highly distorted ^{3}MC states to the ground state is reduced, thereby preserving excited–state population. The result is often room temperature solution luminescence for Pt^{2+} complexes whereas solid state or 77 K emission is observed with Pd^{2+} complexes, although a few examples of room temperature emission are known.[24] The use of a square-planar coordination motif in photoactive arrays have been discussed in recent reviews,[25] and the following discussions concern developments since that time.

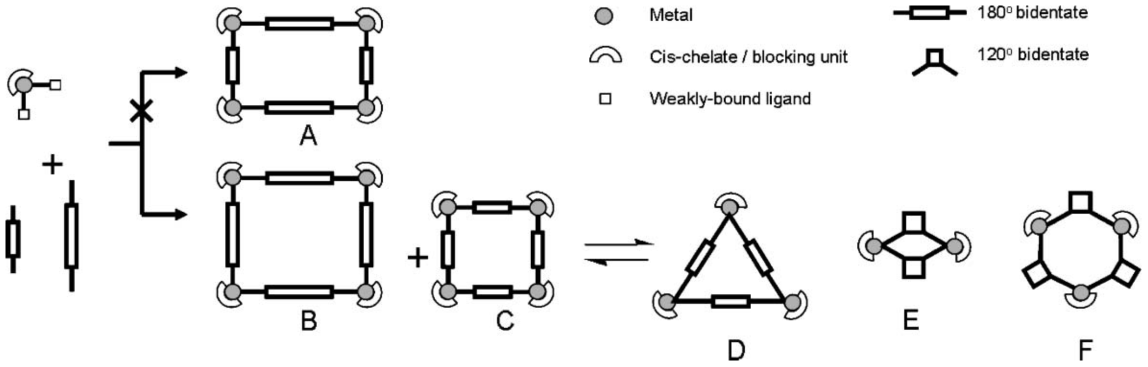
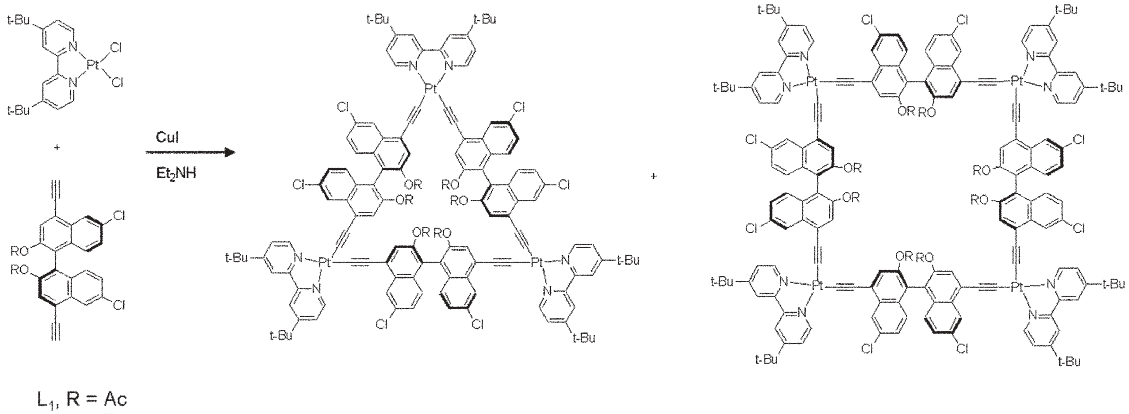


Fig. 3 Metal-directed self-assembly leads to several possible discrete products (A–F).

With regard to forming square assemblies, the conventional self-assembly approach outlined in Fig. 3 has inherent limitations, owing to the relative thermodynamic stabilities of all possible species in solution. This becomes evident in pursuit of larger square assemblies where one relies on longer, linear bridging ligands whose increased flexibility diminishes the enthalpic advantage of square formation (Fig. 3, B and C) over that of a triangle (Fig. 3, D), allowing the entropic advantage of triangle formation to become significant in determining product distribution. An additional disadvantage is the inability to form structures of particular topologies *via* a one-pot self-assembly approach, as exemplified in the construction of chiral, enantiopure squares and triangles composed of Pt^{2+} corners and BINOL-derived, linear bis(4,4′-alkynyl) ligands (L_1 and L_2, Fig. 4).[26] A related square employing the same bridging ligands, but using bulky phosphines in place of 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbPy), was reported earlier and shown to be enantiopure, exhibiting dual room temperature emission from intra-ligand $^1\pi$–π^* (425 nm, $\tau < 400$ ps) and $^3\pi$–π^* (582 nm, $\tau \sim 100$ μs).[27] Considering that the emission from the ligand itself is fluorescence, the effect of Pt^{2+} incorporation has led to efficient singlet–triplet intersystem crossing *via* spin–orbit coupling. The exclusive production of such squares was previously accomplished after multiple steps wherein two mono-nuclear $(Et_3P)_2Pt(L)_2^{2+}$ corner units were covalently coupled to two corner units of $(Et_3P)_2PtCl_2$ in 34–46% yield. More recently, the species shown in Fig. 4 were produced utilizing once again covalent bond synthesis, but in the context of a one-pot self-assembly. Interestingly, although **6a** and **7a** are isolated from the same reaction mixture, dissolution of **6a** cleanly produces **7a** with a half-life of 4 days. The incorporation of the chelating ligand dtbPy was done in pursuit of electroluminescent device applications, since phosphorescence emanating from the ^{3}MLCT [Pt – π^*(diimine)] transition of simple (diimine)–Pt(acetylide)$_2$ complexes has been of interest for the fabrication of light-emitting devices. Square **7a** was shown to be strongly phosphorescent (Φ_p = 9.4%) and stable, giving electroluminescent performance exceeding that for simple (diimine)–Pt(acetylide)$_2$ complexes.[21]

Coordination to a square planar assembling unit is also of interest with regard to the "complex-as-ligand" approach by which transition-metal containing photoactive groups are prepared with suitable secondary functionality to allow for subsequent coordination to other metal ions. This approach has been particularly popular among ruthenium polypyridyl and metallo-porphyrin researchers, owing to the robust nature of the complexes and the potential to perform chemical modifications directly on the complex.[10a,19] Most often, the secondary functionality is installed through preparation of homo- or hetero-ditopic ligands, as illustrated in Fig. 5 and 6. Complex **9**, with a tris-bidentate pseudo-octahedral ligand

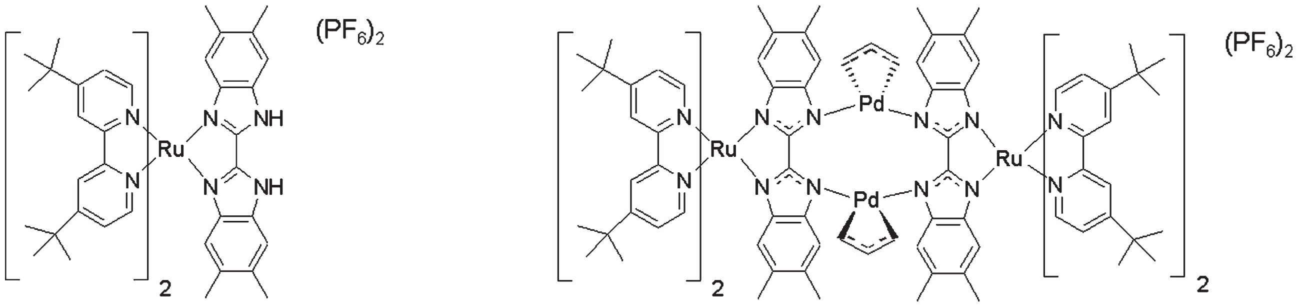


L_1, R = Ac
L_2, R = Et

[Pt(4,4′-dtbPy)(L_1)]$_3$, **6a**, 29 %
[Pt(4,4′-dtbPy)(L_2)]$_3$, 0 %

[Pt(4,4′-dtbPy)(L_1)]$_4$, **7a**, 22 %
[Pt(4,4′-dtbPy)(L_2)]$_4$, **7b**, 17 %

Fig. 4 Topological discrimination: generation of enantio-pure geometries from chiral sub-units with potential electroluminescence application.



8

9

Fig. 5 Model compound exhibiting photo-initiated electron collection at Pd(II) sub-units.

arrangement, and its precursor complex **8**, were synthesized for the purposes of fundamental investigations into electron and energy transfer between subunits of metal-based light harvesting antennas (Fig. 5).[28]

Precursor complex **8** has a ^{1}MLCT excitation at 490 nm, with room temperature solution emission at 650 nm and a luminescence decay of 363 ns, while complex **2** has a red-shifted ^{1}MLCT excitation at 530 nm, with room temperature solution emission at 658 nm and a luminescence decay of 244 ns. Monitoring of the excited-state relaxation processes leading to the equilibrated ^{3}MLCT by time-resolved transient absorption revealed a very fast ($\geqslant$200 fs) process and a slower solvent-dependent process ($\approx$1.5 ps) corresponding to intersystem crossing and solvent reorganization processes, respectively. An additional time constant (50 ps) was observed for **9** corresponding to a mono-exponential transient decay, indicating a charge transfer to the Pd(allyl)$^{2+}$ unit which then equilibrates with the Ru(II) excited-state. Since charge transfer is initiated on the periphery and terminates on the central Pd(allyl) units, which are rather open to substrate binding, this system serves as a functional model for the photosynthesis reaction center in plants.

A recent potential host–guest assembly has been described using the strongly luminescent $[Ru(bpy)_3]^{2+}$ motif in a "complex-as-ligand" approach where the datively unsaturated $[Ru(bpy)_2(qpy)]Cl$ (see Fig. 6, where qpy is 2,2′:4,4″:4′,4‴-quaterpyridyl) is heated with 0.5 equiv. of either the solvated adduct $[M(en)(solv)_2]^{2+}$ (where M = Pd^{2+}(**A**) or Pt^{2+}(**B**), en is 1,2-ethylenediamine) or $ClRe(CO)_5$ (**C**).[29] Considering that every coordination compound is to some degree in an assembly–disassembly equilibrium in solution, the rapid build-up of charge can be a concern as the equilibrium will be affected by such variables as solvent polarity, temperature, and traces of competing ligands. All of the absorption spectra show intense bands at high energy associated with intra-ligand $\pi \rightarrow \pi^*$ processes and lower energy, less intense bands ranging from 350–550 nm arising from Pd/Pt(d) $\rightarrow$ L(π^*) and Ru(d) $\rightarrow$ L(π^*) processes, with relatively intense emissions occurring between 650–670 nm. This is slightly red shifted relative to $[Ru(bpy)_2(qpy)]^{2+}$, as expected since coordination serves to

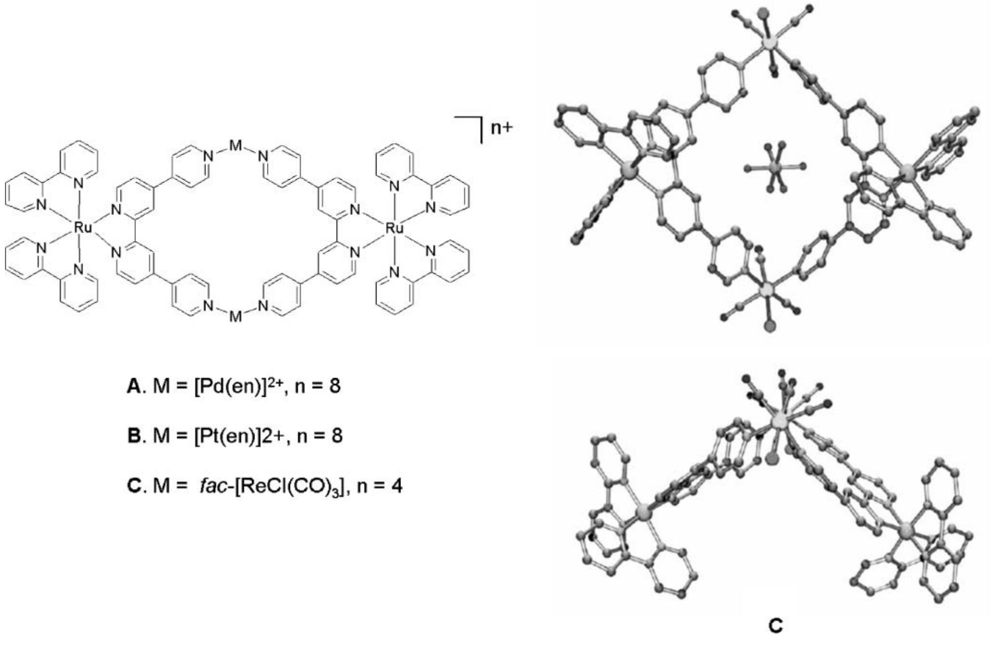


Fig. 6 Kinetically-locked metallomacrocycles based upon $Ru(bpy)_3^{2+}$, assembled from Pd(II) (**A**), Pt(II) (**B**), and Re(I) (**C**) sub-units.

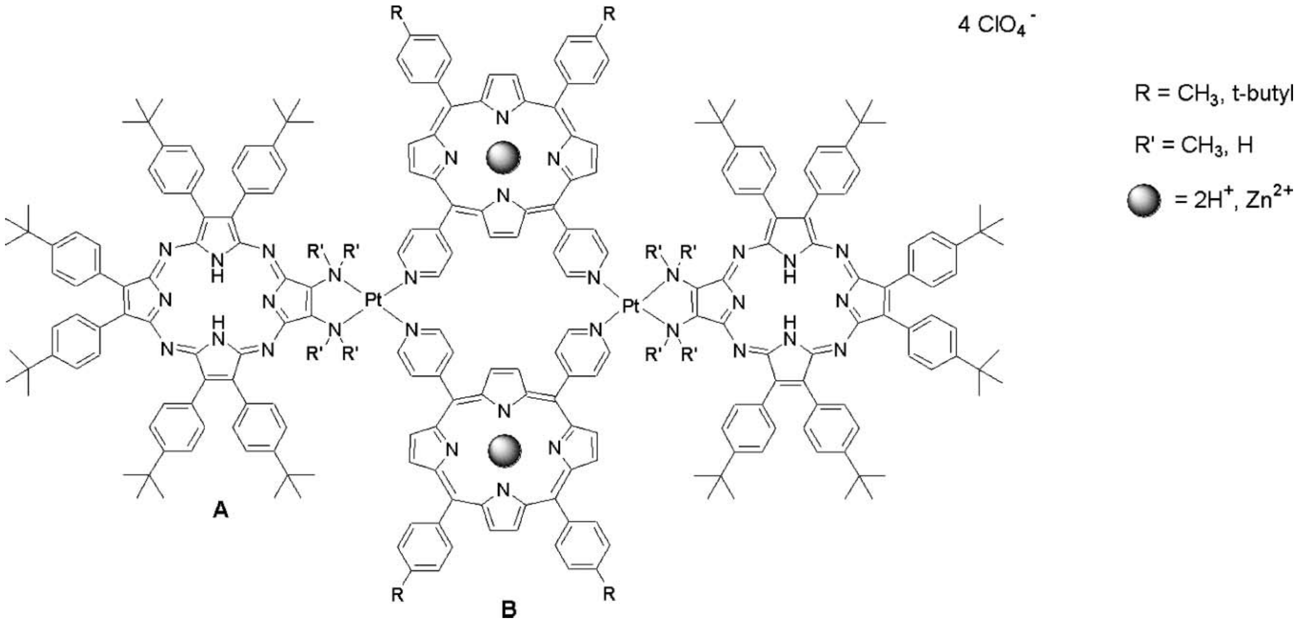


Fig. 7 Dative assembly of porphyrin (**B**) and porphyrazine (**A**) chromophores exhibiting efficient energy transfer phenomena.

stabilize the ligand-centered π^* orbitals (*i.e.* MLCT state). Also, this emission is insensitive to the excitation wavelength which indicates efficient energy transfer from the other excited states to the Ru-^{3}MLCT state. From a structural point of view, in order to accommodate coordination to both octahedral metals, **C** has a bent shape when looking down the Re–Re axis. The room temperature luminescence, particularly in water, and the limited number of counter-anions within the internal cavity for **C** encouraged further host–guest complexation/sensing studies which showed that the ''puckered'' cavity of **C** can enhance binding of guest aromatic molecules.[29]

Much effort has been directed toward the assembly of multinuclear porphyrinoid assemblies, owing to a wide range of potentially exploitable physical properties, including luminescence.[30] Of the existing strategies, metal-directed assembly is particularly attractive considering the influential electronic role played by the linking metal unit(s) and a wide variety of such subunits that can be prepared with secondary dative functionality. A recent, elegant example by Drain and co-workers embodies these synthetic considerations (Fig. 7).[31]

Dipyridyl-porphyrin subunits (**B**, Fig. 7) and diamine-porphyrazine subunits (**A**) were incorporated into a tetra-porphyrinic assembly upon coordination of Pt^{2+}. A one-pot self assembly approach using stoichiometric equivalents of each component yielded only small amounts of the desired structure, since the dative functionality installed on the exterior of the subunits is not exclusively predisposed to discrete structures. Such alternative outcomes are made particularly troublesome considering a distinct difference in binding kinetics between the pyridyls of **B** and the diamine unit of **A**, particularly when dimethylamine is employed. A stepwise synthesis was thus taken, whereby preparation of the precursor $(\mathbf{B})_2Pt_2Cl_4$, followed by dechlorination with $AgClO_4$ in the presence of **A** led to the desired target in 60% yield. Large changes in the electronic absorption profile of this compound relative to those of the subunits **A** and **B** indicate significant electronic mixing between subunits, facilitated by coordination to the Pt^{2+} centers. This is reflected also in the emission spectra, whereby selective excitation of the Zn(II) complexes of **B** results in strong emission from **A** at 740 nm, and *vice versa*, indicating efficient energy transfer.

4. Luminescent assemblies from metal ions with octahedral coordination geometry

4.1 Square structures

The creation of square photoactive structures is inherently facilitated by transition metals predisposed to mutually perpendicular dative bonds. To this end, octahedral metal centers have received much attention, with preference being given to second and third row transition metals owing to their more inert character. Of these, Re(I) has been particularly emphasized as an assembling unit, as we have seen already in Fig. 6c. Its popularity stems from attractive photophysical properties of the *fac*-$[ClRe(CO)_3LL]$ complexes (where LL is a diimine ligand) since they display intense luminescence in the visible region and are stable to photodecomposition.[32] Complexes composed of such units have, therefore, also been of interest for solar energy conversion.[33] In addition, unlike its more prevalent counterparts based on Pt^{2+} and Pd^{2+}, these assemblies can be prepared with charge neutrality which means that the cavities are not occupied by counterions and are available for inclusion of guest molecules. Such events can have large effects on the luminescence of the parent complex, and so solution-phase molecular sensing has become intensely studied of late.[32b] An added feature for such assemblies has been the formation of channels due to stacking of these molecular cavities in the solid state, making applications as solid state chemical sensors[34] and molecular sieving[35] possible as well.

A wide range of assemblies have been prepared from the octahedral coordination motif $XRe(CO)_5$ (X = Cl or Br), where carbonyls are thermally liberated in non or weakly coordinating solvent for coordination to a suitable bis-monodentate ligand. The resultant geometry is often dictated by the flexibility and steric bulk of the bridging ligand. Recently, focus in the literature has shifted from the self-assembly of squares to rectangles, in part because the lower symmetry of a rectangle should lead to greater selectivity and binding, especially for planar aromatic guests.[36]

A promising aspect of coordination-based assemblies is the range of properties that can be introduced and/or perturbed simply by changing the transition metal ion incorporated into a given assembly. The latter has been well illustrated by Hupp and co-workers, where both square and rectangular charge-neutral assemblies have been prepared using moderately fluorescent ($^1\pi \rightarrow {}^1\pi^*$) Zn(salen) complexes and the anionic benzimidazolate bridging ligand (Fig. 8).[37] Considering that Zn(II) possesses a closed shell d^{10} configuration, its incorporation into the salen framework serves more of a structural role as it rigidifies this bridging ligand, making it more suitable for charge delocalization. This effect is evidenced through decreased emission energy and an increase in its intensity relative to the free ligand. However, upon coordination of Re(I), a reduction in emission intensity is observed. This effect is likely due to facilitation of intersystem crossing from the excited singlet to the non-emissive triplet state ($^3\pi^*$) of the salen ligand. Also, no ^{3}MLCT emission is observed from these assemblies even though it lies 3000 cm^{-1} below the salen emissive state, suggesting that the $^3\pi^*$ state lies even lower in energy.

The coordinative flexibility of Zn(II) afforded by its d^{10} configuration also allows for axial coordination and hence the potential to bind guest molecules in a dative fashion. Thus, the bridging ligands are the two variations of the Zn(II)salen complex used to construct the square assemblies. The red-shift in both absorption and emission for the phenyl (yellow) derivative relative to the aliphatic (blue), along with good spectral overlap, prompted the formation of the bridged-square assemblies depicted in Fig. 8. These assemblies demonstrate that the aliphatic derivative behaves as a donor for energy transfer and the phenyl derivative as an acceptor, whereby the outer assembly of Zn(II)salen–aliphatic complexes behave collectively as antennae for efficient energy transfer to the encapsulated Zn(II)salen–phenyl complex for subsequent fluorescence emission.

In addition to Re(I) carbonyls, Ru(II), and Os(II) polypyridyls have been heavily investigated owing to their relatively strong luminescence and the ease with which their photophysical properties may be altered through either synthetic manipulation of their ligands or changes in environmental conditions (*i.e.* temperature, pH, and solvent).[19,38] Their incorporation into larger assemblies can be attained through covalent bond formation, design of polytopic ligands, or using the "complex-as-ligand" approach whereby appropriately-functionalized polypyridyl complexes are used as pre-organized units in self-assembly. With regard to the latter approach, Lees and co-workers have prepared square assemblies in a step-wise synthesis using $(\text{pytpy})_2\text{M}^{2+}$ (where pytpy = 4′-(4-pyridyl)-terpyridine, M = Fe(II), Ru(II), and Os(II)) along with corner units of either *fac*-$\text{Re(CO)}_4\text{Br}$ or *cis*-protected $[1,1'\text{-}(\text{PPh}_2)\text{Fc}]\text{Pd}^{2+}$ (Fig. 9).[39] In this way, the $(\text{pytpy})_2\text{M}^{2+}$ unit behaves as an extended 4,4′-bipyridine.[40] The squares **10–13** were synthesized in high yield by simply heating a 1 : 1 mix of corner unit and $(\text{pytpy})_2\text{M}^{2+}$ in an appropriate solvent, where the highly charged product precipitates from solution. The electronic effect of square formation is reflected in both their solution electrochemistry and their solution absorption and emission spectra. The absorption spectra for **10–12** indicates a red shift for the $(\text{pytpy})_2\text{M}^{2+}$ based MLCT, the origin of which could be either an electronic effect of the Re(I) unit or an extended π-delocalization effect upon formation of the square. Cyclic voltammetry of **10–12** along with their component subunits shows a shift to more positive potential for both the $\text{M}^{2+}/\text{M}^{3+}$ oxidation and the first ligand-centered reduction processes, the latter of which is more pronounced indicating a lowering of the MLCT energy, in accordance with

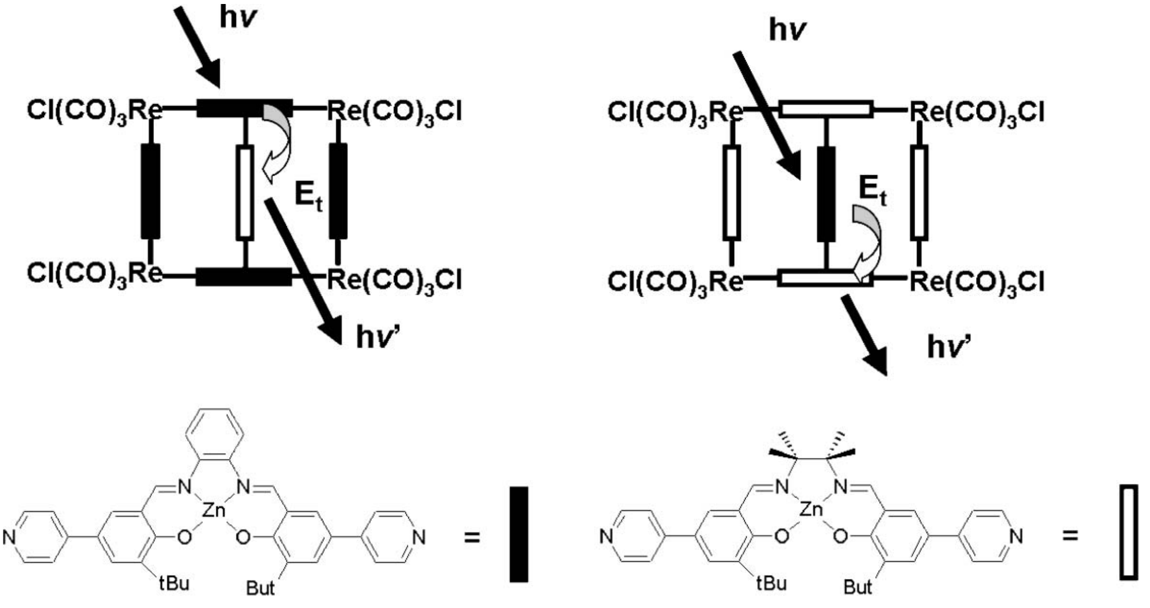


Fig. 8 Mediation of energy transfer in Re(I)-based photoactive assemblies upon installation of Zn(II) (salen) complexes.

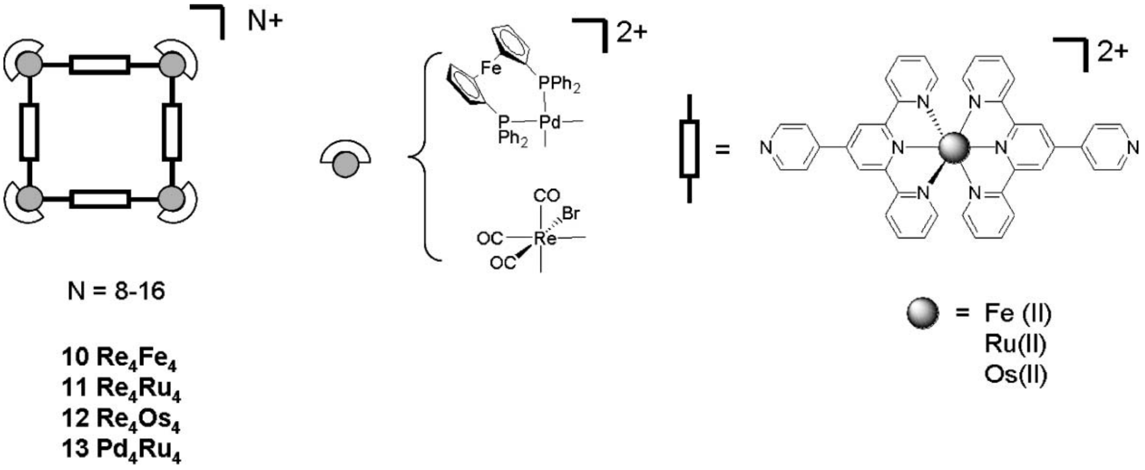


Fig. 9 The "complex-as-ligand" approach: Re(I)-based assemblies using various homoleptic 4-pyridyl-tpy complexes.

electronic absorption spectra. This result suggests an electron-withdrawing effect upon coordination to the Re(I) unit. In terms of luminescence, **10**, **11**, and **13** have no detectable emission at room temperature, as with their mononuclear (pytpy)$_2$Fe^{2+}and (pytpy)$_2$Ru^{2+} starting materials. Despite a net stabilization of the ^{3}MLCT state for (pytpy)$_2$M^{2+}, deactivation *via* non-radiative relaxation from upper-lying ^{3}MC states is significant and, in the case of **13**, there is an additional affect of upper-lying ^{3}MC states centered on the ferrocene units. It is for this reason and the potential reductive quenching of the ^{3}MLCT state by electron donating *cis*-protecting ligands that have precluded the formation of luminescent assemblies based on such preorganized units. On the other hand, the Os(II) based structure **12** is luminescent (Fig. 9). This is due to the stronger ligand field generated by Os(II) compared to both Fe(II) and Ru(II) which results in a higher energy ^{3}MC state that is not as thermally accessible. Newkome and co-workers have prepared related, discrete structures composed of tri-, penta-, and hexa-nuclear bis(terpyridyl)M^{2+} units using appropriately angular ditopic bis(terpyridyl) ligands assembled from Fe(II), Ru(II), and Zn(II) coordination.[41] Again, thermal population of deactivating ^{3}MC states led to efficient quenching in all cases, even when typically fluorescent ligands were employed, the exception being those structures incorporating Zn(II) owing to its closed-shell configuration. In the end, these complexes illustrate some of the factors that govern luminescence in larger assemblies and show that beginning with luminescent components does not necessarily guarantee luminescent products.

4.2 Grid arrays

Polyheterocyclic ligands, such as ligand **14** in Fig. 10, are well suited to assemble into grid-like structures in the presence of metal ions with octahedral coordination geometries.[42,43] As the complexes of polyheterocyclic ligands with metal ions like Ru(II) and Os(II) are characterized by photo-generated MLCT states, such grid-like molecules should be well suited for photonic device applications. Since the energy of the MLCT state is sensitive to the nature of the metal, polymetallic grids offer broad absorption bands in the visible spectrum, a prerequisite for suitable light-harvesting arrays. Equally appealing is the variation of the emissive ^{3}MLCT state simply through selection of the metals employed. Thus, energy gradients can be created to effect vectorial energy transfer, another desired property of such arrays, and the direction of photoinduced energy transfer can even be controlled.[44]

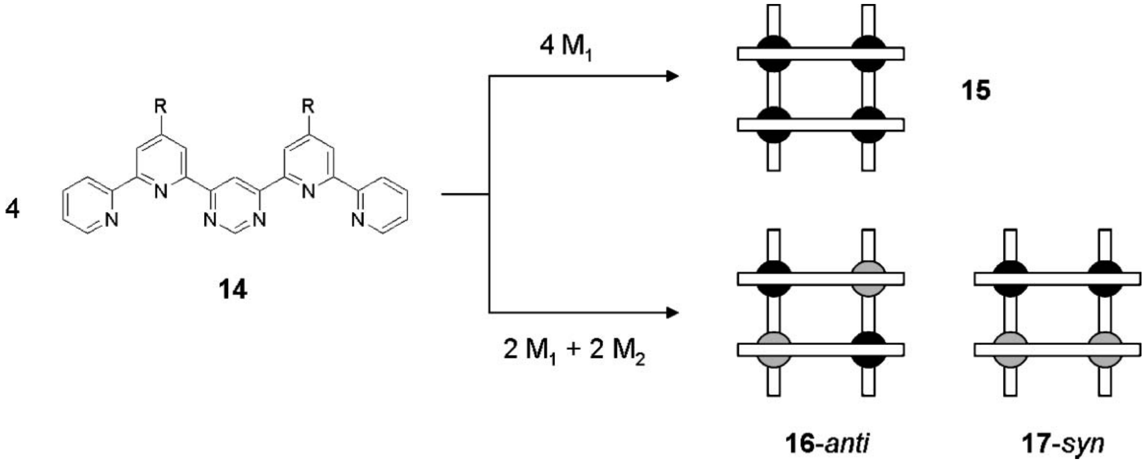


Fig. 10 Potential outcomes to strict self-assembly approach to homo- and hetero-tetrametallic grids.

Energy transfer within grid assemblies can be seen in the mixed-metal grids [Os_2Fe_2] and [Ru_2Fe_2] (**16**-*anti* in Fig. 10), which do not emit due to the presence of the Fe(II) unit which has a ^{3}MC state located below its ^{3}MLCT state.[45] This effectively creates an efficient energy sink upon excitation of Os(II) and Ru(II), resulting in rapid energy transfer to the Fe(II) ^{3}MC state from which deactivation readily occurs. Such energy transfer has been found from pump–probe femtosecond spectroscopy to be less than 200 fs for dinuclear Os–L–Ru and Ru–L–Ru complexes, where L is electronically very similar to **14**.[46] This is a rate on par with ^{1}MLCT–^{3}MLCT conversion,[47] and such rapid transfer is likely present in the grids presented here. When considering large antenna networks for light harvesting devices, such rapid energy transfer is required to effectively compete with excited-state deactivation pathways which, over long distances involving many energy transfer steps, would otherwise render the device inefficient for practical purposes. Unfortunately, to date, such luminescent grids are very rare. However, great advances have been made in recent years toward prolonging the emissive-state lifetime of mononuclear polypyridyl complexes.[10*b*,19] Thus, it stands to reason that a combination of such advancements with intelligent methodology holds tremendous potential for the creation of high nuclearity photoactive grids well suited for device applications.

4.3 Metal dimers

Numerous transition metals exhibit dimeric structures based on a characteristic "paddlewheel" arrangement of four mutually perpendicular bidentate chelates.[48] Depending on the metal and the nature of the chelate, a wide range of physical properties can be exhibited, including long-lived photo-excited states.[49] Considering their use as building blocks in a number of supramolecular architectures,[50] investigation into their potential structural and functional roles toward photoactive assemblies seems to be a natural progression.

Both axial and equatorial coordination sites of metal dimers may be used to assemble larger structures using appropriate bridging ligands. With regard to photoactive assemblies, porphyrins are attractive since a wide range of functionality can be introduced in the course of their synthesis. Dirhodium(II,II) units are attractive as assembling units owing to their rigidity, diamagnetic nature, and an inherent kinetic advantage over other metal dimers regarding ligand displacement.[48] Toward creating directing units for square geometries, the complex *cis*-$Rh_2(form)_2(O_2CCF_3)_2$ (where form = *N*,*N*′-di-*p*-tolylformamidinate) is ideal since it incorporates kinetically inert amidinates as protecting units and kinetically labile trifluoroacetates. Self-assembly of **A** proceeds upon metathesis of *cis*-$Rh_2(form)_2(O_2CCF_3)_2$ with the disodium salt of 15,20-di-(4-carboxyphenyl)-5,10-diphenylporphyrin (Fig. 11).[51] The larger assembly **B** was prepared upon displacement of weakly, axially bound solvent molecules with the stronger bis-monodentate ligand *cis*-5,10-diphenyl-15,20-dipyridylporphyrin.[52] These square assemblies are neutral, which is desired for potential guest uptake analogous to previous discussion pertaining to luminescence detection of host–guest interaction. However, the installation of amidinates leads to electrochemically rich dirhodium(II,II) units, exhibiting facilitated one-electron oxidations relative to their tetracarboxylate counterparts. As such, given the $Rh_2^{4+/5+}$ potential and the excited-state reduction potential for the porphyrin for both **A** and **B**, reductive electron-transfer quenching was found to be energetically favorable in both cases ($\Delta G = -0.4$ eV and

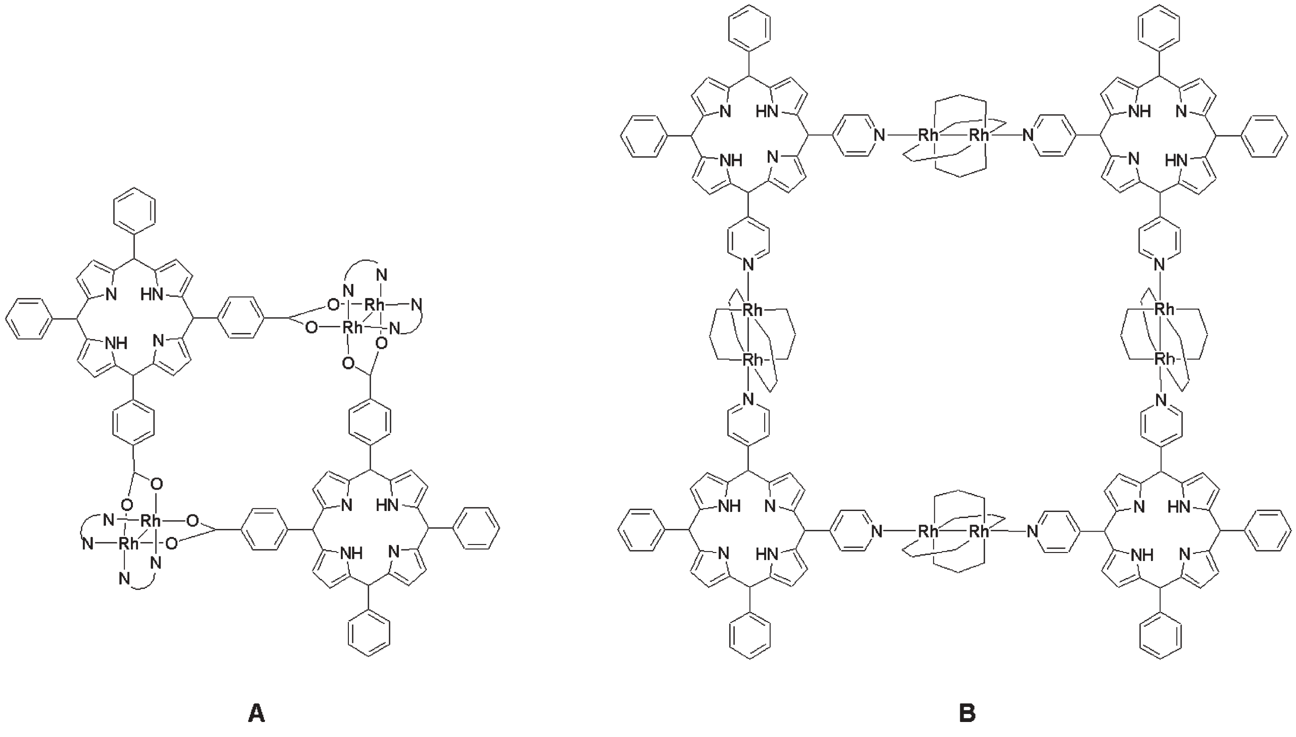


Fig. 11 Dirhodium(II,II)-based porphyrinic assemblies utilizing equatorial (**A**) and axial (**B**) coordination modes of the dimeric unit.

$\Delta G = -0.2$ eV, respectively). The difference in driving force can be attributed to the relatively greater electron richness of the dirhodium(II,II) unit used in **A**. Porphyrin-based emission from **B** is quenched completely, but **A** is very slightly emissive with $\tau < 500$ ps and $\Phi = 7 \times 10^{-5}$ compared to $\tau = 10$ ns and $\Phi = 0.017$ for the parent porphyrin. This trend seems contradictory to the energetic difference for reductive electron transfer, however, given the irreversible nature of the Rh_2 based oxidations for **A**, it is likely that such electron transfer is not as efficient as for that in **B**.

Utilization of such a dirhodium(II,II) unit need not always play the role as a reductive quencher. Hanan and co-workers have identified the di-rhodium(II) tetracarboxylate motif as serving both structural and functional roles toward branched photoactive assemblies (Fig. 12).[53] Photoactive transition metal containing polypyridyl complexes, in particular those based on Ru^{2+}, are robust and can tolerate synthetic modification to a great degree. Of these, those based on terpyridine hold the advantage of being achiral, where otherwise rapid development of isomers can result with arrays based on chiral subunits like $[Ru(bpy)_3]^{2+}$. Carboxylic acid functionalized polypyridyls have been of interest for the dye sensitization of semi-conductor surfaces for the production of solar cells,[21] where such modification allows for adsorption *via* coordination. In a manner akin to typical ligand displacement involving dimetal tetracarboxylates, an excess of the precursor complex $[Ru(4'\text{-}(4\text{-carboxyphenyl})(tpy)]^{2+}$ can be used to displace acetates of dirhodium(II) tetracarboxylate to effect chromophore installation in a controlled manner. These complexes are stable to chromatographic separation and readily identified by well-structured ^{1}H NMR spectra. The dirhodium(II) unit is known to have a non-emissive excited state previously determined to be between 1.34–1.77 eV by energy transfer studies with a long-lived lifetime of up to 5 μs, depending on the solvent and substituent.[49b] Emission studies of the parent chromophore $[Ru(4'\text{-}(4\text{-carboxyphenyl})(tpy)]^{2+}$and of the substituted species suggested an efficient quenching affect by the dirhodium(II) unit. The nature of this quenching was elucidated through the preparation of triazine deficient analogues which exhibited essentially unperturbed emission upon installation of the dirhodium(II) unit.[54] The emissive state for these triazine analogues lies at 1.78 eV, which places the non-emissive state of the dirhodium(II) unit at the upper limit of 1.77 eV. The recent elucidation of other paddlewheel complexes exhibiting long-lived photo-excited states,[49a] in addition to rapid emissive-state modification of the sensitizing unit, bodes well for the creation of photoactive assemblies displaying a wide range of novel physical properties.

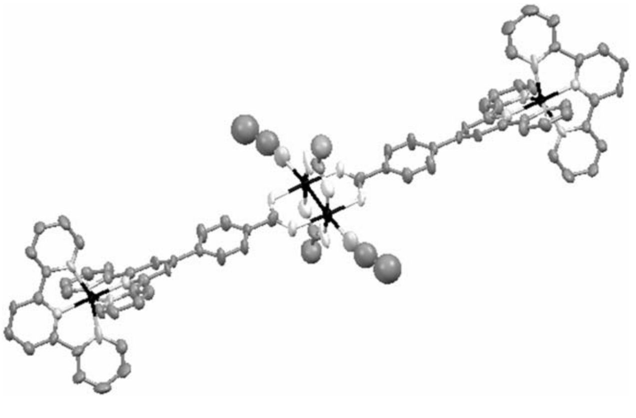


Fig. 12 Convergent assembly of polynuclear Ru(tpy)(4-carboxy-tpy)$^{2+}$ units exhibiting efficient energy transfer to the assembling dirhodium(II,II) core.

5 Luminescent assemblies from metal ions with other coordination geometries

Lanthanides are a natural choice as the metal centre for metal-directed self-assembly of polynuclear luminescent assemblies as their coordination bonds are relatively labile and the f–f transition is strongly luminescent when properly sensitized. However, as lanthanide directed self-assembly of luminescent assemblies has been well described recently, we direct the reader to an excellent review on this topic.[55]

6 Conclusion

The cross-section of current literature regarding metal-directed self-assembly of polynuclear luminescent arrays presented here reflects a rapidly evolving area of research, guided and limited solely by imagination and creativity. Such novel assemblies serve to elucidate those processes subsequent to photo-excitation, which in turn prompts their manipulation toward the fabrication of functional devices. Although the varied coordination geometries of metal ions allow many different structural motifs to be assembled, metal-directed self-assembly of emissive structures in the context of those presented herein is certainly not straight-forward. The best metal ions to assemble discrete luminescent polynuclear assemblies appear to be the second and third row d^8 metal ions, Pd(II) and Pt(II), respectively, as reactions conditions which render their monodentate ligand complexes labile are relatively easy to obtain. In this respect, the Cu(I) complexes of bidentate ligands perhaps hold the greatest promise for future development as suggested by Armaroli.[18]

The compromise between synthetic methodology and function, wherein emphasis on the former has neglected development of the latter, continues to challenge chemists. Nevertheless, considering the great strides made with regard to the manipulation and understanding of the excited states of the complexes described herein, the future of photoactive polynuclear assemblies promises to be a fruitful one.

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