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Review

Self-assembly of discrete metallosupramolecular luminophores

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Contents

Abstract

This review examines the metal-directed self-assembly of luminescent metallosupramolecular structures. A brief overview of the self-assembly process is followed by a discussion of the various types of assemblies based on the nuclearity of the luminophore: dinuclear, trinuclear, tetranuclear and higher nuclearity species. The final assemblies are discussed in light of their synthesis, their photophysical properties, and the role that the metal ion plays: (i) a purely structural role, or (ii) a structural and functional role. While some step-wise syntheses are mentioned, the majority of the polynuclear complexes presented herein are built up by a self-assembly process. Whenever possible, the potential applications of the luminescent metallosupramolecular assemblies are presented and discussed.

Keywords: Metal-directed self-assembly; Metallosupramolecular chemistry; Luminescence; Transition metal ions; Energy transfer; Electron transfer

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1. Introduction

Metal-directed self-assembly has proven to be a powerful tool in the synthesis of functional, discrete assemblies and has been inspired largely by processes found in nature [1]. For example, the harnessing of light energy by photoactive units in natural photosystems has led to the pursuit of artificial light-harvesting systems (LHSs) which may function as catalysts [2], sensitizers for photoactive devices [3], molecular sensors [2b,4], and photodynamic therapeutics [5]. The LHS found in nature have taken eons to evolve to their present complexity, and much can be learned from studying their structure and how they have been assembled. For instance, self-assembly can be seen in light-harvesting complex II (LHII) of purple bacteria, in which non-covalent assembly of eight helical peptide strands, each with 24 bacteriochlorophylls and eight carotenoids, forms a ring approximately 5.6 nm across [6]. The combination of many weak non-covalent interactions, such as hydrogen bonding, electrostatic interactions and metal-ligand coordination, brings the LHII structure together. The LHII subunits assemble with their large LHI counterpart and transfer energy to a central reaction centre. In green plants, photosystem II (PSII) accepts light energy from light-harvesting complexes which transfer energy to the reaction centre. A series of electron transfer steps eventually lead to the reduction of a quinone, with the eventual production of ATP, and the oxidation of water by a tetramanganese cluster. In such complex assemblies, the functional groups which assemble the light-harvesting complexes and the reaction centres must be tolerant of subsequent electron and energy transfer processes.

Nature utilizes many weak supramolecular interactions to produce the connectivity and energetic/electronic relay found in PSII. The reversibility of these supramolecular interactions is fundamental to the self-assembly process as it allows the assembled structure to adapt to changes in its local environment, permitting local minima to be probed and, consequently, the lowest energy structure to be assembled. Within an equilibrating system, the formation of smaller, discrete assemblies are favoured both *enthalpically* (the maximum number of metal ion coordination sites and ligand metal-binding sites interact to form a stable structure) and *entropically* (the smaller the assembly, the more species that will form as opposed to a few oligomers and polymers) [7]. Schematically, this can be readily seen when a metal ion with two convergent coordination sites is brought together with a ligand with two convergent donor sites (Fig. 1). An initially formed oligomer or polymer would not have a maximum number of combined metal–ligand interactions to be favoured enthalpically, and apart from a tetrameric oligomer (as shown in Fig. 1), all oligomers and polymers of greater size would not be favoured entropically.

One could also think in terms of a hyperchelate effect, or ‘supramolecular chelate effect’, which favours the discrete structure. As the intermolecular bonds forming the discrete structure are reversible under the conditions of the reaction, the opening of the discrete structure would only require an intramolecular reaction to close it again (Fig. 2a), whereas an oligomer or polymer would require an intermolecular reaction to reform (Fig. 2b).

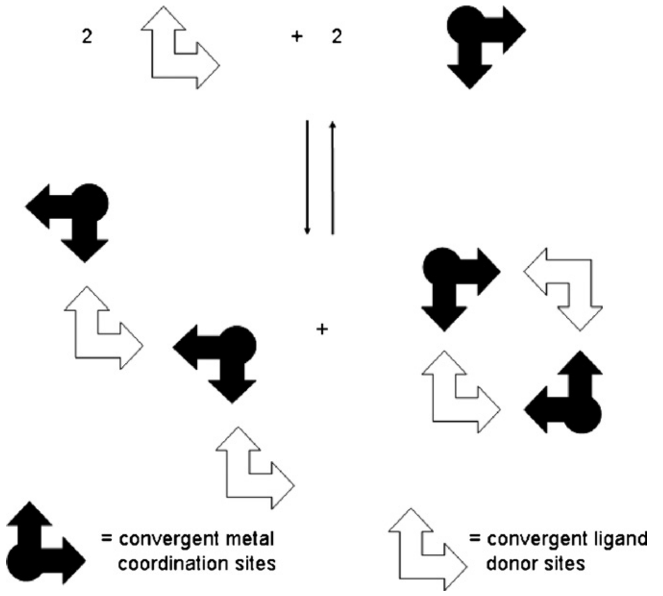


Fig. 1. Enthapically and entropically favoured assembly of discrete structures by the self-assembly of convergent metal sites and convergent ligand donors to give an oligomer (left) and a discrete assembly (right).

Of the intermolecular forces used to assemble natural LHSs, metal–ligand dative bonding covers a wider range of energies, which allows a greater range of self-assembly and step-wise syntheses to be performed. Recent examples of the step-wise assembly of LHSs using metal ions have used elaborate ligand design [8] or have required many iterative chemical transformations [9] with compromised efficiency and demanding purification to reach their targets. Although limitations of this nature have been addressed [10], the synthesis of high nuclearity complexes is still difficult as they often possess a large degree of freedom which can interfere with energy transfer processes. Although the covalent bond gives more durable systems,

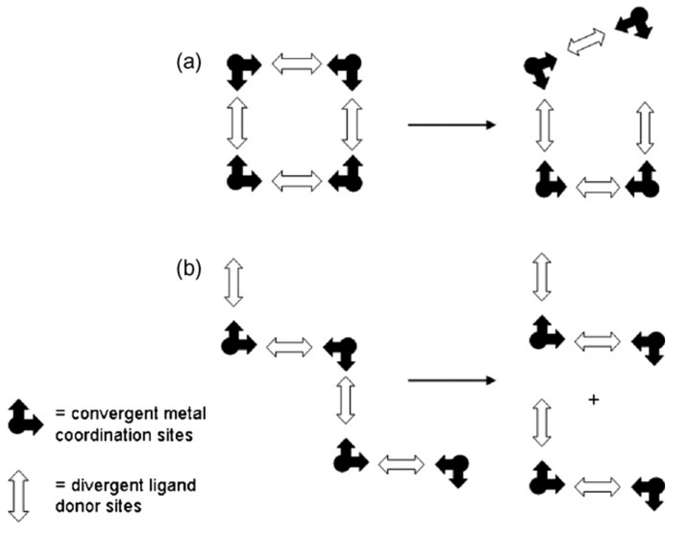


Fig. 2. The metal-directed self-assembly of discrete structures vs. oligomers: (a) “hyperchelate” effect leads to the facile intramolecular closing of an opened discrete assembly and (b) oligomers or polymers would require intermolecular reactions to reform.

the low yields and laborious syntheses of artificial LHSs based thereon often preclude practical applications. Metal-directed self-assembly, in which the reversibility can be tuned by the choice of ligand, metal ion and reaction conditions, allows for discrete structures to be formed while offering bond strengths suitable to afford robust systems. In addition, the vectorial nature of metal–ligand bonding, along with the various possible coordination geometries of metal ions, is conducive to rapid synthesis of multinuclear photoactive arrays with pre-determined architectures. Apart from facilitating construction, incorporation of metal ions into the LHSs can also serve to greatly affect energy and/or electron transfer processes, which ultimately allows their photophysical properties to be fine-tuned.

In this review we present recent achievements in the metal-directed self-assembly of oligometallic luminophores as classified by the number of metal ions found in the final structure and the coordination geometry of the metal ion directing the self-assembly process. The metal ions used to assemble the final structures may play a purely structural role (i.e., they only assemble the structure) or a structural and functional role (i.e., they not only assemble the structure, they also contribute to its photophysical properties). Both structural and functional metal ions have been used with a great degree of success in the self-assembly of oligonuclear luminophores, therefore, examples of both have been included herein.

2. Dinuclear complexes

A dimetallic assembly requires metal ions and ligands with convergent coordination sites and donor atoms, respectively (see Fig. 1), and is, therefore, the simplest oligometallic assembly. Although dinuclear assemblies have been known for a considerable amount of time [11], the investigation of their luminescence is not as well described. The self-assembly of luminescent dinuclear complexes will be examined by the coordination geometry of the metal ion used in the assembly process: square planar, tetrahedral, octahedral, and other. This approach will be used for all of the oligometallic assemblies presented herein. Mention of their role in the assembly, either purely structural, or structural and functional (in a photophysical sense), will be made.

2.1. Assembly by square planar metal ions

Metal ions with square planar coordination geometries are inherently advantageous with respect to the formation of discrete structures [12], particularly with regard to molecular recognition [13]. It is not surprising, then, that transition metal ions predisposed to form square planar complexes are among the most heavily investigated motifs en route to metal-ion assemblies.

Pd^{2+} and Pt^{2+} are the most utilized square planar metal ions with regard to forming assemblies, luminescent or not [12]. Their synthesis relies on a self-assembly strategy in which appropriate precursor transition-metal units possessing labile coordination sites are combined with complementary bridging bidentate ligands to yield a target geometry according to thermodynamic control. Thus, many metallo-supramolecular systems may contain several species in equilibrium where no clear thermodynamic preference is given, the distribution of which depends strongly on the steric demand and flexibility of the bridging ligand as well as on the presence of potential guest molecules [14]. The reversible nature of dative bonds gives rise to persistent kinetically controlled species en route to the final thermodynamically favoured product. Therefore, the choice of metal ion used in the precursor units and its affect on dative bond strength (e.g. $Pt^{2+} > Pd^{2+}$) influences both the stability of the end product and the reaction conditions necessary to generate it efficiently [15].

The role of a square planar metal ion in producing photoactive assemblies is principally structural. Photoactive ligands coordinated to the assembling metal ion may increase in rigidity, which in turn influences their emission energy and intensity by enhancing ligand π-delocalization and minimizing excited-state deactivation through structural perturbations. The larger ligand field strength in Pt^{2+} complexes as compared to Pd^{2+} complexes render the upper lying metal-centred (MC) states less thermally accessible from the emissive metal-to-ligand charge-transfer (MLCT) or intraligand charge-transfer (ILCT) states [16,17]. In this way, efficient non-radiative decay from these distorted MC states to the ground state is reduced, thereby allowing radiative decay of the excited state. The result is often room temperature solution luminescence for Pt^{2+} complexes while only solid state or low temperature emission is observed for Pd^{2+} complexes.

The assembly of porphyrinic arrays is of great interest owing to their wide range of potentially exploitable physical properties, including luminescence [18]. Metal-directed self-assembly is a particularly attractive way to build up these arrays by linking metal unit(s) and a wide variety of porphyrinic subunits [19]. For example, dipyridyl-porphyrin subunits (**B**, Fig. 3) and diamine-porphyrazine subunits (**A**) were incorporated into a tetra-porphyrinic assembly upon coordination of Pt^{2+}. In this case, the self-assembly of $(\mathbf{B})_2Pt_2Cl_4$ is followed by displacement of the chloro ligands by **A**, which leads to the desired tetra-porphyrin in 60% yield. Coordination to the Pt(II) induces large changes in the electronic absorption profile of the component porphyrins, which indicates significant electronic mixing between them.

2.2. Assembly by tetrahedral metal ions

The metal-directed self-assembly of helical complexes, the helicates, has been a very fruitful area of research, yet few of these complexes have shown luminescent properties when assembled with tetrahedral metal ions [20]. Of the metal centres adopting a tetrahedral coordination motif, those with d^{10} configurations are most frequently encountered in the literature owing to the nature and flexibility of the ligands involved. However, the intrinsic tendency of d^{10} metal ions to undergo fluxional processes compromises their potential for applications and necessitates increasingly elaborate ligand design to maintain stable complexes.

A suitable metal–ligand combination for self-assembly is Cu(I) with diimine ligands, in particular 1,10-phenanthroline (phen) or one of its derivatives [21]. As with Ru(II) polypyridyl

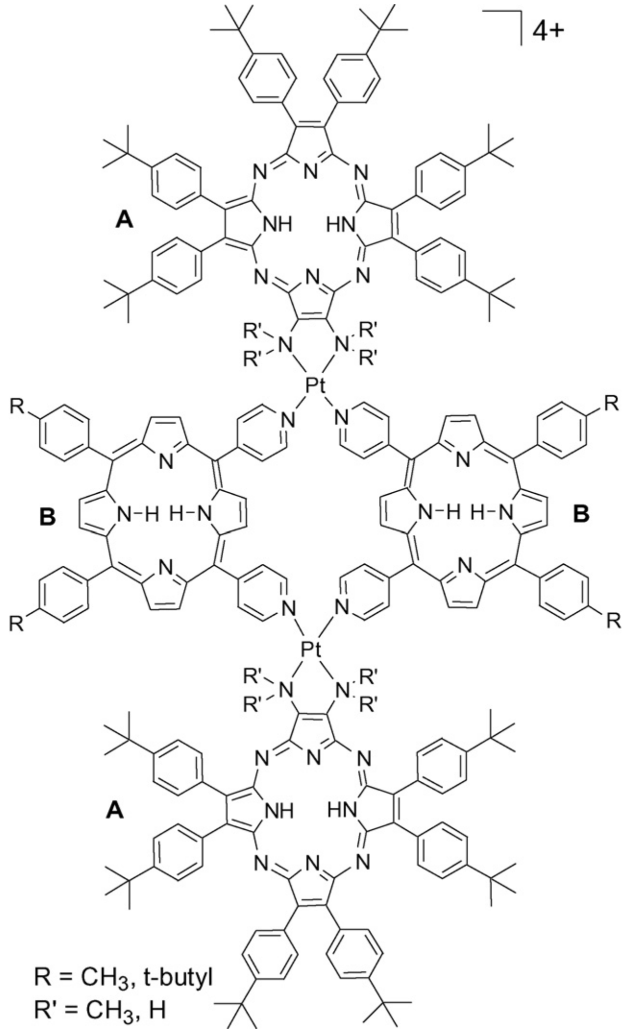


Fig. 3. Diplatinum(II) porphyrinic assembly.

complexes [9,22], Cu(I) phen complexes display MLCT bands in the visible region, however, modification of the phen ligand significantly affects both its MLCT absorption and emission properties. Although $Cu(phen)_2^+$ is non-emissive in solution, increasing ligand delocalization and lowering thermal accessibility of upper-lying deactivating states can render its derivatives luminescent. The main deactivation pathway is a transient Cu(II) centre that is generated upon photo-excitation, which distorts to a square-planar arrangement, making nucleophilic attack by coordinating solvent or anions possible [23]. From this 5-coordinate exciplex species, non-radiative deactivation of the emissive state is rapid and efficient. Modification of the phen ligand can impede nucleophilic attack and lead to substantially improved excited-state properties in its metal complexes [17,24]. In addition, the use of bulky phosphines, and especially diphosphine chelates, has yielded heteroleptic Cu(phen)(P–P) complexes with emission lifetimes of up to 16 μs in dichloromethane at room temperature [25]. Such complexes have proven to be emissive even in strongly coordinating solvent such as methanol and acetonitrile. 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, which leads to potential applications as electroluminescence devices [26,27], photovoltaic devices [28], catalysts, and DNA intercalators [29].

Cu(I) phenanthroline complexes have been incorporated into multicomponent photoactive systems such as rotaxanes, catenanes, and dendrimers [21]. With regard to these systems, fullerenes have been an attractive partner for Cu(I) phenanthrolines considering that C_{60} is fluorescent, exhibits diagnostic singlet and triplet transient absorption spectra, and is an excellent electron acceptor. The combination of Cu(I) phenanthroline and C_{60} has lead to dinuclear helicate formation of bis-fullerene complexes [30], with the absorption spectra of each dicopper helicate found to be the sum of the spectra of their individual components, thus suggesting no ground-state electronic interaction between the Cu(I)-phenanthroline and C_{60} moieties.

Fluorescence from the bis-fullerene was unaffected relative to a related model compound consisting of nearly the same ligand but without the bis-fullerene portion, 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 bis-fullerene, 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 bis-fullerene, the persistence of the fullerene emission upon helicate formation suggests an electron transfer from the ^{3}MLCT of the Cu(I) core to the fullerene.

Another interesting class of dimetallic assembly is based on copper(I) oligonuclear racks (Fig. 4) [31]. This structure represents an important synthetic achievement considering that such architectures have typically been assembled in a step-wise fashion using kinetically inert 2nd and 3rd row transition metal ions, such as Ru(II) or Os(II) [32]. The synthesis of dicopper(I) racks relies on the introduction of bulky substituents into the 2- and 9-positions of phen on one of the ligand components, which limits the potential formation of homoleptic oligomers that are otherwise accessible using tetrahedral metal ions such as Cu(I) and Ag(I).

Four dicopper(I) complexes based on 1,10-phenanthroline and diphosphine ligands were assembled and shown to absorb between 338 and 355 nm [33]. The absorption band was ascribed to a MLCT absorption, and, thus, the Cu(I) ions play both a structural and functional role in the assembly process. The complexes were shown to emit between 565 and 644 nm from the ^{3}MLCT state in a similar fashion to mononuclear Cu–N_2P_2 complexes. The use of 2,9-dimethyl-1,10-phenanthroline with diphosphine ligands lead to a dicopper(I) complex with enhanced photophysical properties [34]. The absorption (382 nm) and emission (590 nm) bands were MLCT based and similar to those of the 1,10-phenanthroline complexes mentioned above, however, the quantum yields and excited state lifetimes were an order of magnitude greater due to the increased steric bulk around the metal centres.

Silver(I) is another d^{10} metal ion that has been of great use in the self-assembly of metallosupramolecular structures. The formation of discrete di-, tri- and tetra-nuclear met-

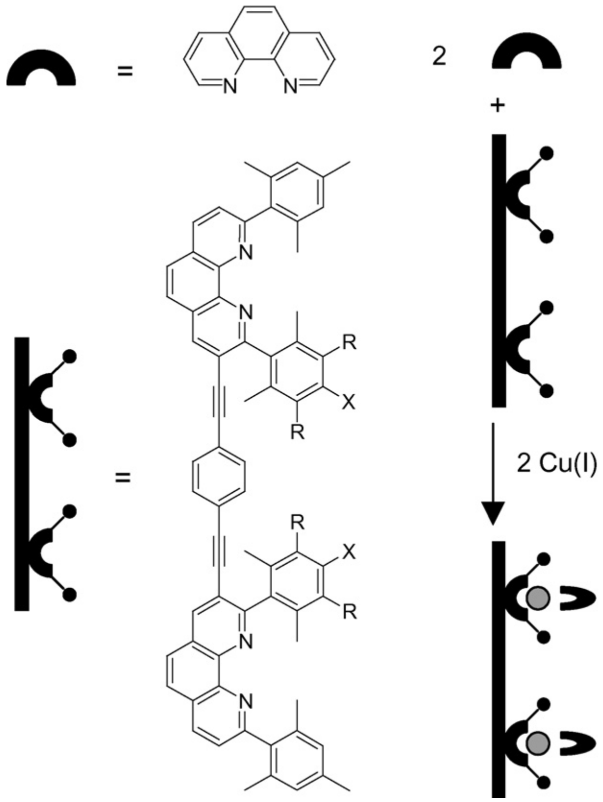


Fig. 4. Tetrahedral assembly of dicopper rack complex.

allomacrocycles and metallopolymers based on the ligand 9,10-bis(diphenylphosphino)anthracene and a variety counteranions such as OTf$^-$, ClO$_4^-$, PF$_6^-$, and BF$_4^-$ has been described (Fig. 5) [35]. The reaction was very simple and involved room temperature mixing of the chosen silver(I) salt with the diphosphine in equimolar amounts. However, the potential products were varied, yielding either discrete metallo-macrocycles of variable size and nuclearity or helical polymers. The product isolated upon crystallization was dictated by the choice of silver(I) salt and the solvent(s) used for crystallization [35]. The dinuclear metallo-macrocycle was formed using PF$_6^-$ as counter-anion with subsequent crystallization from CH$_2$Cl$_2$/Et$_2$O CH$_3$CN, while crystallization from Et$_2$O/CH$_3$CN produced the helical polymer. Such diversity points to solution equilibria between metallo-cycles and polymers, as indicated by NMR studies in both CD$_3$CN and CD$_2$Cl$_2$. Clearly the use of better donors, such as CH$_3$CN, favours polymer formation. In the case of the dinuclear metallocycle in CD$_3$CN, a ring-opening mechanism was proposed as shown, involving just one intermediate (Fig. 5). All isolated complexes display intense luminescence from an emissive π–π* state localized on the anthracene ligand.

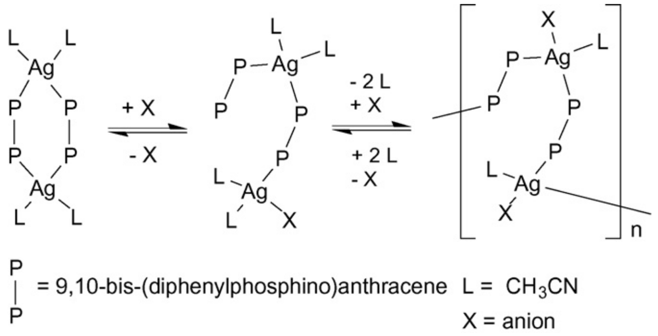


Fig. 5. The opening of disilver(I) metallomacrocycle leads to a silver(I)-based polymer.

In general, a variety of ligands can assemble disilver and digold(I) complexes, with ligand-based emission in solution and in the solid state being noted in most cases as Ag(I) plays a mostly structural role in the assembly process [36].

2.3. Assembly by octahedral metal ions

Numerous transition metal ions exhibit dimeric structures based on a characteristic "paddlewheel" arrangement of four mutually perpendicular bidentate chelates [37]. Depending on the metal ions and the nature of the chelating ligands, a wide range of physical properties are exhibited, including long-lived photo-excited states [38]. They are building blocks in a number of supramolecular architectures [39], and their potential structural and functional roles in photoactive assemblies has only recently been investigated [38].

As previously mentioned, porphyrins are attractive ligands with respect to photoactive assemblies, as 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 with regards to ligand displacement [37,40]. The *cis*-protected complex *cis*-Rh$_2$(form)$_2$(O$_2$CCF$_3$)$_2$ (where form = *N*,*N*′-di-*p*-tolylformamidinate) is an ideal building block with kinetically inert amidinates and kinetically labile trifluoroacetates. Self-assembly proceeds upon metathesis of *cis*-Rh$_2$(form)$_2$(O$_2$CCF$_3$)$_2$ with the disodium salt of 15,20-di-(4-carboxyphenyl)-5,10-diphenylporphyrin (Fig. 6) [41]. The amidinates lead to electrochemically rich dirhodium(II,II) units, exhibiting facilitated one-electron oxidations relative to their tetracarboxylate counterparts. Based on the Rh$_2^{4+/5+}$ oxidation potential and the excited-state reduction potential for the porphyrin, reductive electron-transfer quenching was found to be energetically favorable ($\Delta G = -0.4$ eV). As such, porphyrin-based emission from this structure is very weak with $\tau < 500$ ps and $\Phi = 7 \times 10^{-5}$ compared to $\tau = 10$ ns and $\Phi = 0.017$ for the parent porphyrin.

3. Trinuclear complexes

3.1. Assembly by square planar metal ions

Luminescent trinuclear assemblies based on square-planar metal ions are more readily assembled with long, linear bridging ligands whose increased flexibility allows the entropic advantage of triangle formation to become significant in determining product distribution (Fig. 7) [42].

The combination of Pt^{2+} corners and BINOL-derived, linear bis(4,4′-alkynyl) ligands in a one-pot self-assembly process leads to chiral, enantiopure triangles and squares (L$_1$ and

L_2, Fig. 8) [43]. Interestingly, although **1a** and **2a** are isolated from the same reaction mix, dissolution of **1a** cleanly produces **2a** 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 [4a]. Here, square **2a** was shown to be strongly phosphorescent ($\Phi_p = 9.4\%$) and stable, giving electroluminescent performance exceeding that for simple (diimine)–Pt(acetylide)$_2$ complexes [44].

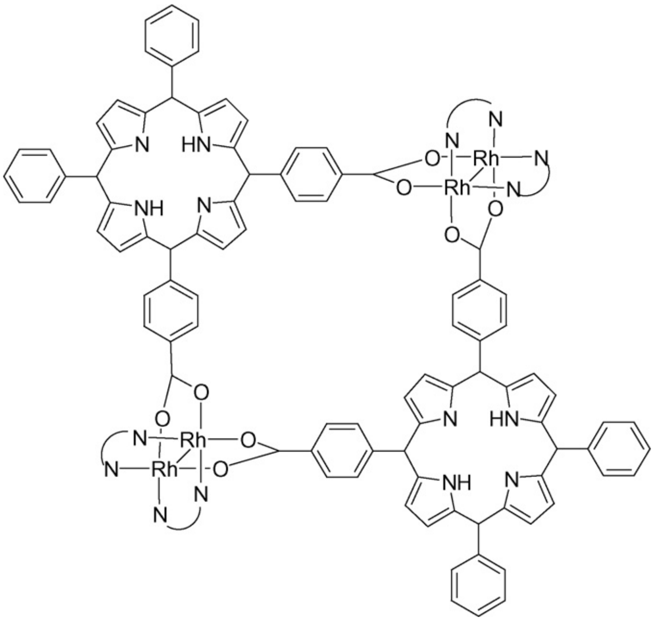


Fig. 6. Convergent Rh(II) dimers direct convergent porphyrinic ligands into a dimetallic assembly.

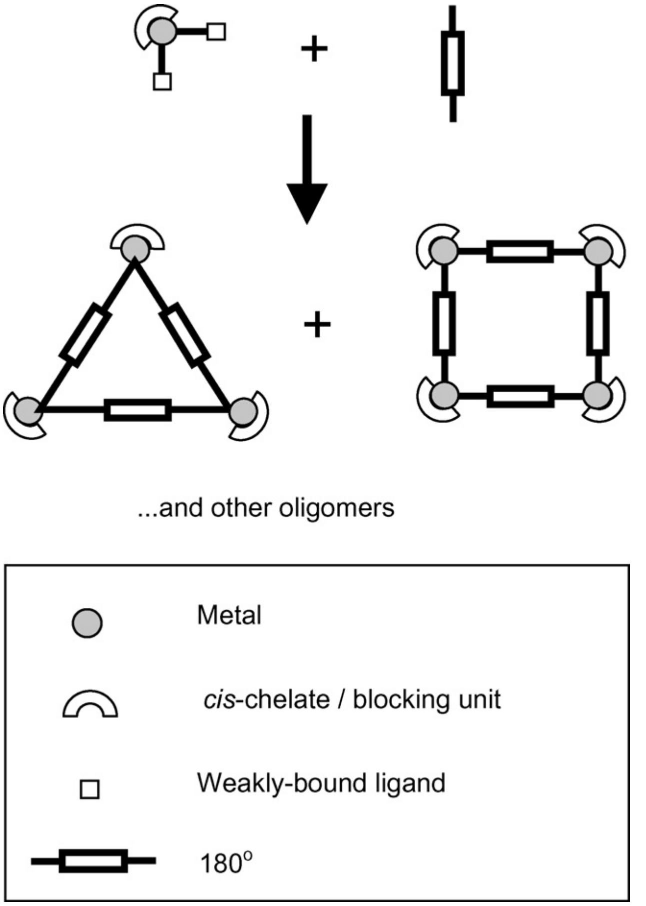


Fig. 7. Long, flexible ligands can afford triangular assemblies whereas short, rigid ligands usually lead to squares.

Luminescent trimetallic complexes can be assembled by judicious choice of ligands without generating tetrametallic complexes [45,46]. In the first case, bridging benzimidazolate ligands provided a 150 degree angle from which a triangular complex was assembled (Fig. 9) [45]. The absorption spectrum of the complex contained a spin-allowed ligand centred band (270 nm), and both spin-allowed and spin-forbidden MLCT bands (^{1}MLCT = 400 nm, ^{3}MLCT = 480 nm, respectively). The complex was emissive at 301 K in CH_2Cl_2, with peak maxima at 560, 606 and 661 nm (MLCT transitions). In the second case (not shown), a bis-diphenylphosphino anthracene was assembled with $[Rh(CO)_2Cl]_2$ to give a bowl-shaped trirhodium assembly which exhibited anthracene-based fluorescence [46].

3.2. Assembly by tetrahedral metal ions

Multinuclear Cu(I) complexes may be prepared using 2,5-di(2-pyridyl) pyrazine (2,5-dpp), or its regioisomer 2,3-dpp, of which the 2,5-dpp isomer is depicted in Fig. 10 [47]. Assembly of dinuclear ruthenium polypyridyl complexes (where L–L = bpy) is directed by coordination of Cu(I) upon the addition of the precursor [(2,5-dpp)Ru(bpy)$_2$](PF$_6$)$_2$ to [Cu(CH$_3$CN$_4$)]PF$_6$ in 1,2-dichloromethane at room temperature. Interestingly, the MLCT region of the absorption profile is broad, extending from 400 to 580 nm, which is due primarily to the red-shift of the Ru → 2,5-dpp transition stemming from lowering of the bridging ligand π* level upon Cu(I) complexation. This was confirmed by comparison of the 2,5-dpp reduction potential for the precursor complex [(2,5-dpp)Ru(bpy)$_2$](PF$_6$)$_2$ to that of the dinuclear ruthenium complex, which showed an anodic shift of 0.4 V. However, the complex was non-emissive in both the solid state and solution, presumably due to deactivation through exciplex formation in the absence of sterically encumbered substituents. Moreover, irradiation of this complex with visible light under ambient conditions in 1,2-dichloromethane results in the oxidation of the complex to produce a Cu(II) species.

In other examples, the techniques developed to synthesize kinetically stable Cu(phen)$_2^+$ complexes have been applied to diruthenium(II)–copper(I) complex based on spirophenathroline ligands, however, no photophysical properties for the trinuclear assembly were reported [48]. A diiridium(III)–copper(I) trinuclear complex was assembled in a similar fashion to the previous example. In this case, the Ir(III) excited state was also quenched by the Cu(I) centre [49].

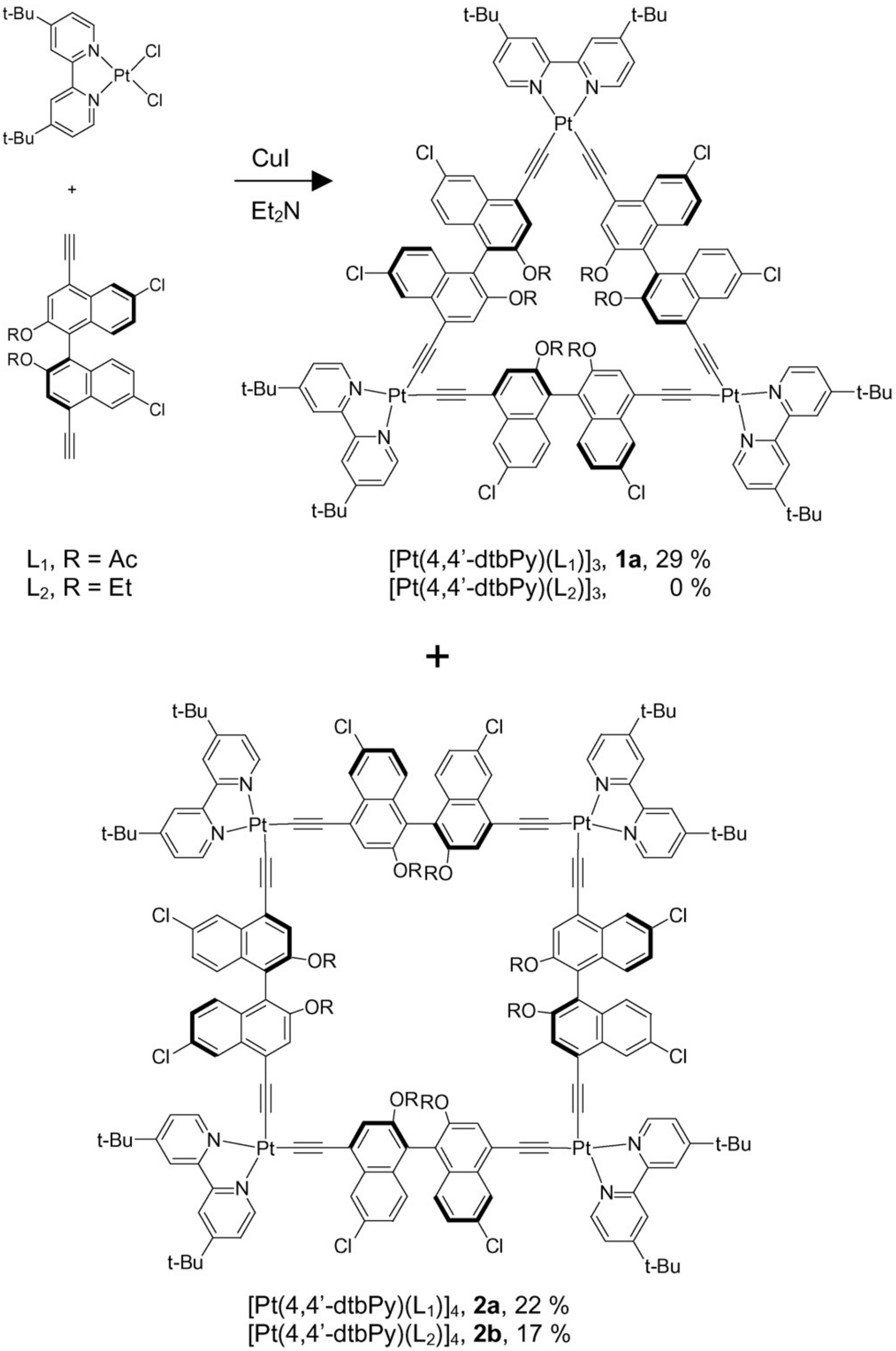


Fig. 8. Rigid divergent ligands can lead to both tri- and tetra-metallic assemblies.

3.3. Assembly by octahedral metal ions

Tetracarboxylate metal dimers may also be used as building blocks that serve both structural and functional roles in photoactive assemblies [50]. Photoactive Ru^{2+} complexes based on terpyridine are achiral [51], and their incorporation into polynuclear assemblies does not generate diastereomeric mixtures [52,53]. Carboxylic acid functionalized polypyridyls have been of interest for the dye sensitization of semiconductor surfaces [3a], but can also be used for ligand displacement involving tetracarboxylate metal dimers. $[(4'\text{-}(4\text{-Carboxyphenyl-tpy})Ru(tpy)]^{2+}$ can be used to displace acetates of dirhodium(II) tetracarboxylate to introduce chromophores into polymetallic assemblies [50]. Emission studies of the parent chromophore $[(4'\text{-}(4\text{-carboxyphenyl-tpy})Ru(tpy)]^{2+}$ and of similar species substituted about a dirhodium(II) core sug-

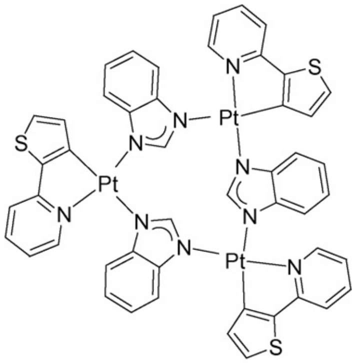


Fig. 9. Triplatinum(II) complex assembled with the anionic benzimidazolate ligand.

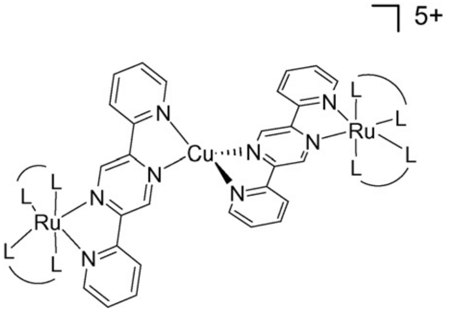


Fig. 10. Cu(I) coordination of two Ru(II) complexes leads to a simple trinuclear system.

gest that energy transfer from the exterior Ru(II) units to the dirhodium(II) core is efficient. The emissive state of the triazine analogue [(4′-(4-carboxyphenyl-tpy)Ru(6-phenyl-2,4-dipyridyl-1,3,5-triazine)]$^{2+}$ lies at 1.78 eV and maintains its luminescence in its Rh–Rh assemblies [54], which places the non-emissive state of the dirhodium(II) unit at the upper limit of 1.77 eV [38b]. The recent elucidation of other paddlewheel complexes exhibiting long-lived photo-excited states [38a], 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. A *trans*-diruthenium(II)–dirhodium(II) complex was also structurally characterized (Fig. 11) [50,54].

4. Tetranuclear complexes

4.1. Assembly by square planar metal ions

Coordination to a square planar assembling unit is also of interest with regard to the "complex-as-ligand" synthetic approach in which metal-ion containing photoactive groups are prepared with additional donor sites to allow for subsequent coordination [9,55]. This approach has been particularly popular for ruthenium polypyridyl and metallo-porphyrin complexes owing to their robust nature and the possibility to perform chemical modifications directly on the metal complex [56]. The additional donor sites can be introduced through the preparation of homo- or hetero-ditopic ligands. Complex **4** and its precursor complex **3** were synthesized to study electron and energy transfer processes between subunits of metal-based light-harvesting antennas (Fig. 12) [57]. Complex **3** has a ^{1}MLCT absorption band at 490 nm and emits at 650 nm with a lifetime of 363 ns, while complex **4** has a red-shifted ^{1}MLCT absorption band out to 530 nm and emits at 658 nm with a lifetime of 244 ns. Monitoring of the excited-state relaxation processes leading to the equilibrated ^{3}MLCT state by time-resolved transient absorption spectroscopy revealed both fast (≈200 fs) and slow processes (≈1.5 ps) corresponding to intersystem crossing and solvent reorganization processes, respectively. An additional process was observed for **4** corresponding to a mono-exponential transient decay (50 ps), indicating a charge transfer to the Pd(allyl)$^{2+}$ unit.

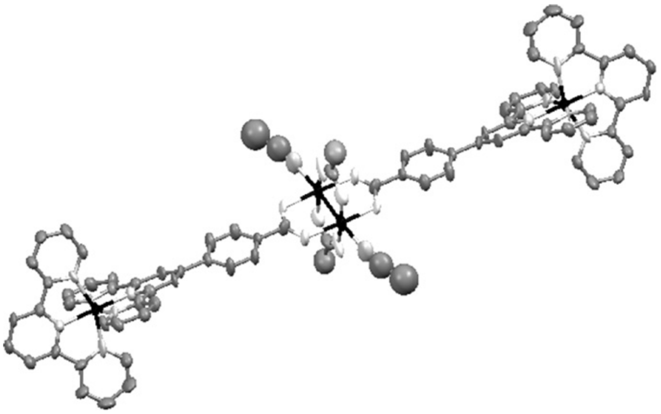


Fig. 11. Two Ru(II) complexes are assembled about a Rh(II) dimer by a simple displacement reaction.

A square related to that shown in Section 3.1, Fig. 8 was assembled using the same bridging ligands, but employing bulky phosphines in place of 4,4′-di-tertbutyl-2,2′-bipyridine (dtbPy). It exhibited dual room temperature emission from intra-ligand $^1\pi$–π^* (425 nm, $\tau < 400$ ps) and $^3\pi$–π^* (582 nm, $\tau \sim 100\ \mu$s) [58]. Considering that the ligand itself is only fluorescent, the effect of Pt^{2+} incorporation has led to efficient singlet–triplet intersystem crossing via spin-orbit coupling, and plays a direct role in increasing the excited state lifetime of the assembly.

A recent potential host–guest assembly has been described using the strongly luminescent [Ru(bpy)$_3$]$^{2+}$ motif [59]. Here, the "complex as the ligand" approach is once again utilized where the datively unsaturated [Ru(bpy)$_2$(qpy)]Cl (see Fig. 13, in which qpy is 2,2′:4,4″:4′,4‴-quarterpyridyl) is heated with 0.5 equivalents 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**). All of the complexes show strong, characteristic absorption and solution luminescence in both organic and aqueous solvent. 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 to 550 nm arising from Pd/Pt M(d) → L(π^*) and Ru M(d) → L(π^*) processes. A relatively intense emission occurs between 650 and 670 nm and is slightly red shifted relative to [Ru(bpy)$_2$(qpy)]$^{2+}$, as expected since coordination serves to stabilize the ligand-centred π^* orbitals (i.e. MLCT state). Also, this emission is insensitive to the

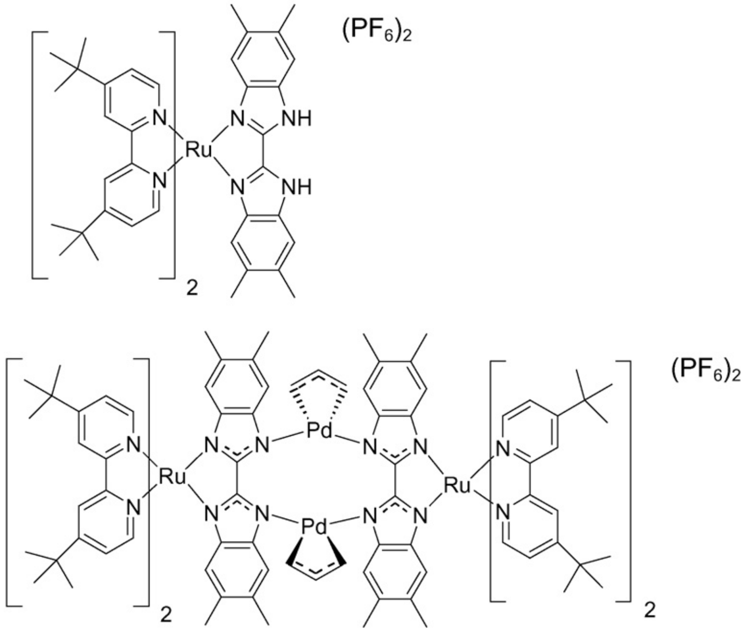
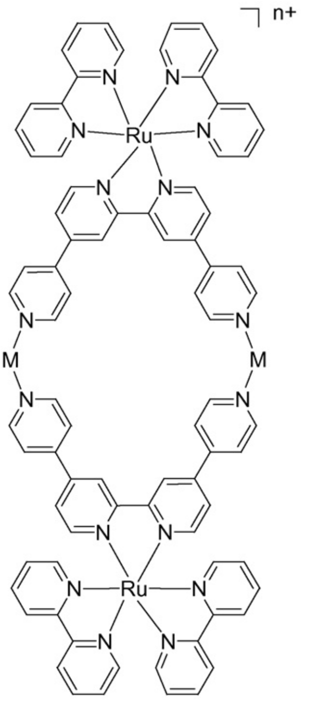


Fig. 12. Pd(allyl)$^+$ directed assembly of a tetrametallic complex (**4**).

excitation wavelength, which indicates efficient energy transfer from the other MLCT states to the Ru-^{3}MLCT state.

Pd(II) and Pt(II) can also be used in a structural role to assemble tetrametallic perylenebisimide complexes with ligand-based fluorescence [60]. Pd(II) was also used to self-assemble a ‘complex-as-ligand’ type structure incorporating a Re(CO)$_3$Cl centre and two 4,4′-bipyridines [61]. The tetrametallic Pd$_2$Re$_2$ complex exhibited a 25-fold luminescence quenching as compared to the Re(I) starting material due to the Pd(II) centres. The absence of spectral overall between the absorption and emission spectra of the tetrametallic complex and its starting materials ruled out a Forster-type energy-transfer quenching mechanism.



A. M = $[Pd(en)]^{2+}$, n = 8;
B. M = $[Pt(en)]^{2+}$, n = 8;
C. M = *fac*-$[ReCl(CO)_3]$, n = 4

Fig. 13. Rapid assembly of tetrametallic Ru(II)-based emitters (en = ethylenediamine).

4.2. Assembly by tetrahedral metal ions

Tetrahedral metal ions have been combined with substituted bis- and tris-phenantholine-based ligands to produce oligonuclear grids [62], boxes [63], and baskets [64] as shown in an example of a box-like structure (Fig. 14) [63]. As mentioned in Section 2.2, the synthesis of these complexes relies on the incorporation of bulky substituents in the 2 and 9 positions of phenanthroline on one of the ligand components, which limits the formation of homoleptic oligomers that are otherwise quite accessible using Cu(I) and Ag(I). The “one-pot” self-assembly of polynuclear structures possessing large voids and internal cavities is efficient and they are ideally suited for applications in molecular sensing and catalysis. The box-like structure in Fig. 14 was assembled using both Cu(I) and Ag(I) [63]. The Ag(I) complexes are relatively less stable as the structure assembled by Ag(I) was cleanly transformed into the isostructural compound composed of Cu(I) by addition of equimolar quantities of CuI at room temperature despite obvious steric barriers.

In the case of Ag(I), much work has been devoted to coordination of phosphine- and sulfur-based ligands [65], which are complementary to such a soft metal centre, while relatively little work has been directed toward luminescent assemblies based on *N*-heterocyclic ligands and Ag(I) [66]. Tetranuclear grid-like

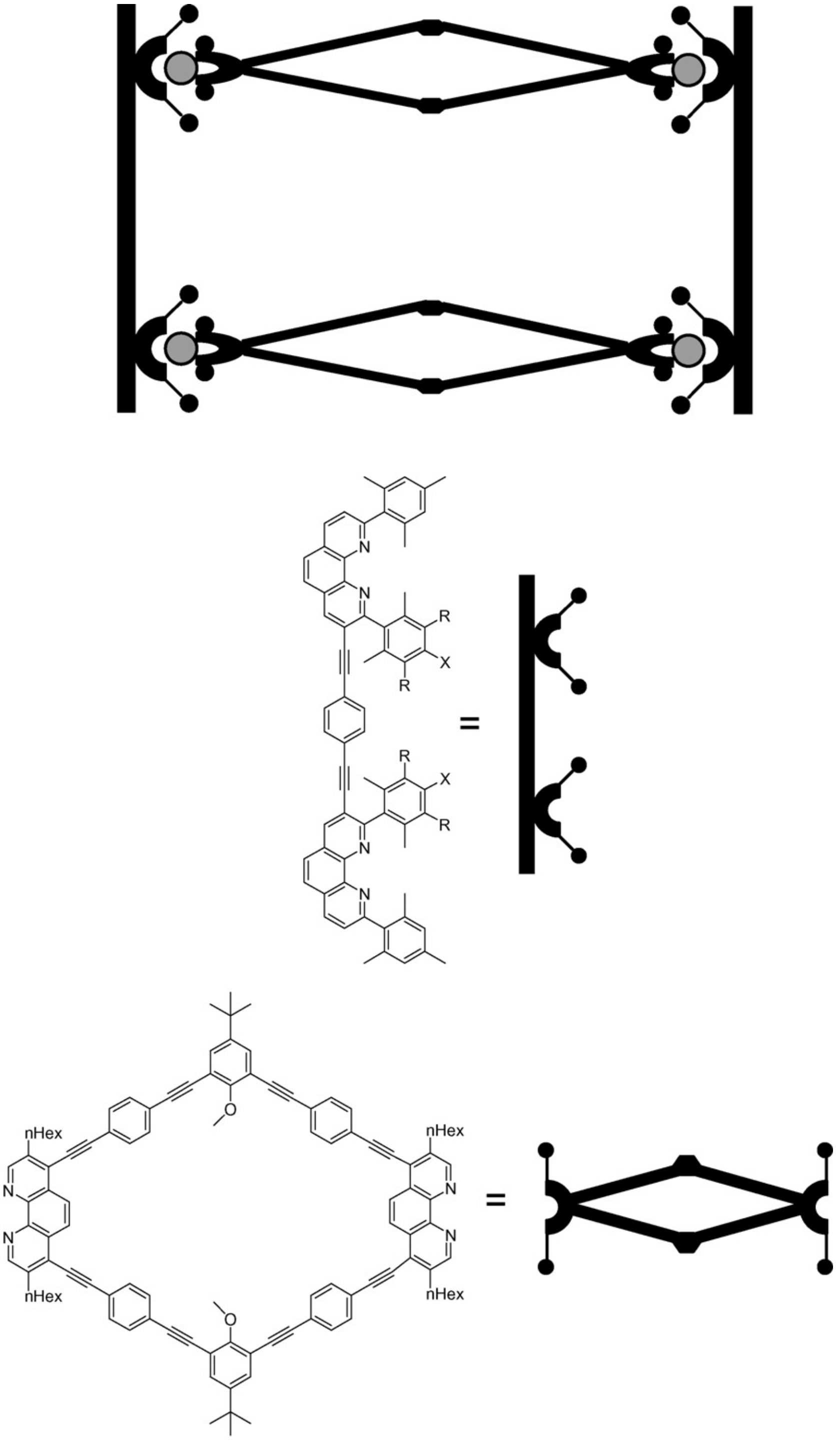


Fig. 14. Cu(I) directed assembly of a box-like tetrametallic complex.

structures can be assembled with bis-bidentate Schiff-base ligands, which are readily obtained by condensation of diamines with 2-formyl pyridine (Fig. 15) [67]. A material comprised of a 1D chain exhibiting intermolecular π–π stacking interactions was crystallized from an equimolar amount of ligand **5** and $AgClO_4$ (Fig. 15, **6**). Upon dissolution in polar media, the polymer was observed to rearrange into a [2 × 2] grid structure (Fig. 15, **7**), as evidenced by a symmetric ^1H NMR spectrum and confirmed by FAB-MS.

Ag(I) containing complexes, like those presented here, do not exhibit MLCT bands in their absorption spectra due to the d^{10} nature of the metal ion, and so luminescence must derive from the ligand itself. In this case, ligand **5** is not luminescent in the solid state nor in solution, however, upon complexation to form the polymer or grid, luminescence from ligand-centred π–π* states is observed in the solid state and in acetonitrile solution ($\tau = 1.2$–12.7 ns). Complexation of Ag(I) increases the rigidity of the ligands and leads to less structural perturbation

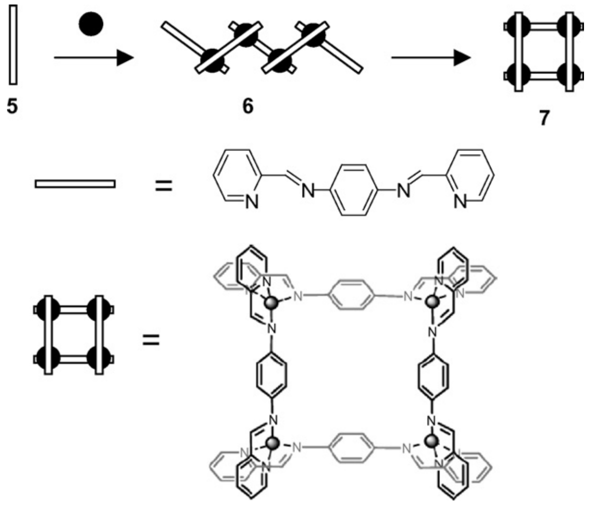


Fig. 15. Metal-directed self-assembly of an entropically favoured 2 × 2 grid.

upon excitation. 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 stemming from heavy-atom relaxation of spin-forbidden processes. This case is rare considering that most Ag(I)-based systems display luminescence only in the solid state or at 77 K.

4.3. Assembly by octahedral metal ions

Metal-ion arrays with regular grid-like patterns have potential as information storage devices when it can be demonstrated that external triggers reversibly produce distinct physicochemical states [8,68]. Their synthesis relies primarily on a self-assembly approach whereby the ligand binding motif is repeated regularly to give *N* binding sites [69]. Metal ions are selected and combined in the correct stoichiometry such that placement of a second ligand with *N* binding sites mutually perpendicular to the first satisfies the preferred coordination sphere(s) of all metal(s) added, to afford a grid of *N* × *N* nuclearity. However, if one adds different metal ions that have the same coordination geometry, the differences in the relative kinetic stability of these metal ions may be exploited to achieve structural control in the self-assembly process. To this end, rigid aromatic *N*-heterocycles such as pyridines offer both kinetically labile intermediate complexes and thermodynamically stable end products with most metal ions (M^{1+}, M^{2+}, and M^{3+}), and so many examples are based on chelating aromatics related to pyridine, bipyridine, and terpyridine. Since many transition metal polypyridyl complexes exhibit a photo-induced MLCT state, such networks should be well suited for photonic device applications. The synthetic strategies and potential applications of such grids are considerable [8,68,70,71].

A ditopic hexadentate ligand based on bis-terpyridine satisfies octahedral coordination mutually perpendicular to itself (Fig. 16). Generation of homometallic grids would then simply entail a one-step reaction using an octahedral metal ion (M_1 in Fig. 16). However, if incorporation of two different octahedral metal ions is attempted in such a manner (M_1 and M_2 in Fig. 16), both *syn* and *anti* topoisomers could result. A sequential strategy towards the *anti*-isomer, based on kinetically inert Ru(II) and Os(II) complexes and the kinetically labile Fe(II) complex, would entail coordination of the inert metal ions first to form a precursor complex (**10**) (Fig. 17) [72]. Subsequent coordination of the second, more labile metal ion under mild conditions would avoid scrambling of ligand **8** to yield the desired structure **11**. The formation of **10** is straightforward in the case of Os(II) when ligand **8** is refluxed directly with 0.5 equivalents of NH_4OsCl_6 gives the Os(II) precursor complex in 40% yield. However, such an approach with the more kinetically labile Ru(II) results in scrambling and the undesired $[Ru_4]^{8+}$ grid [68a]. Therefore, it was necessary to invoke a protection sequence by reacting trimethyloxonium tetrafluoroborate with **8** (Fig. 17), which preferentially methylates the outer pyridines due to lower steric encumbrance and a higher basicity of these nitrogens relative to those of the electron-deficient pyrimidine. The mono-protected ligand **9** can then be coordinated to give the desired corner unit **10** after deprotection with 1,4-diazabicyclo[2.2.2] octane (DABCO) and can then be reacted under mild conditions with hexaaqua iron(II) to yield the *anti* isomer of the tetranuclear assembly **11** (Fig. 17).

As the energy of the MLCT state is sensitive to the nature of the metal ion and the ligand, polymetallic grids offer broad absorption in the visible spectrum, which is a prerequisite for functional light-harvesting arrays. Equally appealing is the variation of the energy of the emissive ^{3}MLCT state simply through variation of the metal ions involved in the self-assembly process. Vectorial energy transfer, another desired property

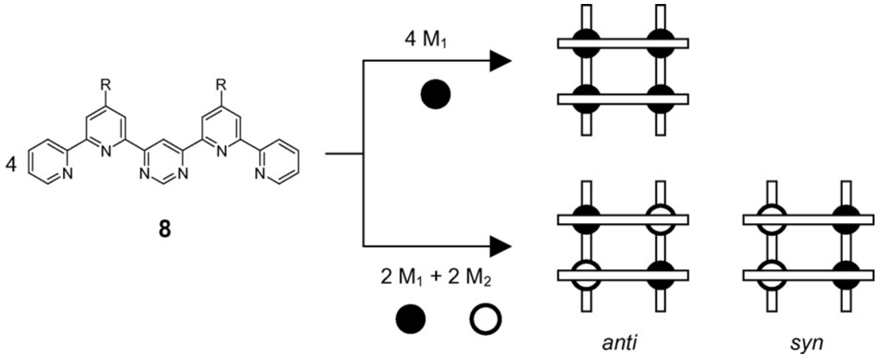


Fig. 16. Synthesis of hetero- and homo-metallic tetranuclear complexes.

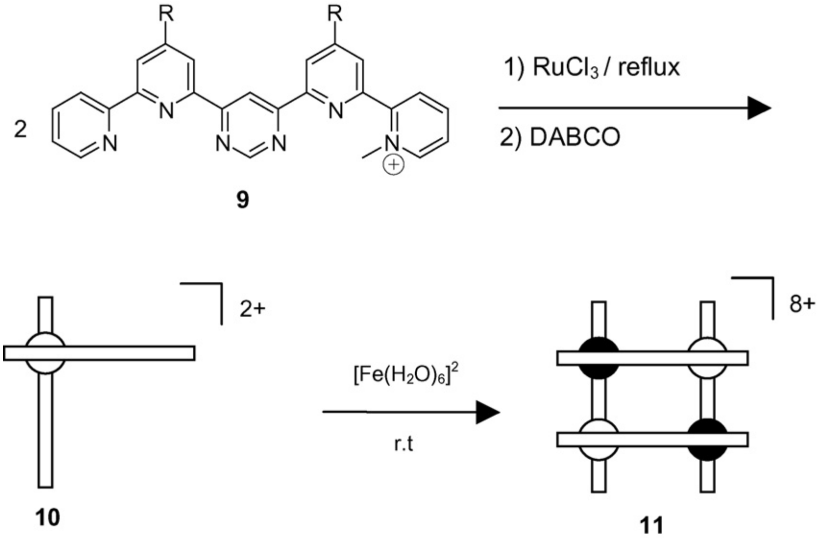


Fig. 17. The step-wise assembly of mononuclear **10** is followed by the self-assembly of tetranuclear complex **11**.

of such arrays, can therefore be induced [73]. In this example (Fig. 17), however, the mixed-metal grids $[Os_2Fe_2]$ and $[Ru_2Fe_2]$ of type **11** do not emit due to the presence of the Fe(II) unit which has a relatively weak ligand field strength and consequently a ^{3}MC state located near its ^{3}MLCT state. This 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 time-resolved 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 **8** [74]. This is similar to that of ^{1}MLCT–^{3}MLCT conversion [75], and such rapid transfer is likely present in the grid presented here. When considering large antennae 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, could otherwise render the device inefficient for practical purposes.

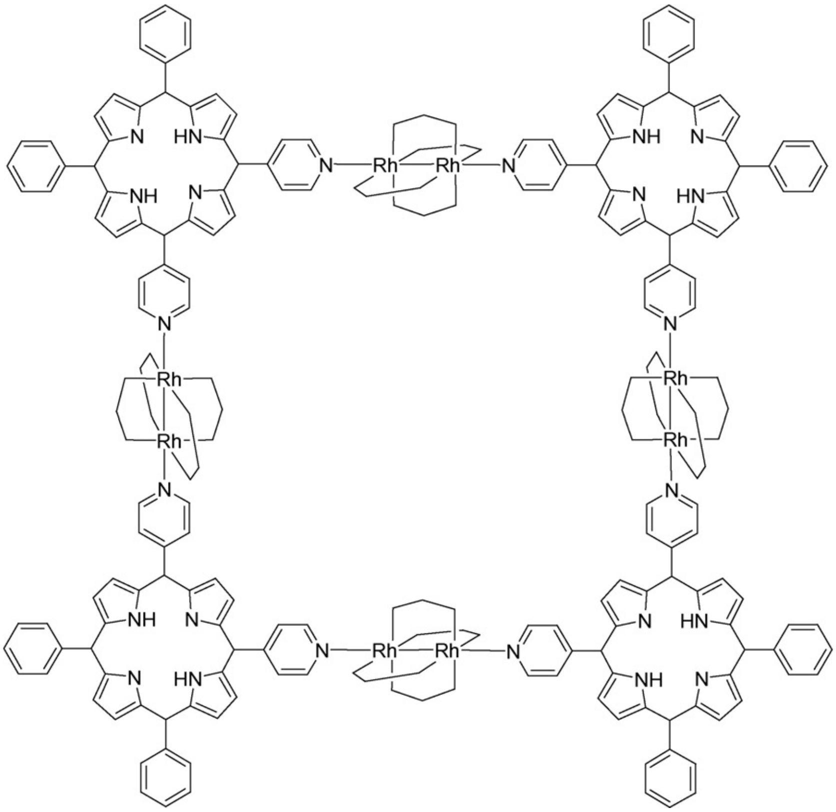


Fig. 18. Axial coordination of Rh(II) dimer leads to a tetraporphyrinic assembly.

To date, such luminescent grids are rare, the luminescence usually being based on the ligand itself [76].

A tetra dirhodium(II) assembly similar to that described in Section 2.3 was prepared by displacement of axially bound solvent molecules with the more strongly coordinating bis-monodentate ligand *cis*-5,10-diphenyl-15,20-dipyridylporphyrin (Fig. 18) [77]. The *trans*-coordinating dirhodium(II) centres assemble the porphyrins into neutral square assemblies, which are desired for potential guest uptake. The porphyrin-based emission from the tetraporphyrinic assembly is completely quenched by the dirhodium(II) units. Other photoluminescent porphyrinic assemblies have been prepared and reviewed recently [78].

Re(I) has been particularly emphasized as an assembling unit of tetranuclear assemblies due to its attractive photophysical properties and its stability towards photodecomposition [4c,79,80]. In addition, unlike its more prevalent counterparts based on Pt^{2+} and Pd^{2+}, these assemblies can be prepared with charge neutrality, which may permit stronger interactions with guest molecules. Such events can have large effects on the luminescence of the parent complex, and so solution-phase molecular sensing has been intensely studied [79]. 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 [4c,81] and molecular sieving possible as well [78b,82].

Trimetallic and tetrametallic squares based on Re(I) have also been prepared using similar strategies to those described in Section 3.1 and Section 4.1 [4,83,84], and have been reviewed recently [78b,81], and so will not be presented here.

4.4. Metal ions with other coordination geometries

Au(I) can use its linear coordination sphere to assemble a wide variety of different structures, ranging from polymeric to discrete [85]. Although various digold(I) complexes can be assembled by a step-wise approach [86], a self-assembly approach seems particular well suited to the assembly of luminescent tetragold(I) complexes [87a,b]. In most cases, bis-pyridyl ligands are used to bridge the Au(I) centres and diphosphines are used as the ancillary ligands. The luminescence of the complexes is ligand-based and, therefore, varies according to the ligand type: between 423 and 424 nm for oxalamide-bridged pyridines [87a] and 390–410 nm for ethene-bridged pyridines [87b].

5. Higher nuclearity complexes

5.1. Hexanuclear complexes

5.1.1. Assembled by square planar metal ions

Hexanuclear complexes can be assembled around a dianionic 2,2′-biimidazolate ligand (biim) which adopts a back-to-back mode of coordination in the presence of metal ions with linear and octahedral coordination spheres (Fig. 19). The datively unsaturated precursor complex $[Ru(bpy)_2(biim)]$ (where bpy is 2,2′-bipyridine) can then react smoothly with $Cu(ClO_4)_2$ in refluxing methanol to produce the di-copper(II) species supported by a linear coordination mode of the $biim^{2-}$ ligand (M_1, Fig. 19), while the opposite side is coordinated via a chelating mode reminiscent of bpy to Ru^{2+}, albeit with relatively more strain. The resulting square structure is twisted about the di-copper(II) centre, with the $biim^{2-}$ and di-copper(II) deviating from co-planarity by ∼40°. This twist is repeated in a staggered manner about the di-copper(II) centre and generates enantiomers, both of which are found in the X-ray crystal structure. This is in contrast to the eclipsed conformation of the related $Cu_2(OAc)_4$ [37]. The electronic absorption spectrum of this tetramer displayed a red-shift of the Ru $M(d) \rightarrow L(\pi^*)$ MLCT and a fourfold increase in its intensity relative to $[Ru(bpy)_2(biim)]$, due to the presence of four photoactive units. Unfortunately, no emission studies were conducted to investigate energy transfer phenomena, and so the potential of these units toward the development of photoactive arrays cannot be assessed.

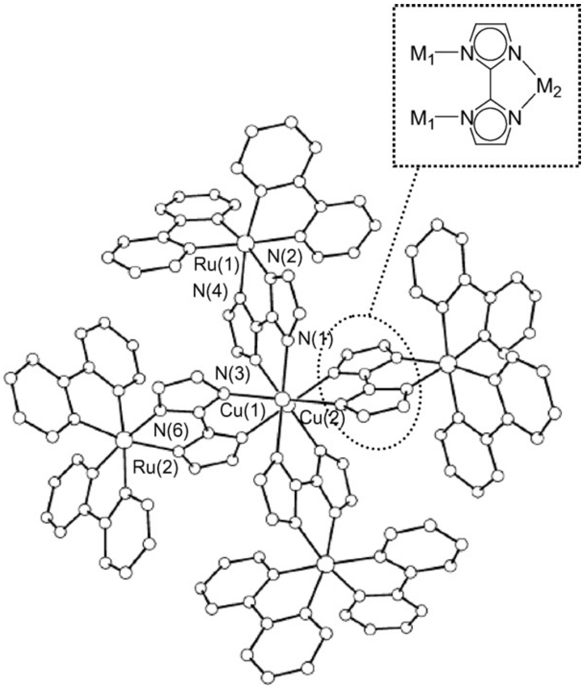


Fig. 19. Hexanuclear Ru_4Cu_2 complex.

5.1.2. Assembled by octahedral metal ions

Related discrete structures composed of tri-, penta-, and hexa-nuclear bis(terpyridyl)M^{2+} units have been prepared using appropriately angular ditopic bis(terpyridyl) ligands assembled from Fe(II), Ru(II), and Zn(II) coordination (Fig. 20) [88]. Thermal population of deactivating ^{3}MC states led to efficient quenching of the Fe(II) and Ru(II) excited states, even when typically fluorescent ligands were employed. The assemblies incorporating Zn(II) were luminescent due to its d^{10} closed-shell configuration.

Some hexanuclear torus complexes (circular helicates) are known, but no luminescence studies have been published [89].

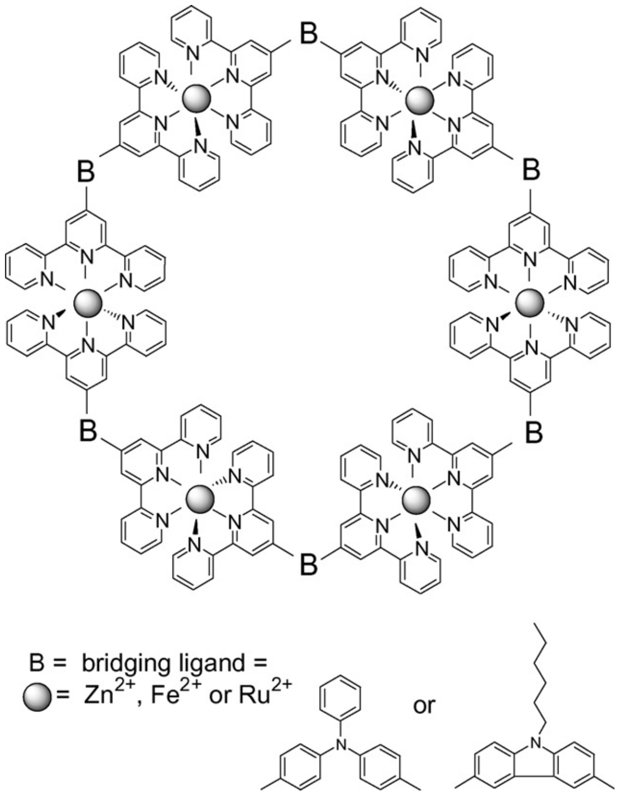


Fig. 20. Molecular hexagons assembled with bis-terpyridyl complexes.

5.2. *Heptanuclear complexes*

The absorption of a large quantity of light energy would be beneficial for efficient operation of a photonic device. As such, it is inherently more advantageous to develop spherically dense photoactive assemblies, and to this end dendritic arrays have been prepared utilizing photoactive subunits. However, to make the structure functional, the assembly should possess an available "docking" site where the substrate can receive the redox equivalents to the initial photoexcitation. This requires the design of lower symmetry assemblies, relative to their potential dendritic counterparts. Where catalysis is concerned, photoreduction of the substrate requires an electron acceptor site capable of collecting and relaying redox equivalents while at the same time maintaining structural integrity. The incorporation of photoactive units displaying photo-initiated charge transfer is obviously required, and as such ruthenium(II) and osmium(II) polypyridyl complexes have, amongst others, received particular attention [74]. Suitable electron acceptor sites may also be served by various transition metal units based upon, for instance, iridium(III), rhodium(III), and platinum(IV). The advantage of their incorporation over purely organic acceptor sites is their capacity to transmit charge directly through dative bonding interactions, the consequence thereof should be enhanced efficiency over other scenarios involving hopping or tunneling processes. To do this requires that such a metal-containing motif be, or become, datively unsaturated for substrate binding subsequent to photo-excitation. In addition, to promote and facilitate ^{3}MLCT excitation and subsequent charge transfer, it is required that the ligand systems employed be rigid, aromatic, and amenable to minimizing donor–acceptor internuclear distance, considering the distance dependence of electron and energy transfer. Several of these systems have been reported (Fig. 21) [90]. Although built-up by a step-wise process, these systems warrant mentioning as they show considerable promise as photocatalysts for the production of H_2 [91].

The ditopic ligand 2,3-di-2-pyridylpyrazine is used to coordinate simultaneously to ruthenium(II) centres in the reference complex **B** and to the rhodium(III) centre in **A**. Cyclic voltammetry of **B** shows no significant electronic interaction between Ru(II) centres as evidenced by superimposed and reversible Ru(II/III) couples at 1.63 V (vs. Ag/AgCl), while the Rh(III) centre undergoes typical irreversible reduction to Rh(I) at −0.37 V, along with two reversible dpp$^{0/-}$ reductions at −0.76 and −1.00 V. The irreversibility of the Rh(III) reduction illustrates the Rh(dσ*) nature of the LUMO of the acceptor unit. The lowest energy absorption band is at 520 nm, due to a Ru → dpp CT transition. Emission from this ^{3}MLCT state (760 nm) is slightly red-shifted with respect to that of **A** (744 nm), reflecting the stabilizing influence of the Rh(III) centre on the dpp π^* orbital. Moreover, **B** Exhibits 95% quenching of the ^{3}MLCT emission and concurrent excited-state lifetime reduction relative to that of **A**, indicating efficient charge transfer to Rh(III), thereby populating the lower lying ^{3}MMCT state. Since the ^{3}MLCT states for **A** and **B** are similar in energy, it is reasonable to estimate that k_r and k_{nr} are equivalent for **B**, giving a rate constant for electron transfer of $k_{et} = 1.2 \times 10^8\ s^{-1}$. Upon forming a Rh(I) centre, a square planar coordination motif is preferred and so two chloride ions are lost, making room for potential substrate binding. The capacity for such an assembly to serve as an efficient photocatalyst for substrate reduction was tested in the context of water reduction to form hydrogen. This is a thermodynamically uphill process and requires multiple electron exchange. To ensure reasonable device efficiency, then, it is advantageous to construct an assembly bearing more photoactive units, such as for the related assembly **C** in Fig. 21. As mentioned previously, this complex was prepared using a step-wise approach whereby the terminal ruthenium(II) units are assembled first containing available coordination sites via the bridging ligand dpp, and these complexes are then in turn used as "ligands" in subsequent complexation steps to render controlled design of the assembly. For the catalyst to function, it is necessary to complete the redox cycle, and so a sacrificial electron donor, *N*,*N*-dimethylaniline (DMA) is added, which serves to regenerate the catalyst by reducing Ru(III) back to Ru(II). In the presence of DMA in a H_2O/CH_3CN mix, irradiation of complex **C** was found to produce significant amounts of hydrogen gas, detected by gas chromatography, upon irradiation at the MLCT excitation wavelength or any wavelength overlapping with the absorption spectrum of **C**.

5.3. *Octanuclear complexes*

5.3.1. *Assembled by square planar metal ions*

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

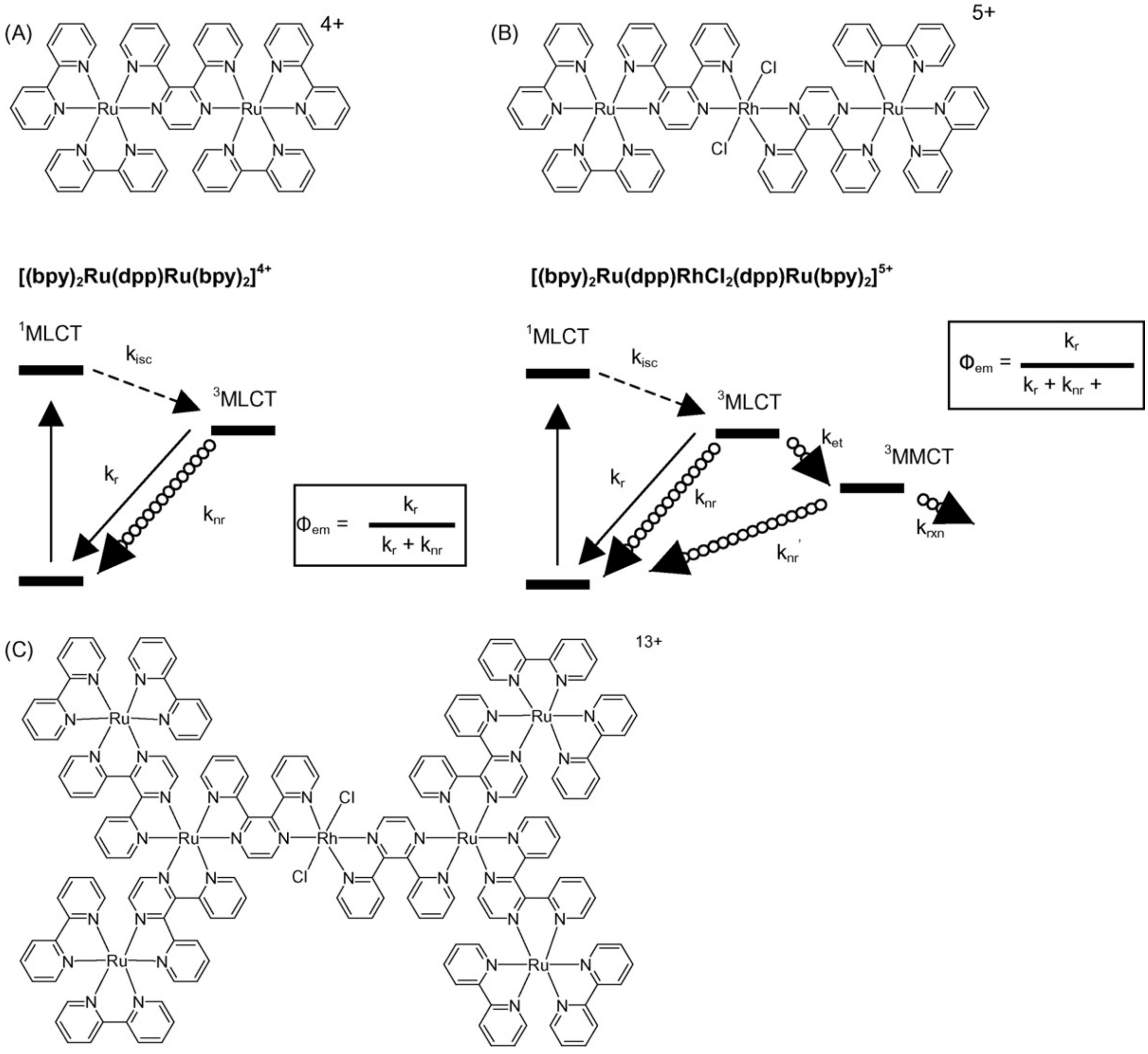


Fig. 21. Heptanuclear complex used for the photocatalyst for the production of H_2.

properties may be altered through either synthetic manipulation of their ligands or changes in environmental conditions (i.e. temperature, pH, and solvent) [22,92]. Their incorporation into larger assemblies can be attained through the 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 [9,55]. Using the latter approach, square assemblies have been prepared by the self-assembly of a $(pytpy)_2M^{2+}$ building block (where pytpy = 4′(4-pyridyl)terpyridine, M = Fe(II), Ru(II), and Os(II)) along with corner units of either *fac*-$Re(CO)_4Br$ or *cis*-protected $[1,1'-(PPh_2)Fc]Pd^{2+}$ (Fig. 22) [93]. The absorption spectra for **12–14** indicates a red shift for the $(pytpy)_2M^{2+}$ based MLCT, the origin of which may be due to an extended π-delocalization effect upon formation of the square. Cyclic voltammetry of **12-14**, along with their component subunits, shows a shift to more positive potential for both the M^{2+}/M^{3+} oxidation and the first ligand-centred reduction processes. The latter reduction processes exhibit a more pronounced shift which generates a net lowering of the MLCT energy, in accordance with electronic absorption spectra. In terms of luminescence, **12**, **13**, and **15**

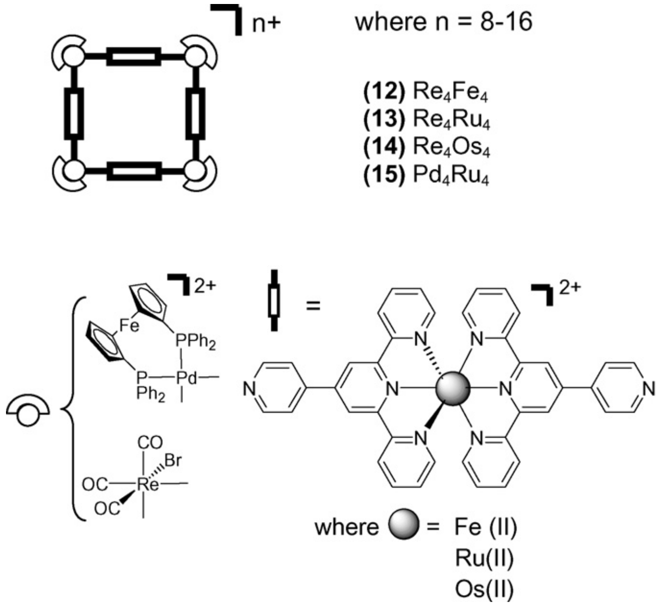


Fig. 22. Bis-tpy metal complexes assembled into octanuclear complexes by Pd(II) and Re(I).

have no detectable emission at room temperature, as with their mononuclear $(pytpy)_2Fe^{2+}$and $(pytpy)_2Ru^{2+}$ starting materials. Despite a net stabilization of the ^{3}MLCT state for $(pytpy)_2M^{2+}$, deactivation via non-radiative relaxation from upper-lying ^{3}MC states is significant and, in the case of **15**, there is an additional affect of upper-lying ^{3}MC states centred on the ferrocene units. On the other hand, the Os(II)-based structure **14** is luminescent due to the stronger ligand field effected by Os(II) compared to both Fe(II) and Ru(II), which results in a higher energy ^{3}MC state that is not as readily thermally accessible (Fig. 22).

5.3.2. Assembled by octahedral metal ions

A series of octanuclear complexes in the form of square and rectangular charge-neutral assemblies have been prepared using moderately fluorescent ($^1\pi \rightarrow {}^1\pi^*$) Zn(salen) complexes (Fig. 23) [94]. The incorporation of Zn(II) into the salen framework serves a structural role as it rigidifies this bridging ligand, decreasing the emission energy and increasing its intensity relative to the free ligand. Zn(II) also allows for axial coordination and hence the potential to incorporate guest molecules in a dative fashion. Thus, the bridging ligands in the octanuclear complex are the two variations of the Zn(II)salen complex used to construct the square assemblies (Fig. 23). The red shift in both absorption and emission for the phenyl derivative relative to the aliphatic, along with good spectral overlap, prompted the formation of the bridged-square assemblies depicted in Fig. 23. 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 can behave collectively as antennae for efficient energy transfer to the encapsulated Zn(II)salen-phenyl complex for subsequent fluorescence emission.

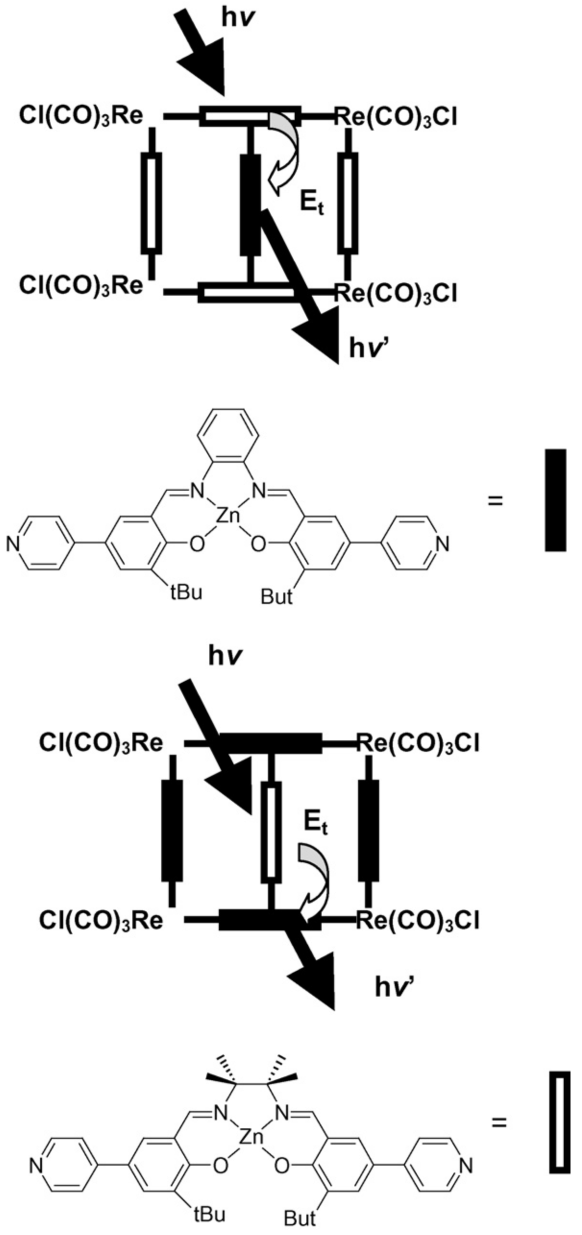


Fig. 23. Octanuclear Re_4Zn_4 complexes can be used as a host for metal complexes which modify its excited state properties.

Re(I) was also used as its alkoxide dimer to assemble an octametallic complex based on a tetrakis-4-pyridyl ligand [95]. The octarhenium(I) assembly emitted between 645 and 667 nm depending on the chain length of the alkoxide bridging ligand with corresponding excited state lifetimes on the order of 50 ns at room temperature.

5.4. Dodecanuclear complexes

A dodecanuclear Zn(II) complex was assembled using a naphthalene containing bis-bidentate ligand. It exhibited a ligand-based ‘excimer-like’ emission at 400 nm that could be used to monitor its self-assembly in solution [96].

6. Conclusion

The metal-directed self-assembly of oligo- and poly-nuclear complexes mimics the fundamental assembly processes found in natural photosystems. In general, the assembly process can be directed by metal ions that play solely a *structural* role (e.g., Pd(II)) or by metal ions that also provide a *functional* role (e.g., Re(I)) to the final assembly. For example, the use of diamagnetic metal ions as the metal-directing unit would favour the assembly of luminescent structures, whereas the use of paramagnetic metal ions would favour vectorial electron transfer in donor-acceptor systems. Although the choice of metal ion provides good control of the overall properties of the assembly, the appropriate ligand type must be selected in order to obtain the right conditions for self-assembly. The denticity of the ligand (e.g., monodentate vs. didentate) will depend on the lability of the metal–ligand complex: the more inert the metal–ligand combination, the greater the need for lower denticity ligands. Thus, metal-directed self-assembly has made its largest strides forward using bridging ligands with monodentate sites. Recent advances, however, suggest that appropriate reaction conditions for a variety of polydentate ligands with various metal ions may also be found [88,89]. The polynuclear assemblies found herein also illustrate some of the factors that govern luminescence in larger assemblies and show that beginning with luminescent components does not necessarily guarantee luminescent products.

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