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HIGHLIGHT

Luminescent metal complexes of d^6 , d^8 and d^{10} transition metal centres

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This highlight focuses on various luminescent complexes with different transition metal centres of d^6 , d^8 and d^{10} electronic configurations. Through the systematic study on the variation of ligands, structural and bonding modes of different metal centres, the structure-property relationships of the various classes of luminescent transition metal complexes can be obtained. With the knowledge and fundamental understanding of their photophysical behaviours, their electronic absorption and luminescence properties can be fine-tuned. Introduction of supramolecular assembly with hierarchical complexity involving non-covalent interactions could lead to research dimensions of unlimited possibilities and opportunities. The approach of “function by design” could be employed to explore and exploit the potential applications of such luminescent transition metal complexes for future development of luminescent materials.

Introduction and general aspects

The field of photophysics and photochemistry of coordination complexes of transition metals has experienced a great blossom and has received an increasing

interest since the last few decades for the understanding of the excited state properties and photochemical reactions.¹ In the earlier studies, transition metal complex photochemistry was mainly confined to and dominated by photosubstitution reactions typical of ligand field (LF) excited state reactivities of chromium(III) complexes^{1b,2,3} and metal carbonyls.^{1b,3} It wasn't until 1971 that photoredox reactivities characteristic of the metal-to-ligand charge transfer (MLCT) excited states of ruthenium(II) bipyridine complexes became apparent.⁴ This work first reported by Adamson and

coworkers has opened up a totally new and fascinating area of research in luminescent transition metal complexes and their photochemistry. This has also eventually led to the emergence of a new branch of supramolecular photochemistry.¹⁻⁵ The fast growing field has been accelerated by the pioneering development of the ligand field theory and the in-depth understanding of electronic transitions and spectroscopy of transition metal compounds led by Gray, Ballhausen and others,⁶ as well as the rapid development of high grade spectrophotometers and lasers.

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Transition metal photochemistry was then mainly dominated by studies of the MLCT excited state of luminescent ruthenium(II) polypyridine complex systems. Amongst the vast library of luminescent transition metal complexes known, the class of ruthenium(II) polypyridyls, such as $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine), is definitely one of the most extensively studied systems.¹⁻⁵ Since the first discovery of their photophysical and photochemical behaviours, numerous studies of the related systems were further developed and elaborated by Balzani,^{1a,5a} Meyer,^{5b} Crosby,^{5c} Watts,^{5d} Endicott,^{5e} Scandola,^{5f} De Cola,^{5g} von Zelewsky,^{5h} Campagna,⁵ⁱ and others.³ The MLCT excited state was generally considered as an involvement of the oxidation of ruthenium(II) to ruthenium(III) and the reduction of a diimine ligand. Taking the advantages of the advances of various ultrafast techniques, recent reports suggested that a promoted electron upon excitation is shared by all polypyridine ligands at the early-time dynamics in homoleptic ruthenium(II) polypyridine species.⁵ⁱ The inverse relationship between the MLCT emission energy and the rate of non-radiative decay processes was found to follow the energy gap law as demonstrated by Meyer and coworkers.^{5j} Photoinduced electron and energy transfer processes have been studied across the bridge in a number of dinuclear heterometallic ruthenium(II)–osmium(II), –iridium(III) and –rhodium(III) polypyridine complexes containing rigid and conjugated as well as photoresponsive spacers.^{5k,l} While the d^6 metal-to-ligand charge transfer (MLCT) excited states of these ruthenium(II) polypyridyl complexes are widely explored, they suffer from the presence of a close-lying $d-d$ ligand field (LF) excited state that can lead to photosubstitution reactions, especially for those polypyridines that do not have a low enough π^* orbital energy or a high enough LF strength. Thus the tuning of a delicate balance between MLCT excited states and LF excited states can lead to interesting control of the excited state properties and a change in the photo-reactivity. An elegant example has been demonstrated by Sauvage and coworkers in making use of the difference in the MLCT and LF excited states to construct interesting molecular machines.^{5m,n}

As the congener of ruthenium(II), the photophysics and photochemistry of

osmium(II) complexes have also been extensively studied.^{1d} Similar to the ruthenium(II) tris-diimine model complexes, the excited state of $[\text{Os}(\text{bpy})_3]^{2+}$ has been ascribed to the $d\pi(\text{Os}) \rightarrow \pi^*(\text{bpy})$ MLCT character. In general, lower emission energy, relative to the ruthenium(II) analogues, has been observed in osmium(II) complexes, resulting from the higher-lying HOMO of the osmium(II) orbital. In view of the energy gap law, shorter luminescence lifetime will also be anticipated. On the other hand, there has been a long history of the photophysical and photochemical studies of chromium(III) complexes of polypyridine, acetylacetonate, polycyanide, polyamine, porphyrin and macrocyclic ligands.^{1b,c} The fields of photosubstitution, photoactivated redox processes, cross-exchange energy transfer, thermally activated excited state relaxation and ultrafast dynamics still remain active research areas.^{1c}

Although the iridium(III) bis-diimine complexes, $[\text{Ir}(\text{N}^{\wedge}\text{N})_2\text{Cl}_2]\text{Cl}$ have been known for a long time,⁷ the related photophysical studies are relatively rare. Another class of iridium(III) complexes bearing two bidentate cyclometallating ($\text{C}^{\wedge}\text{N}$) ligands, e.g. the deprotonated form of 2-phenylpyridine (Hppy) was first reported by Watts.^{8a} In the past decade or so, the dominating position of ruthenium(II) polypyridyl complexes in many photophysical and photochemical investigations has gradually been replaced by cyclometallated iridium(III) complexes $[\text{Ir}(\text{C}^{\wedge}\text{N})_2\text{X}_2]^+$ and $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{L}^{\wedge}\text{L})]^n+$ ($\text{C}^{\wedge}\text{N}$ = cyclometallating ligand; $n = 1$ when $\text{L}^{\wedge}\text{L}$ = neutral bidentate ligand; $n = 0$ when $\text{L}-\text{L}$ = monoanionic bidentate ligand),⁸ which benefit from their broader colour-tuning possibility, less thermally accessible ³MC state, high electrochemical reversibility, synthetic versatility and photo- and chemical stabilities. Continuation of their extensive studies is mainly associated with the revival of interest in this system that stems from the application of such luminescent iridium(III) systems as triplet emitters and dopants in the development of phosphorescent organic light emitting devices (PHOLEDs),^{8d,9} pioneered by Thompson and Forrest^{9a} and later elaborated by others.^{9b-d} Although the polypyridyl and cyclometallated rhodium(III) and iridium(III) complexes share the similar synthetic methodology, structural characteristics and some physical and chemical

properties, the luminescence studies of rhodium(III) systems have comparatively been much less explored.^{1e} The lack of luminescence behaviour at room temperature in solution has been ascribed to the presence of non-emissive $d-d$ ligand field (LF) state, which is at a comparable energy level to those of the luminescence excited states of ligand-centred (LC) and/or metal-to-ligand charge transfer (MLCT) characters, as revealed by temperature-dependent lifetime measurements.

Apart from ruthenium(II) and its heavier congener, osmium(II), and iridium(III), another d^6 MLCT system that has attracted wide interest is the rhenium(I) tricarbonyl bipyridine chromophore, $[\text{Re}(\text{CO})_3(\text{N}^{\wedge}\text{N})\text{X}]^{n+}$ ($\text{N}^{\wedge}\text{N}$ = diimine; X = anion, $n = 0$; X = neutral ligand, $n = 1$), first pioneered by Wrighton^{10a} and extensively developed by Meyer^{10b} and others.^{1b,10c,d} These complexes were found to show intense luminescence and the origin has been attributed to the rhenium(I) to diimine MLCT excited state. Ultrafast spectroscopic studies of such rhenium(I) system have also been investigated in order to gain more insights in the excitation kinetic profile.^{10e,f} While most of the studies are focused on the d^6 metal polypyridine system, metal centres of different electronic configurations that are capable of exhibiting MLCT excited states have also been explored. Early works include the spectroscopic and luminescence studies of d^{10} copper(I) diimine system by McMillin,^{11,12b,c} Sauvage,¹² Karpishin,^{12d} and others.¹³ Very strong luminescence has been observed for the systems of $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$, $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ and $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{POP})]^+$ [$\text{N}^{\wedge}\text{N}$ = 2,9-disubstituted 1,10-phenanthroline; $\text{P}^{\wedge}\text{P}$ = bis(diphenylphosphino)methane and bis(diphenylphosphino)ethane; POP = bis[2-(diphenylphosphino)phenyl]ether with sterically hindered substituents at the 2,9-position of 1,10-phenanthroline ligands. Such enhanced luminescence properties are due to the restriction of the excited state distortion and steric protection from exciplex formation.^{12d,13c} On the other hand, corresponding spectroscopic studies have been done on the d^8 platinum(II) polypyridine system by Miskowski,¹⁴ Gray,¹⁵ Lippard,¹⁶ Vogler,¹⁷ Che,¹⁸ Eisenberg¹⁹ and others,²⁰ and the cyclometalated d^8 platinum(II) analogue²¹ first reported by Maestri.^{21a} Such class of square-planar platinum(II) complexes have

been shown to exhibit interesting and intriguing photophysical behaviours associated with the strong tendency to form π - π stacking and Pt...Pt interactions.¹⁴⁻²⁰

In addition to the rich and interesting photophysical and photochemical properties of the MLCT excited states, another type of excited state that has fascinated researchers is the excited state associated with non-covalent metal-metal interactions found in d^8 and d^{10} metal complex systems. The early classical examples include the d^8 rhodium(i) isocyanide oligomers,²² and the discrete dinuclear d^8 - d^8 diplatinum(ii), $[\text{Pt}_2(\text{pop})_4]^{4+}$ (pop = $\text{P}_2\text{O}_5\text{H}_2^{2-}$ diphosphonate),²³ and the d^{10} - d^{10} $[\text{M}_2(\text{dppm})_3]$ (M = Pd(0), Pt(0); dppm = bis(diphenylphosphino)methane)²⁴ and $[\text{Au}_2(\text{dppm})_2]^{2+}$.²⁵

In the next sections, we will highlight some of our recent efforts in the exploration and exploitation of new classes of luminescent metal-ligand chromophores and their excited state properties. In particular, we will focus on the strategic design of the various classes of luminescent metal complexes not only through chemical modifications of the ligands and metal centres at the molecular level, but also at the supramolecular level to bring in hierarchical complexity to tune the excited state properties. Due to the huge number of luminescent transition metal complexes reported since last decade, selected examples will be drawn from various luminescent metal complexes developed in our laboratory with different transition metal centres of d^6 , d^8 and d^{10} electronic configurations, such as rhenium(i), platinum(ii), gold(iii), copper(i), silver(i) and gold(i). Based on an understanding of the spectroscopic origin and their structure-property relationships, the potential for the development of luminescent metal complexes for a variety of functions and applications will be described and discussed. Finally, the discussion on the future outlook and perspectives on the luminescent transition metal complexes will be made towards the end of this article.

Basic luminescence properties of the metal complexes with carbon donor ligand

As one of the issues in d^6 and d^8 metal complexes with MLCT excited states involves the possible presence of

close-lying non-radiative d - d LF excited states that compete with the population of the emissive MLCT states, one strategy to improve the population of the MLCT states to generate emissive behaviour will be either to raise the energy of the d - d LF excited states by incorporation of strong σ -donor ligands or to lower the energy of the MLCT states through the introduction of strong π -acceptor ligands. We have been particularly interested in employing alkynyl ligands to achieve this goal. Organic alkynes (poly-yne)s, with extended or conjugated π -systems and rigid structure with linear geometry, have become a significant research area due to their novel electronic and physical properties and their potential applications in nanotechnology. The study of transition metal σ -bonded alkynyl complexes has grown rapidly due to their technological potentials that may differ from those of conventional organic counterparts. By introduction of the linear alkynyl group with strong σ -donor ability into luminescent transition metal complexes, fine-tuning and perturbation of emission behaviours are anticipated. For some d^6 and d^8 transition metal complexes such as rhenium(i), platinum(ii) and gold(iii), the presence of low-lying thermally accessible d - d LF state would result in the quenching of the excited state *via* non-radiative decay and hence the lack of or diminution of luminescence. Coupling of strong σ -donating alkynyl ligands should render the metal centre more electron-rich, which would enhance the luminescence properties of these complexes by increasing the population of the emissive excited state resulting from the raising of the energy of the d - d state.

As mentioned earlier, since the first report on the luminescence behaviour appeared in 1974 by Wrighton and Morse,^{10a} the rhenium(i) tricarbonyl diimine system, $[\text{Re}(\text{CO})_3(\text{N}^{\wedge}\text{N})\text{X}]^{n+}$ ($\text{N}^{\wedge}\text{N}$ = diimine; X = halide or pyridine, $n = 0$ or 1), has been extensively studied for the rich photophysical properties of the metal-to-ligand charge transfer (MLCT) excited state^{10b-d} and its ability to effect electrocatalytic reduction of carbon dioxide.²⁶ Mono-, di- and triynyl complexes with various diimine ligands, $[\text{Re}(\text{CO})_3(\text{N}^{\wedge}\text{N})((\text{C}\equiv\text{C})_n\text{R})]$ ($n = 1, 2, 3$; R = alkyl or aryl), have been synthesized.²⁷ Upon excitation at $\lambda > 350$ nm, these alkynylrhenium(i) complexes all show

intense and long-lived orange-red luminescence, which originates from the ³MLCT [$d\pi(\text{Re}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})$] excited state, with some mixing of [$\pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})$] ligand-to-ligand charge transfer (LLCT) character. In general, a more electron-donating alkynyl ligand will give a lower energy MLCT emission band and this is consistent with the σ - and π -donating ability of the alkynyl moieties. It is interesting to note that a blue shift in emission energies has been observed upon increasing the $\text{C}\equiv\text{C}$ unit from a monoynyl to a diyynyl to a triynyl ligand for such alkynylrhenium(i) systems.^{27c} Such a luminescence shift to higher energy with increasing number of $\text{C}\equiv\text{C}$ units is in contrast to the common observation of the red shift in transition energy with increasing $\text{C}\equiv\text{C}$ chain length in organic polyynes²⁸ and in other metal alkynyl systems.²⁹

Similarly, introduction of the strong electron-donating alkynyl ligand to the platinum(ii) terpyridyl moiety has led to an interesting class of phosphorescent metal complexes.³⁰⁻³⁴ The platinum(ii) terpyridine complexes have attracted considerable attention in recent years, mainly due to their interesting spectroscopic behaviour^{14c,15a-c,18} and useful physical³⁵ and biological properties.¹⁶ For example, the chloroplatinum(ii) terpyridyl complex, $[\text{Pt}(\text{terpy})\text{Cl}]^+$ (terpy = 2,2':6',2''-terpyridine), has been reported to exhibit strong luminescence in the solid state and in low-temperature glass.^{15a,18b,36} However, such a complex was found to be non-emissive in the solution state at room temperature, probably due to the presence of a low-energy d - d ligand field (LF) state. By the reaction of the acetonitrile coordinated precursor complex, $[\text{Pt}(\text{terpy})(\text{MeCN})]^{2+}$, with various organic alkynes under basic condition, the synthesis of alkynylplatinum(ii) terpyridyl complexes, $[\text{Pt}(\text{terpy})(\text{C}\equiv\text{CR})]^+$, was first accomplished and reported by us.^{30a} They are found to display intense luminescence in solution on excitation at $\lambda > 360$ nm at room temperature. An emission origin of a [$d\pi(\text{Pt}) \rightarrow \pi^*(\text{terpy})$] ³MLCT excited state, with some mixing of a [$\pi(\text{C}\equiv\text{CR}) \rightarrow \pi^*(\text{terpy})$] ³LLCT state, is assigned.^{30a,b} Incorporation of strong σ -donating alkynyl ligands into the platinum(ii) metal centre would perturb their emission properties. First, the d - d LF state would be destabilized as a

result of the enlargement of d–d orbital splitting by such strong field ligand. Second, destabilization of the HOMO orbital, comprising of the alkynyl and Pt(II) characters, would result from the filled–filled π – $d\pi$ interaction. Accordingly, the emissive ${}^3\text{MLCT}/{}^3\text{LLCT}$ state would be stabilized. Thus the enhancement of luminescence properties with the emission maxima at 560–665 nm in acetonitrile solution at 298 K has been achieved not only by destabilization of the non-emissive d–d LF state but also by stabilization of the emissive excited state of ${}^3\text{MLCT}/{}^3\text{LLCT}$ character (Fig. 1).

A related isoelectronic chlorogold(III) bis-cyclometalated diphenylpyridine complex has also been reported to show emissive behaviour in the solid state and in low-temperature glass.³⁷ In contrast to the related gold(I)³⁸ and the isoelectronic platinum(II)^{14–21,23,30–34,36} compounds which are known to show rich luminescence properties, very few examples of luminescent gold(III) compounds have been reported,^{37,39} probably again due to the presence of low-energy d–d LF states and the electrophilicity of the gold(III) metal centre. There are very few examples of gold(III) compounds that would emit at room temperature in solution.^{39b,c} Using a similar strategy, a new class of alkynylgold(III) bis-cyclometalated diarylpyridine complexes, $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})(\text{C}\equiv\text{CR})]$ ($\text{HC}^{\wedge}\text{N}^{\wedge}\text{CH} = 2,6\text{-diphenylpyridine}$ or its derivatives; R = alkyl or aryl), has been obtained and shown to display rich phosphorescence behaviour in solution at room temperature.⁴⁰ The luminescence is assigned as originating from a metal-perturbed ${}^3[\pi-\pi^*(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})]$ intraligand state. On the other hand, the complex with an amino-phenyl alkynyl group shows a lower-energy structureless emission band centred at ca. 610 nm, which is tentatively assigned as being derived from an excited state of ${}^3\text{LLCT}[\pi(\text{C}\equiv\text{CC}_6\text{H}_4\text{NR}_2) \rightarrow \pi^*(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})]$ origin.^{40a–c}

Apart from the alkynyl ligand, other strong electron-donating ligands can also be employed to raise the energy of the

non-radiative d–d LF excited states. A new class of luminescent mononuclear and dinuclear *N*-heterocyclic carbene-containing gold(III) complexes has also been synthesized and characterized (Fig. 2).⁴¹ These complexes are also found to exhibit intense luminescence in dichloromethane solution at room temperature and the low-energy emission bands are ascribed to be mainly derived from the intraligand $\pi-\pi^*$ states with an aryl-to-pyridine charge transfer character of the cyclometalating $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$ ligand, similar to the related alkynylgold(III) cyclometalated system.⁴⁰ It is interesting to note that one of the dinuclear complexes exhibits two distinct reduction couples instead of one with the first reduction occurring at a less cathodic potential, probably related to the splitting of the π^* orbital-based LUMO resulting from intramolecular $\pi-\pi$ interaction that also led to the red shift of its emission band relative to that of the mononuclear complex.

Excited state tuning via supramolecular assembly with hierarchical complexity

The square planar geometry of d^8 metal complexes with its open structure is well-known to show a strong tendency to stack and to form non-covalent metal–metal interactions. This has been exemplified by the early examples such as $[\text{Pt}(\text{bpy})\text{Cl}_2]$,^{15d,20e,f} $[\text{Pt}(\text{N}^{\wedge}\text{N})(\text{CN})_2]$,^{14b,c,17} $[\text{Rh}(\text{CNR})_4]^+$ (CNR = isocyanide),²² and others, which mainly exist in the solid state, with the exception of $[\text{Rh}(\text{CNR})_4]^+$ which can occur in solution as oligomers. Model complexes such as $[\text{Pt}_2(\text{pop})_4]^{4-}$,²³ $[\text{Rh}_2(\text{bridge})_4]^{2+}$ (bridge = 1,3-diisocyanopropane)^{42a–c} and $[\text{Rh}_2(\text{TMB})_4]^{2+}$ (TMB = 2,5-dimethyl-2,5-diisocyanohexane)^{42c,d} have been studied to provide an understanding of the effect of metal–metal interactions on the spectroscopic and luminescence properties associated with these non-covalent interactions. With the incorporation of the strongly electron-donating as well as solubilizing alkynyl

moiety in $[\text{Pt}(\text{terpy})(\text{C}\equiv\text{CR})]^+{}^{30–34}$ and $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})(\text{C}\equiv\text{CR})]^{40}$ or the *N*-heterocyclic carbene (NHC) moiety in $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})(\text{NHC})]^+$,⁴¹ an understanding of their aggregation behaviour in the solution state at room temperature and at low temperature becomes possible. This is because the d–d LF state has become more high-lying in energy and the enhanced solubility has enabled high concentrations of these compounds to exist in solutions or in mixed solvents without precipitation. For example, low-energy metal–metal-to-ligand charge transfer (MMLCT) absorption and emission bands that impart the drastic colour changes from yellow to blue or magenta and near infra-red (NIR) emission in $[\text{Pt}(\text{terpy})(\text{C}\equiv\text{CR})]^+$ upon aggregation³¹ and excimeric emission due to $\pi-\pi$ stacking interactions in $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})(\text{C}\equiv\text{CR})]$ upon an increase in concentration in the thin films⁴⁰ have been observed. Red shifts in the electronic absorption and emission bands in a dinuclear model complex, $[\{\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\}_2\text{(bis-NHC)}]^{2+}$, have also been observed.⁴¹ Interesting and rich solid-state polymorphic behaviour has also been observed in the platinum(II)-butadiynyl complex of terpyridine, $[\text{Pt}(\text{terpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})\text{OTf}]$.^{31a} Two forms, a dark green form and a red form, exist; both of which have been structurally characterized and shown to exhibit different crystal packing arrangements. The dark green form exists as a linear-chain with the platinum atoms equally spaced, with short intermolecular Pt···Pt contacts of 3.388 Å, while the red form shows a dimeric structure in a zigzag arrangement with alternating Pt···Pt distances of 3.394 and 3.648 Å.^{31a} Short $\pi-\pi$ stacking interactions of 3.38–3.57⁴⁰ and 3.42 Å⁴¹ are also evident in the respective $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})(\text{C}\equiv\text{CR})]$ and $[\{\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\}_2(\text{bis-NHC})]^{2+}$. The hierarchical supramolecular architecture and complexities found in these d^8 square planar complexes have enriched the spectroscopic and luminescence properties of these classes of compounds by adding on a secondary supramolecular control beyond that of a simple molecule.^{32–34}

Similarly, d^{10} metal centres with their low-dimensional coordination geometry are also known to display non-covalent metal–metal interactions; the most well-known is that of gold which has

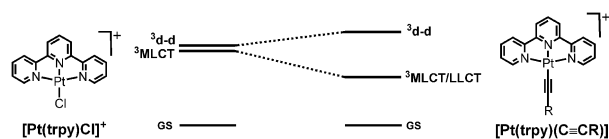


Fig. 1 Proposed excited state energy level diagram of $[\text{Pt}(\text{terpy})\text{Cl}]^+$ and $[\text{Pt}(\text{terpy})(\text{C}\equiv\text{CR})]^+$.

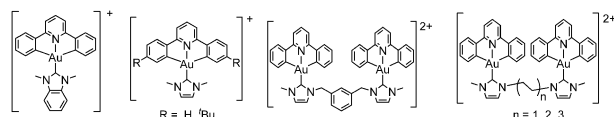


Fig. 2 Luminescent mononuclear and dinuclear *N*-heterocyclic carbene-containing gold(III) complexes.

been coined as “aurophilicity” by Schmidbaur,⁴³ with theoretical studies and insights provided by Pyykko.⁴⁴ These d^{10} - d^{10} metal–metal interactions have led to unique spectroscopic features in the electronic absorption and emission spectra. Classical examples include the $[M_2(dppm)_3]$ ($M = Pd(0), Pt(0)$) pioneered by Gray,²⁴ $[Au_4(pip)_4Cl_4]$ ($pip = piperidine$) by Vogler,⁴⁵ $[Cu_4(py)_4I_4]$ by Hardt⁴⁶ and Ford,⁴⁷ $[Ag_4(PPh_3)_4I_4]$ by Zink,⁴⁸ and $[Au_2(dppm)]^{2+}$ studied independently by Che^{25a,b} and Fackler.^{25c} The electronic absorption spectra and magnetic circular dichroism (MCD) spectra of $[Au_2(dmpm)]^{2+}$ ($dmpm = bis(dimethylphosphino)methane$) and $[Au_2(dppm)]^{2+}$ have been studied in depth by Mason.⁴⁹ We have extended the work to trinuclear gold(I) phosphine systems⁵⁰ and studied the effect of nuclearity and the effect of coordination number and geometry on the electronic absorption and luminescence of these gold(I) phosphine complexes, namely $[Au_2(dmpm)]^{2+}$ and $[Au_2(dppm)]^{2+}$ versus $[Au_3(dmmp)]^{3+}$ ($dmmp = bis(dimethylphosphinomethyl)methylphosphine$) and $[Au_3(dmmp)]^{3+}$.⁵⁰ Exploration of the spectroscopic studies of metal–metal interactions of Au(I), Ag(I) and Cu(I) has also been reported for the optically transparent dcpm analogues.⁵¹ The remarkable report on the solvoluminescence of trinuclear gold(I) stacks by Balch⁵² has also aroused immense interest in the chemical community.

Various luminescent alkynyl complexes of Cu(I),^{38c,53} Ag(I)^{38c,53} and Au(I)^{38c–e,53} phosphines have been described, which show phosphorescence originated either from ligand-to-metal

charge transfer (LMCT) mixed with metal-centred (MC) ds/dp character or intraligand (IL) π - π^* character. By making use of the unique conformation of diethynylcalix[4]crown pre-organized in a 1,3-alternate fashion, interesting phosphorescence behaviour has also been observed in a very unusual class of homoleptic tetranuclear gold(I) bis-alkynylcalix[4]crown complexes that displays a discrete non-polymeric structure (Fig. 3), in which both σ - and π -coordinated gold(I) centres are present with planar η^2, η^2 -bonding mode and short intramolecular $Au \cdots Au$ contacts.⁵⁴ The emission with large Stokes shift and lifetime in the microsecond range has been assigned as derived from states of metal-cluster-centred character modified by $Au \cdots Au$ interactions and mixed with metal-perturbed $[\pi \rightarrow \pi^*(C \equiv C)]$ intraligand states.

Apart from alkynyl as bridging ligands, chalcogen atoms have also been shown to exhibit bonding with transition metal centres in various bridging modes. The interest in the d^{10} metal chalcogenido system has partly been due to the growing importance of metal chalcogenide nanostructured thin films and nanoparticles in semiconductor and optical applications. Model compounds of d^{10} metal chalcogenides and their spectroscopic studies will provide an understanding of their rich intrinsic optical and photoluminescence properties. A number of luminescent tetranuclear copper(I) and silver(I) μ_4 -chalcogenide and the isoelectronic phosphinidene clusters, $[M_4(dppm)_4(\mu_4-E)]^{2+}$ [$dppm = bis(diphenylphosphino)methane$], have been prepared, isolated and structurally

characterized (Fig. 4).^{38c,53b,55} All of them adopt a similar saddle-like structure with four bridging $dppm$ ligands, in which the four metal centres form a distorted rectangle with a μ_4 -bridged chalcogenide or phosphinidene projected above the M_4 plane. Photoexcitation of such a class of clusters both in the solid state and MeCN solution results in intense long-lived luminescence. Their luminescence colour/energies are found to be dependent on the nature of metal centres and chalcogenide or phosphinidene bridge. Their isoelectronic and isostructural nature has allowed a systematic comparison of their spectroscopic and luminescence properties. The luminescence is believed to originate predominantly from the ligand-to-metal charge-transfer LMCT $[E^{2-} \rightarrow M_4]$ excited state, with mixing of a metal-centred MC ($d-s/d-p$) state modified by metal–metal interactions. Such an assignment is consistent with the trend observed in the luminescence energy with $E = S^{2-} > Se^{2-} > Te^{2-} > PPh^{2-}$ and $M = Ag(I) > Cu(I)$.

With gold(I), the strong tendency to form aggregates through aurophilic $Au \cdots Au$ interaction has led to an even wider interest. This is particularly the case given the widespread interest in the study of alkythiol-gold monolayer-protected clusters (MPCs)⁵⁶ and self-assembled monolayers (SAMs);⁵⁷ the former of which have been reported to show interesting intrinsic optical and photoluminescence properties.⁵⁶ Molecular model compounds of gold(I) chalcogenides are believed to provide insights to these studies. Soluble luminescent hexanuclear, decanuclear, dodecanuclear and octadecanuclear gold(I) sulfido complexes of phosphines, $[Au_6\{Ph_2PN(^iPr)PPh_2\}_3(\mu_3-S)_2]^{2+}$,^{58a} $[Au_{10}\{Ph_2PN(^iPr)PPh_2\}_4(\mu_3-S)_4]^{2+}$,^{58b} $[Au_{12}(dppm)_6(\mu_3-S)_4]^{4+}$ ^{58c} and more recently, $[Au_{18}(\mu-dpepp)_6(\mu_3-S)_6]^{6+}$ ($dpepp = bis(2-diphenylphosphinoethyl)phenylphosphine$)^{58d} (Scheme 1) have been synthesized and isolated by us. Short intramolecular $Au \cdots Au$ distances typical of aurophilic interactions are revealed in their X-ray crystal structures.⁵⁸ All of them exhibit an orange to red luminescence, which is attributed to be derived from states of a $^3LMMCT [S \rightarrow Au \cdots Au]$ origin. Dual luminescence behaviour with an additional emission band in the green region has been

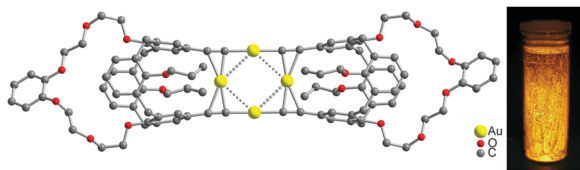


Fig. 3 (Left) Crystal structure of a luminescent tetranuclear gold(I) alkynylcalixarene complex. (Right) Solid sample of the gold(I) complex showing luminescence upon UV irradiation. Reproduced with permission from ref. 54.

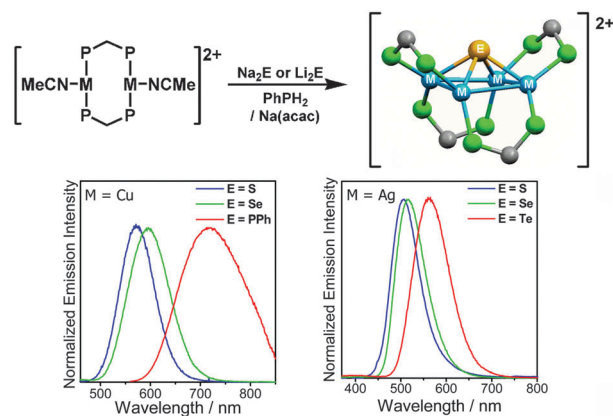
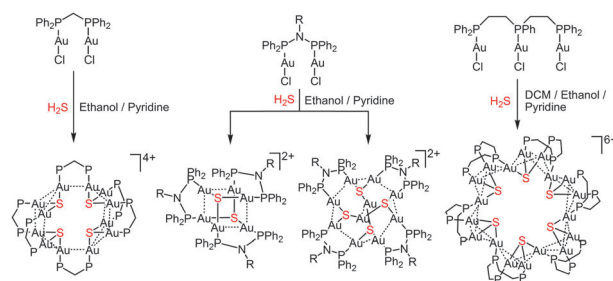


Fig. 4 Synthetic route and emission spectra of tetranuclear copper(I) and silver(I) μ_4 -chalcogenide or phosphinidine clusters.

observed for the decanuclear complexes,^{58b} attributed to the metal-perturbed ³IL(diphosphine) phosphorescence. On the other hand, an abnormally large Stokes shift of 15052 cm^{-1} (1.87 eV) has been observed for the hexanuclear complexes, arising from a highly distorted excited state structure. Reversible binding of Ag^+ ions and spectroscopic changes can be readily achieved upon addition of CH_3CN to a methanolic solution without disruption of the Au_{18} macrocycle.^{58d} A related series of gold(I) selenido clusters, $[\text{Au}_{10}\text{Se}_4(\text{dppm})_4]^{2+}$ and $[\text{Au}_{18}\text{Se}_8(\text{dpppe})_6]^{2+}$ [dpppe = bis(diphenylphosphino)pentane], have been synthesized,^{58e,f} and their photoluminescence and photosensitization of singlet oxygen have been studied. The former complex $[\text{Au}_{10}\text{Se}_4(\text{dppm})_4]^{2+}$ was found to exhibit near infra-red (NIR) luminescence, which is associated with the configuration of the $\text{Au}_{10}\text{Se}_4$ core.^{58f} On the other hand, the latter complex $[\text{Au}_{18}\text{Se}_8(\text{dpppe})_6]^{2+}$ was found to show intense red luminescence in the solid state and to possess effective photosensitization of singlet oxygen in solution.^{58f}

Apart from the supramolecular interactions observed in the solid state and in solution, supramolecular chemistry also plays a very important role in governing the properties of soft matter. As MLCT excited state properties are well-known to be sensitive towards the environment and the nature of the media, their spectroscopic and luminescence studies in soft matter will be interesting to explore. In this regard, supramolecular gels represent one class of these soft matters. While there has been a growing interest in the study of organogels,⁵⁹ corresponding studies in metallogels based on metal complexes are still relatively rare and are rather unexplored,^{27e,f,60,61} despite numerous works on transition metal complexes with rich spectroscopic properties being known. Through the functionalization of the alkynyl ligand with three long alkyl chains, an alkynylrhenium(I) tricarbonyl diimine system (Chart 1) was found to form metallogels.^{27e} During the sol-gel transition, the colour and emission properties of the rhenium(I) tricarbonyl diimine MLCT system are found to vary with the rigidity and the microenvironmental changes of the media.



Scheme 1 Synthetic route of luminescent high nuclearity gold(I) sulfido clusters.

By making use of the possible η^2 - π -coordination of alkynyls to metal centres such as copper(I) or silver(I), a novel alkynylrhenium(I) tricarbonyl diimine system with metal coordination-assisted crosslinking-induced metallogelation behaviour has been demonstrated.^{27f} The sol-gel transitions and luminescence turn-on switching are induced by copper(I) or silver(I) coordination. This luminescent supramolecular gel assembly process can also be considered as a molecular AND logic gate. The fine balance and the interplay of the non-covalent interactions in these gelators can be readily modified by the judicious choice and rational design of the coordinating ligands in the organometallic system.

Moreover, despite recent growing interest in the development of low molecular-weight organogels, most of the work has been directed towards the utilisation of noncovalent van der Waals' forces, π - π stacking and hydrogen bonding interactions as the driving force for gelation.⁵⁹ In view of the propensity of the platinum(II) terpyridyl system to form $\text{Pt} \cdots \text{Pt}$ and π - π interactions,^{14-21,23,30-34} it is anticipated that such interactions will provide an additional driving force for the gelation process. Since remarkable spectroscopic changes have been well-documented upon conformational and microenvironmental changes, associated with inter- or intramolecular $\text{Pt} \cdots \text{Pt}$ and π - π interactions in solution, interesting changes in the spectroscopic and luminescence behaviour are anticipated in addition to the inherent sensitivity of the MLCT transitions to the environment. A series of alkynylplatinum(II) terpyridyl system has been designed and prepared for the study of metallogel formation (Fig. 5).^{61a} Such kinds of complexes show drastic colour and luminescence changes during the sol-gel transition. Counter-anion dependent colour changes and metallogel stability have been observed which is attributed to the different degrees of aggregation derived from the $\text{Pt} \cdots \text{Pt}$ and π - π interactions involved in the gelation process.^{61a} The complex with OTf^- counter anion has been found to form the most stable gel, together with the observation of the most drastic red shift in colour and luminescence, indicative of the presence of the largest extent of the $\text{Pt} \cdots \text{Pt}$ and π - π interactions. On the other

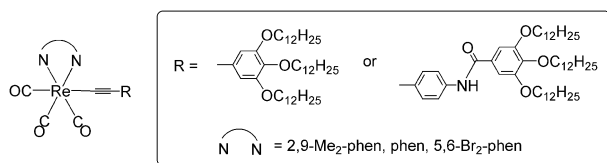


Chart 1 Luminescent metallogels of alkynylrhenium(I) complexes.

hand, the complex with three *tert*-butyl substituents showed a slight blue shift in MLCT energy during gel-to-sol transition, suggesting the lack of Pt...Pt and π - π interaction involvement in gel formation due to the steric bulk imparted by the *t*Bu₃-terpy ligand.

Functions and potential applications

Chemosensing function

Taking into consideration their high luminescence quantum yield, long luminescence lifetime and large Stokes shift, oxygen sensors based on phosphorescent metal complexes of ruthenium(II) polypyridines,⁶² and platinum(II) porphyrins^{62a} have also been extensively developed for analytical, medicinal and environmental applications. DeGraff and Demas have worked extensively in this area of research.⁶² Some of these compounds have been immobilized onto various solid phase supports and the sensing mechanism is based on the quenching of luminescence intensity and/or lifetime that are strongly sensitive to the concentration of oxygen. Suslick and coworkers have reported a series of colorimetric sensor arrays based on the ligand binding on different metalloporphyrins for the detection and identification of various volatile organic compounds and toxic gases.⁶³

As the metal-to-ligand charge-transfer (MLCT) excited states of luminescent rhenium(I) tricarbonyl diimine complexes

and platinum(II) terpyridyl complexes are mixed with ligand-to-ligand charge-transfer (LLCT) character by the attachment of alkynyl unit onto the metal centre, their absorption and luminescence properties are known to be affected by the electronic effect of the substituents on the alkynyl group. Upon incorporation of various functional groups on the alkynyl ligand, such as crown ether, amino and triarylboron moieties, the rich photophysical properties of the MLCT/LLCT excited state of these metal complex systems can be used to serve as versatile spectroscopic reporters and probes for metal ion,^{30a,c-e} proton^{30b,e} and fluoride ion,^{27g} respectively. A series of alkynylrhenium(I) tricarbonyl diimine complexes with a triarylboron moiety has been synthesized^{27g} (Fig. 6) and is found to be capable of binding F⁻ ions with spectral changes in the UV-vis absorption and emission spectra, and is further supported by ¹⁹F NMR binding experiment. The alkynylplatinum(II) terpyridyl complexes with crown ether,^{30a,c} calix[4]-crown-5,^{30d} and amino^{30b} moieties are found to be non-emissive in fluid solution, resulting from the presence of a quenching process by the lower-lying non-emissive ³LLCT state as well as by reductive electron transfer quenching due to the presence of the strong electron-donating group.^{30a-e} These platinum(II) complexes show colour changes and emission enhancement upon the addition of metal ion (Fig. 7) or acid. It has been suggested that the $d\pi(\text{Pt})$ orbital energy is lowered as a result of the reduced electron-donating ability of

the metal ion-bound crown ether or ammonium group. As a result, a blue shift in the lowest energy absorption band and a revival of luminescence are observed, which have been ascribed to the blocking of reductive PET quenching pathway.

Biological activity

With the superior advantages possessed by luminescent transition metal complexes, such as large Stokes shift, kinetic inertness, high photochemical stability and low excitation energy, there has been a growing interest in the design and studies of luminescent transition metal-based immunoassays. Various systems including ruthenium(II),⁶⁴ rhenium(I),^{65,66} osmium(II),⁶⁷ platinum(II),^{18g,20g-i,68} rhodium(III),⁶⁹ and iridium(III)^{66,70} have been shown to be promising candidates for bioanalytical applications. Utilization of such transition metal complexes as luminescent labelling reagents and probes for biological molecules such as DNA, peptides, proteins, avidin and estrogen receptors have been explored and reported.⁶⁶ Some of them have been demonstrated to serve as *in vivo* luminescent bioimaging agents for live cell imaging.^{66a,70} Photorelease of nitric oxide has also been reported in some transition metal complexes,⁷¹ which could be exploited for potential photoinduced delivery of bioregulatory compounds. Barton and co-workers have also extensively studied a number of metal complexes for the recognition, metallointercalation and photo-redox reactions with DNA.^{72a,b} A number of metal complexes containing aromatic side arms as metallointercalators have been reported by Sadler and coworkers to show dual binding functions.^{72c} Intercalation into the DNA bases by the aromatic side arms as well as the direct coordination to DNA base by the metal centre would cause DNA distortion and hence influence the biological activity.^{72c} Extensive studies on several classes of platinum(II), gold(I) and gold(III) complexes have been reported to show *in vitro* and *in vivo* therapeutic behaviours by Che and coworkers.⁷³

Vapochromic and vapoluminescent functions

Beyond the molecules, supramolecular non-covalent metal-metal interactions can also be exploited for sensing purposes.

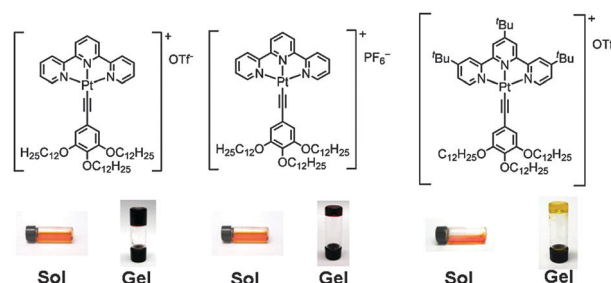


Fig. 5 Luminescent metallogels based on platinum(II) terpyridyl alkynyl complexes.

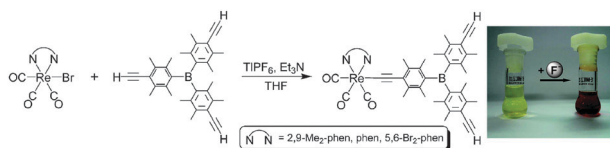


Fig. 6 (Left) Synthetic route of luminescent alkynylrhenium(I) tricarbonyl diimine complexes with a triarylboron moiety for the fluoride ion-binding properties. (Right) Photograph showing the colour change upon addition of fluoride ion. Reproduced with permission from ref. 63.

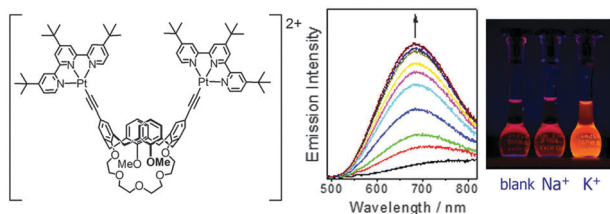


Fig. 7 Alkynylplatinum(II) terpyridyl complexes with a calix[4]-crown-5 functional group showing luminescence enhancement upon selective potassium ion sensing. Reproduced with permission from ref. 30d.

For example, the optical properties of the classical Magnus' salt of $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ have been studied for many years and its unique green colour in the solid state has been attributed to the presence of $\text{Pt} \cdots \text{Pt}$ interactions.⁷⁴ A number of related double salts of platinum(II), $[\text{Pt}(\text{CNR})_4][\text{Pt}(\text{CN})_4]$ and $[\text{Pt}(\text{phen})(\text{CNR})_2][\text{Pt}(\text{CN})_4]$, have been reported by Mann and coworkers to show interesting vapochromic and vapoluminescent behaviours for the development of a practical "electronic nose".⁷⁵ The changes in the solid state colour and luminescence are ascribed to the solvent-chromophore interactions as well as the alteration of $\text{Pt} \cdots \text{Pt}$ distance upon penetration of solvent vapours. Other classes of square-planar platinum(II) complexes containing terpyridine,^{19f} 2,6-bis(*N*-methylbenzimidazol-2-yl)pyridine,⁷⁶ cyclometalating^{77a} and bipyridine^{77b-d} ligands have also been demonstrated by various research groups including Eisenberg, Connick, Che and

Kato to display vapochromic and vapoluminescence phenomena that are related to the perturbation of the metal-metal interactions.

Luminescent probes associated with non-covalent π - π stacking and/or metal \cdots metal interaction

The changes in solution colour and luminescence of the class of alkynylplatinum(II) complexes, $[\text{Pt}(\text{terpy})(\text{C}\equiv\text{C}-\text{R})]^+$, upon aggregation as a result of reduced solvation have been shown to be dependent on the nature of the anions.³¹ This indicates that counterions can play an important role in governing the degree of aggregation and the extent of metal-metal and π - π interactions within these aggregates. In light of this, the use of an ordered assembly of counter-anions arranged in a preorganized fashion as in the anionic polyelectrolytes such as polyacrylate, poly(vinyl sulfonate), and poly(4-styrene sulfonate) carrying

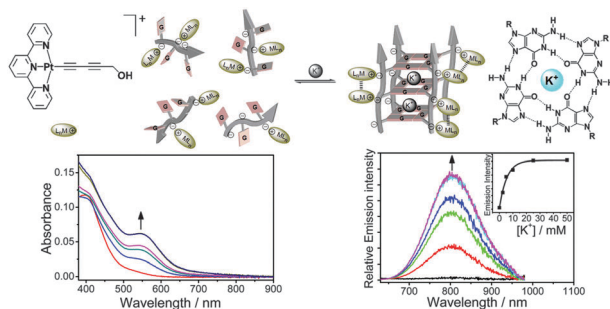


Fig. 8 G-Quadruplex-induced self-assembly of alkynyl-platinum(II) terpyridyl complexes. Reproduced with permission from ref. 34a.

multiple negative charges, has been employed to induce the self-assembly or aggregation of the positively charged alkynylplatinum(II) terpyridyl units, without the need to change the solvent composition.³² The remarkable electronic absorption and emission spectral changes associated with the aggregation and self-assembly of the complexes are driven by electrostatic interactions between the polymer and the complex, and by terpyridine ligand π - π stacking and $\text{Pt} \cdots \text{Pt}$ interactions. Similarly, poly(L-glutamate), poly(L-aspartate), and oligonucleotides, such as poly(dT)₂₅, poly(dC)₂₅, poly(dG)₂₅, and poly(dA)₂₅,³³ have also been shown to induce such aggregation and self-assembly of the complexes to give drastic colour changes and NIR emission, provided that the number of repeating units of such poly-anionic biomolecules is above a certain critical length. Employment of the concept of the self-assembly of platinum(II) complexes which shows a new MMLCT absorption band and NIR luminescence attributed to the presence of $\text{Pt} \cdots \text{Pt}$ and π - π stacking interactions in solution has been further extended for the detection of various other biomolecules such as nucleases,^{34a} G-quadruplex formation,^{34a} K^+ ions^{34a} (Fig. 8), glucose and proteins.^{34b,c} Apart from the intermolecular self-assembly properties of mononuclear alkynylplatinum(II) terpyridyl complexes brought about by changes in the counter-anions^{31b} and the microenvironment,^{18f,30a,c,32-34} the design of model compounds for the intramolecular self-assembly study of the aggregation properties of only two isolated units in fluid solution has been achieved *via* the appropriate design of dinuclear platinum(II) complexes of this class with flexible bridges on the terpyridyl ligand, $[(4\text{-}^n\text{Bu-C}_6\text{H}_4\text{C}\equiv\text{C})\text{Pt}(\text{tpy-R-terpy})\text{Pt}(\text{C}\equiv\text{C-C}_6\text{H}_4\text{-}^n\text{Bu-4})](\text{PF}_6)_2$ ($\text{R}=\text{O}(\text{CH}_2\text{CH}_2\text{O})_2$, $\text{O}(\text{CH}_2\text{CH}_2\text{O})_3$, $\text{O}(\text{CH}_2\text{CH}_2\text{O})_4$ and $\text{O}(\text{CH}_2)_{10}\text{O}$).^{30f} Drastic colour changes and NIR emission enhancement as well as broad and poorly resolved resonance signals in the ¹H NMR spectra were observed for the intra-molecular self-assembly in fluid solution state even at room temperature.

Using a similar strategy, utilization of the switching on and off of $\text{Au} \cdots \text{Au}$ interactions has been demonstrated for

chemosensing. Examples include the use of dinuclear gold(i) crown ether-containing complexes for metal ion sensing *via* the on/off switching of Au...Au interactions.^{78a,b} Extension of the concept has been made using a simple trinuclear alkynylgold(i) complex with three oligoether pendants^{78c} (Fig. 9). The encapsulation of the Mg²⁺ ions in between the three intramolecular oligoether pendant units would force the three rigid and linear arylalkynylgold(i) units into close proximity, and as a result would lead to the turning on of the Au...Au interactions, leading to the switching on of a low-energy absorption and emission band.

Phosphorescent organic light-emitting diodes

Apart from exploiting luminescent transition metal complexes for chemosensing and imaging functions, their phosphorescence behaviour would render them to function as attractive candidates as triplet emitters for the fabrication of phosphorescent organic light-emitting diodes (OLEDs). OLEDs have aroused a great interest in the fields of chemistry, physics and engineering in the past two decades as there is a huge potential for the development of this new technology in flat panel display and solid state lighting applications. In principle, phosphorescent metal organic complexes can generate 100% internal quantum efficiency, resulting from both singlet and triplet exciton formation. Such class of complexes has attracted considerable interest for their employment as efficient phosphorescent materials in OLEDs. In light of the requirement for large spin-orbit coupling imparted by the heavy atom effect, transition metal

complex systems of iridium(III),^{8d,9,79} platinum(II),⁸⁰ ruthenium(II),⁸¹ and osmium(II)⁸² have been widely studied in this research area. The most commonly employed system is the cyclometalated iridium(III) complexes, with the best device showing an external quantum efficiency of 19.2% in a doped device.^{79g} A series of cyclometalated platinum(II) complexes acting as a dopant in OLEDs have been found to exhibit blue monomeric and orange excimeric electroluminescence simultaneously.^{80a,b} By controlling the dopant concentration, the ratio of monomeric and excimeric emissions can be varied and white organic light emitting diodes (WOLEDs) can be achieved from a single emissive dopant. De Cola and coworkers^{81a} have been making use of a ruthenium(II) polypyridine phosphorescent dopant and semiconducting PPV polymer to fabricate a light-emitting electrochemical cells (LEECs), which showed red emission from the ruthenium(II) phosphor at forward bias and green emission from the PPV at reversed bias. A number of highly luminescent and long-lived osmium(II) complexes containing diimine and carbonyl ligands have been synthesized and utilized as phosphorescent dopants in high performance green and blue OLEDs.^{1d,82} Recently, phosphorescent biscyclometalated alkynylgold(III) complexes have been reported to show electroluminescence.^{40c,d} Interestingly, these square-planar gold(III) complexes also show a concentration-dependent PL and EL behaviour (Fig. 10). A biscyclometalated alkynylgold(III) complex has been shown to act as an emissive dopant and to give promising EL performance in OLEDs.^{40d} At an

optimized dopant concentration of 4%, a device with a maximum EQE of 11.5%, corresponding to a current efficiency of 37.4 cd A⁻¹ and a power efficiency of 26.2 lm W⁻¹ has been obtained. Such a high EQE is comparable to that of Ir(ppy)₃-based devices.

Clean and renewable energy

Similarly, the diversity of metal-ligand chromophoric systems with tunable electronic absorption and excited state redox properties has made transition metal complexes attractive candidates for solar energy conversion. Because of the environmental aspect and rising demand of energy, development of clean and renewable energy is one of the grand challenges in scientific research. Conversion of a solar energy source, either to electricity or chemical fuels such as hydrogen, provides a promising solution, given the abundant and unlimited supply of solar energy. Dye-sensitized solar cells (DSSCs) comprising of nanocrystalline TiO₂ semiconductors and panchromatic dye have received fast-growing interest since the first report on the Grätzel cell.^{83a} Ruthenium(II),⁸³ osmium(II),^{84a} rhenium(I),^{84b} iridium(III),^{84c} platinum(II)^{84d} and copper(I)^{84e} complexes with appropriate ligands for anchoring and charge separation functions have been designed and utilized as the dye for photosensitizing function. In the past few years, Grätzel and co-workers have made significant progress in improving the conversion efficiency of the DSSCs.^{83e} On the other hand, photo-generation of hydrogen from water represents another kind of conversion of solar energy into stored chemical fuels. Platinized TiO₂ particles with attachment of various metal-ligand chromophores, such as ruthenium(II) polypyridine,^{85,86} cyclometalated iridium(III)^{85,87} and zinc(II) porphyrin,^{85,88} have been investigated for the study of such water photosplitting processes. Recently, the MLCT state of platinum(II) terpyridine complexes has been demonstrated to serve as the chromophore for the light-driven production of hydrogen from aqueous protons in the presence of a sacrificial electron donor.⁸⁹ The same class of complexes has also been found to possess photocatalytic properties, such as oxidation of oximes into their

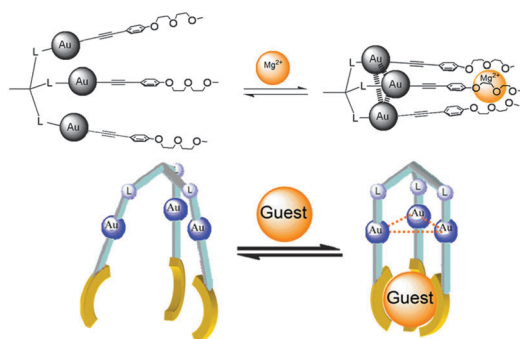


Fig. 9 Selective ion probe for Mg²⁺ based on Au...Au interactions in a tripodal alkynylgold(i) complex with oligoether pendants. Reproduced with permission from ref. 78c.

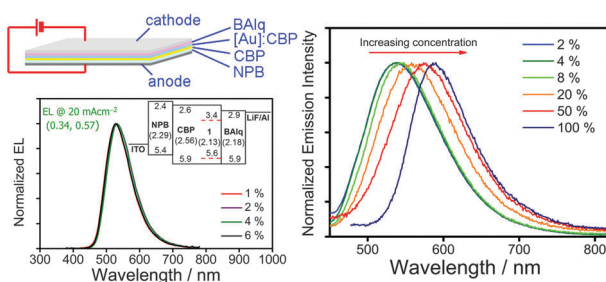


Fig. 10 (Left) Electroluminescence and (right) photoluminescence of alkynylgold(III) cyclometalated complex. Reproduced with permission from ref. 40d.

corresponding carbonyl compounds,^{90a} photooxidation of olefins^{90b} and homogeneous photocatalytic hydrogen production from Hantzsch 1,4-dihydropyridines.^{90c} Another molecular device consisting of platinum(II)⁹¹ or palladium(II)⁹² coupled with ruthenium(II) polypyridyl hybrid has been reported to show photo-driven hydrogen evolution. Photo-catalyzed hydrogen evolution from solutions by a promising class of cobalt has been reported and the related potential pathways have also been thermodynamically analysed from the results of electrochemical and photochemical investigation.⁹³ Nocera and coworkers have reported mono- and bimetallic gold(III) complexes which showed facile multi-electron photoelimination of halogen upon LMCT excitation.⁹⁴ Photocatalytic reduction of carbon dioxide has also been investigated for solar fuels by using polypyridyl ruthenium(II)⁹⁵ and rhenium(I),^{96,97} as well as other transition metal complex systems.^{95,98}

Future outlook and perspectives

Transition metal–ligand chromophoric complexes represent an important class of building block. By making use of the diversity and versatility of ligand design and synthesis as well as the variety of the different structural and bonding modes of metal complexation, various metal–ligand chromophoric systems with tunable electronic absorption, emission and excited state redox properties can be obtained. In addition to tuning the molecular properties of metal complexes, introduction of supramolecular assembly with hierarchical complexity involving non-covalent interactions could lead to research dimensions of unlimited possibilities and opportunities. Through the systematic study on the variation of

ligands with different functionalities, one could attempt to study the structure–property relationships of the various classes of luminescent transition metal complexes. With the knowledge and fundamental understanding of their photophysical properties, their electronic absorption and luminescence properties could be fine-tuned. New knowledge could be generated from the synergism of innovative molecular design and synthesis, physical characterization and measurements, and photophysical and photochemical studies. The approach of “function by design” could be employed to explore and exploit the potential applications of such luminescent transition metal complexes. Future development of luminescent transition metal complexes with improved and optimized functions in the widely diverse fields of immunoassay, chemosensing, OLEDs, OPVs and DSSCs, multimodal imaging, diagnostics, therapy, photocatalysis, and photosensitizers for clean and renewable energy is envisaged.

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