

# Luminescent metal alkynyls – from simple molecules to molecular rods and materials

Vivian Wing-Wah Yam \*

*Centre for Carbon-Rich Molecular and Nano-Scale Metal-Based Materials Research and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, People's Republic of China*

Received 14 November 2003; accepted 17 December 2003

## Abstract

This review describes the design and synthesis of a number of luminescent transition metal alkynyls by this laboratory. The luminescence properties of the complexes have been studied and their emission origin elucidated. Some of these complexes have been shown to be ideal building blocks for the design and construction of luminescent molecular rods and materials, in which the luminescence properties can be readily tuned by changing the alkynyl ligands. Some of them also exhibited luminescence switching behaviour with the “ON–OFF” luminescence states modulated by redox processes, metal ion-binding or solvent composition.  
© 2004 Elsevier B.V. All rights reserved.

*Keywords:* Luminescence; Alkynyl; Copper(I); Silver(I); Rhenium(I); Platinum(II)

## 1. Introduction

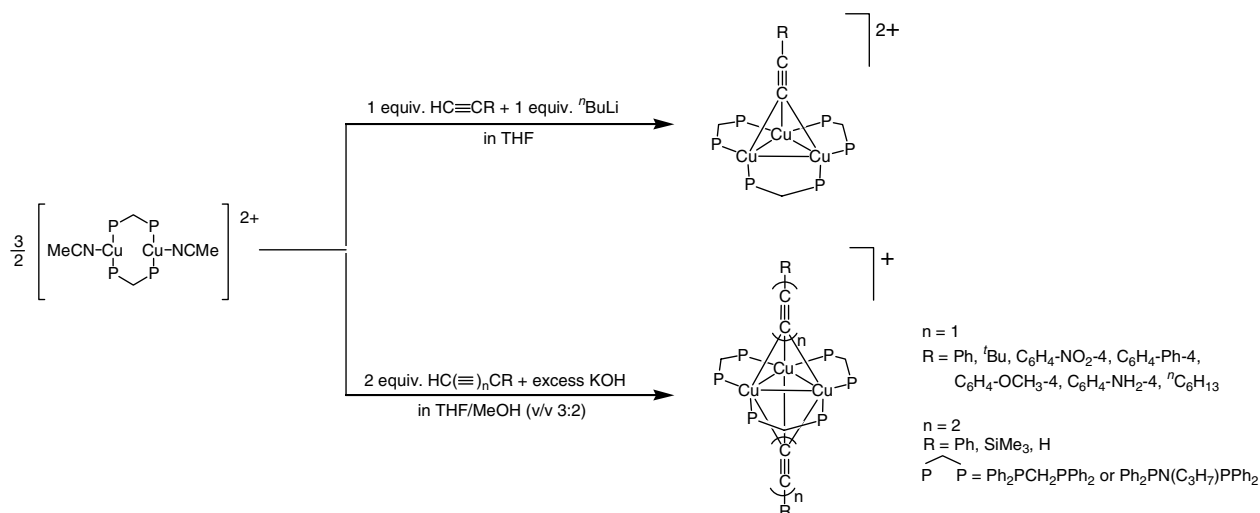
The present article focuses on some of our recent efforts in the molecular design and synthesis of luminescent metal alkynyls of selected metal centres, the study of their luminescence properties and the fundamental understanding of the underlying spectroscopic origins of their luminescence behaviour. Organic polyynes are molecules of interesting electrical and optical properties [1–7]. In particular, there has been a growing interest in the study of polyphenyleneethynes (PPE), which has a rigid-rod structure with extended  $\pi$ -conjugation [8] and is an alkyne analogue of the very important class of polyphenylenevinyls (PPVs) [8]. The chemistry of metal alkynyls has attracted enormous attention, in particular, with the emerging interest in their potential applications in the field of materials science [9–31]. The linear geometry of the alkynyl unit and its  $\pi$ -unsaturated nature have made the metal alkynyls attractive building blocks for molecular wires [13–19] and organometallic oligomeric [20] and polymeric materials, [21–23] which may possess unique properties such as

optical nonlinearity, electrical conductivity, and liquid crystallinity [24–31]. Despite the growing interests and extensive studies in metal alkynyls, relatively less attention was focused on the luminescence behaviour of this class of compounds [17,18,32–52]. In this context, we have directed our research specifically to the design and synthesis of luminescent metal alkynyls and, with a judicious design and choice of ligands and metal functionalities, to employing them as versatile building blocks for luminescent molecular materials.

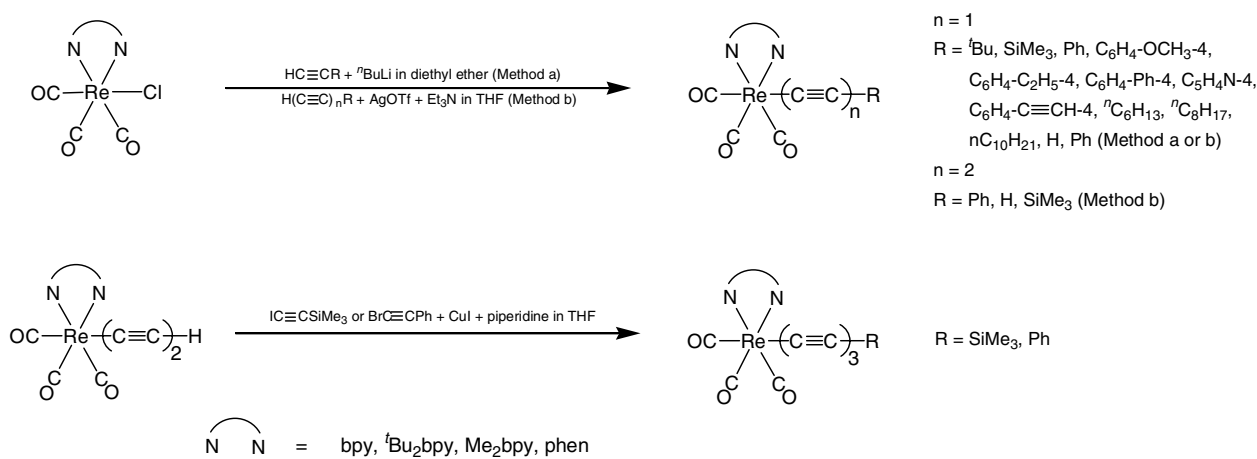
## 2. Copper(I) alkynyls and rhenium(I) alkynyls

Recent works by us have shown that luminescent metal-based carbon-rich materials could be constructed from copper(I) alkynyls [34–38] and rhenium(I) alkynyls [18,39–44]. The former consist of triangular arrays of copper(I) centres bridged by the alkynyl units in a  $\mu_3$ - $\eta^1$ -type of bridging mode either in a mono-capped or bi-capped fashion (Scheme 1), while the latter involve the coordination of the alkynyl unit to the rhenium(I) center in a terminal  $\sigma$ -bonding mode (Scheme 2). These compounds were found to be strongly phosphorescent.

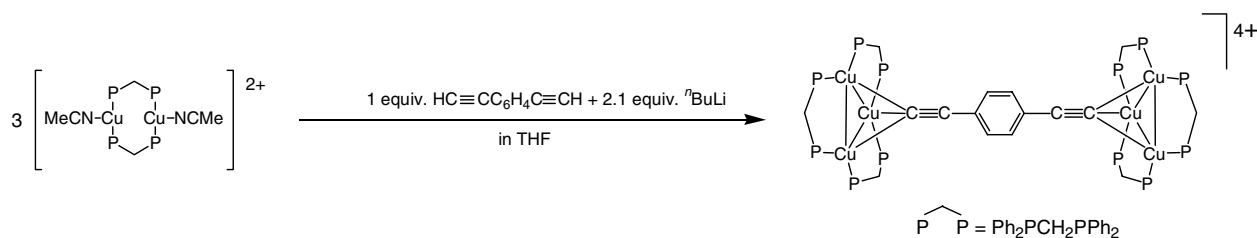
\* Corresponding author. Tel.: +852-2859-2153; fax: +852-2857-1586.  
E-mail address: [wvyam@hku.hk](mailto:wvyam@hku.hk) (V.W.-W. Yam).



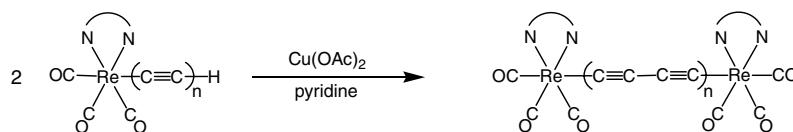
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

Extension of the work to link two triangular copper(I) arrays via a diethynylbenzene unit to give a luminescent hexanuclear complex (Scheme 3) [36] and the

coupling of two mononuclear rhenium(I) units to give luminescent dinuclear rhenium(I) alkynyls (Scheme 4) [40,44] has also been made.

Excitation of these complexes in the solid state and in fluid solutions resulted in long-lived and intense luminescence. The copper(I) monoynyls showed strong phosphorescence at 416–697 nm, with the emission energy dependent on the electron-donating ability of the alkynyl ligand. In general, the complexes with electron-rich alkynyls emitted at a lower energy. The origin of the emission has been proposed to involve substantial ligand-to-metal charge-transfer (LMCT) [alkynyl  $\rightarrow$  Cu $_3$ ] character, with mixing of some metal-centred  $3d^94s^1$  character, i.e. the lowest-lying emissive state could best be described as an admixture of LMCT triplet state and a metal-centred (MC)  $3d^94s^1$  state modified by copper–copper interaction, and in cases when the alkynyls are less electron-rich or have more extended  $\pi$ -conjugation, probably a mixing of a ligand-centred  $\pi-\pi^*$  (alkynyl) excited state is also involved. On the other hand, the rhenium(I) alkynyls showed intense phosphorescence typical of the metal-to-ligand charge transfer (MLCT) excited state properties of rhenium(I) polypyridines, probably 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, the better is the electron-donor ability of the alkynyl ligands, the lower is the  $^3\text{MLCT} [d\pi(\text{Re}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})]$  emission energy.

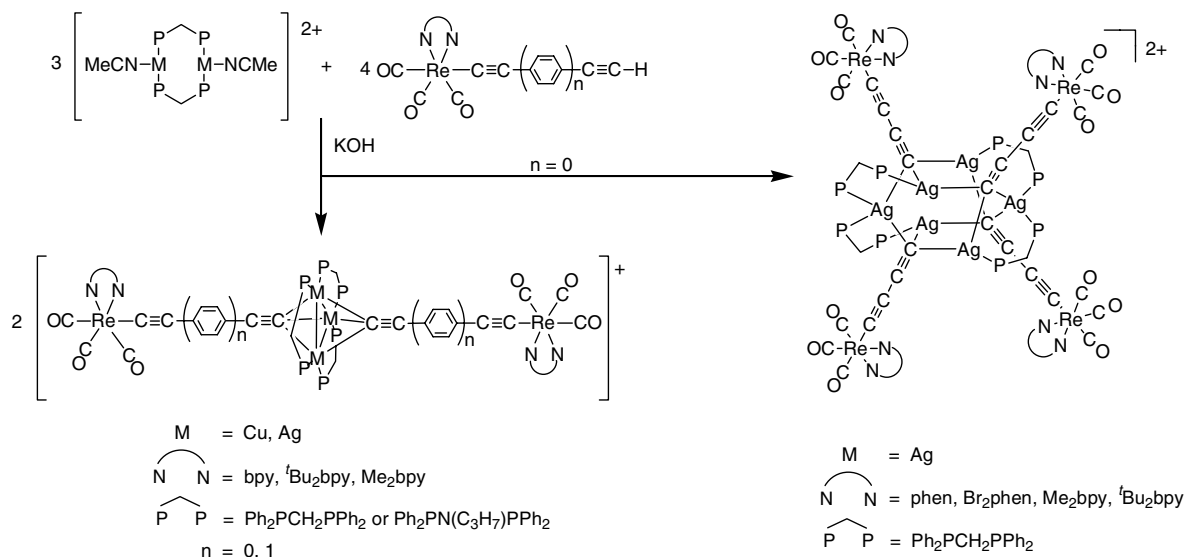
### 3. Pentanuclear mixed-metal Re(I)–Cu(I) and –Ag(I) alkynyl complexes and decanuclear Re(I)–Ag(I) alkynyl complexes

With our interest in both polynuclear Cu(I) and Ag(I) alkynyl and rhenium(I) alkynyl complexes, an extension of the work to the design and synthesis of interesting luminescent mixed-metal molecular rods and materials

of rhenium–copper and –silver has been made. The synthesis of novel series of pentanuclear mixed-metal Re(I)–Cu(I) and –Ag(I) alkynyl complexes,  $[\text{M}_3(\mu\text{-P}^{\wedge}\text{P})_3\{\mu_3\text{-}\eta^1\text{-C}\equiv\text{C-C}_6\text{H}_2\text{R}_2\text{-C}\equiv\text{C-}p\text{-Re}(\text{N}^{\wedge}\text{N})(\text{CO})_3\}_2]^+$  and  $[\text{M}_3(\mu\text{-P}^{\wedge}\text{P})_3\{\mu_3\text{-}\eta^1\text{-C}\equiv\text{C}\equiv\text{C-Re}(\text{N}^{\wedge}\text{N})(\text{CO})_3\}_2]^+$  [45,46], and decanuclear Re(I)–Ag(I) alkynyl complexes,  $[\text{Ag}_6(\mu\text{-dppm})_4\{\mu_3\text{-C}\equiv\text{C}\equiv\text{C-Re}(\text{N}^{\wedge}\text{N})(\text{CO})_3\}_4](\text{PF}_6)_2$  [47], has been accomplished based on the employment of the ‘metal complex as ligand’ or the so-called metalloligand approach (Scheme 5). Through a systematic variation of the nature of the trinuclear or hexanuclear metal core and the diimine ligands on the Re(I) centre, the emission properties of these classes of compounds have been systematically and readily tuned.

The complex cations of the pentanuclear mixed-metal Re(I)–Cu(I) and –Ag(I) alkynyl complexes consist of an isosceles triangle of copper or silver atoms with a dppm ligand bridging each edge to form a roughly planar  $[\text{M}_3\text{P}_6]$  core, with two Re(I) butadiynyl metalloligands capping the triangular M(I) in a  $\mu_3\text{-}\eta^1$  fashion, while the complex cations of the decanuclear Re(I)–Ag(I) alkynyl complexes show a hexanuclear Ag(I) core decorated with four Re(I) diimine complex fragments on the periphery, with each of the silver atoms linked to two bridging dppm ligands and each butadiynyl group has one end coordinated to the three silver atoms in a  $\mu_3\text{-}\eta^1$ -bridging mode and the other end coordinated to a rhenium atom. The hexanuclear Ag(I) core consists of two  $\text{Ag}_3$  triangular planes that are arranged in a near perpendicular fashion.

The electronic absorption spectra of the penta- and decanuclear mixed-metal alkynyl complexes in dichloromethane solution exhibited, in addition to the high-energy absorption bands typical of intraligand  $\pi \rightarrow \pi^*$  transitions of the diphosphines, alkynyl and di-



Scheme 5.

mine ligands, low-energy absorption bands at ca. 434–482 nm. The energy of the low-energy absorption band was found to depend on the nature of the diimine ligands, with an order in line with the  $\pi$ -acceptor orbital energy of the diimine ligands:  $\text{Br}_2\text{phen} < \text{phen} < \text{Me}_2\text{bpy} \leq {}^t\text{Bu}_2\text{bpy}$ , and are assigned as  $[\text{d}\pi(\text{Re}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})]$  MLCT transition [ $\text{phen} = 1,10\text{-phenanthroline}$ ,  $\text{Br}_2\text{phen} = 4,7\text{-dibromo-1,10-phenanthroline}$ ,  $\text{Me}_2\text{bpy} = 4,4'\text{-dimethyl-2, 2'-bipyridine}$ ,  ${}^t\text{Bu}_2\text{bpy} = 4,4'\text{-di-tert-butyl-2,2'-bipyridine}$ ]. The slightly higher MLCT absorption energy for the silver(I) complex (473 nm) than the related copper(I) analogue (482 nm) in the pentanuclear complexes is consistent with the poorer electron-donating ability of the  $\text{Ag}_3^{\text{I}}$  core than the  $\text{Cu}_3^{\text{I}}$  counterpart, which would render the Re(I) centre less electron rich, leading to a larger MLCT energy gap.

Excitation of both the penta- and decanuclear mixed-metal alkynyl complexes in the solid state and in solution at  $\lambda > 400$  nm resulted in strong orange to red luminescence. The emission energies were found to be sensitive to the nature of the diimine and diphosphine ligands and the nature of the central tri- or hexanuclear metal core. The emission energies of the complexes with the same diphosphine ligands but different diimine ligands in dichloromethane in general follow the  $\pi^*$  orbital energies of the diimine ligands, with the better  $\pi$ -acceptor diimine ligands showing the lower energy emission (Fig. 1). With reference to previous spectroscopic works on the rhenium(I) diimine systems, the intense low-energy emission has been assigned as derived from states of  ${}^3\text{MLCT} [\text{d}\pi(\text{Re}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})]$  origin, probably mixed with some  ${}^3\text{LLCT} [\pi(\text{C}\equiv\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})]$  character. With the same diimine ligand, a slight blue shift in emission energy was observed on going from  $[\text{Cu}_3(\mu\text{-dppm})_3\{\mu_3\text{-}\eta^1\text{-C}\equiv\text{C}\equiv\text{C-Re}(\text{bpy})(\text{CO})_3\}_2]^+$  (706 nm) to  $[\text{Cu}_3(\mu\text{-dppa})_3\{\mu_3\text{-}\eta^1\text{-C}\equiv\text{C}\equiv\text{C-Re}(\text{bpy})(\text{CO})_3\}_2]^+$  (701 nm) and from  $[\text{Cu}_3(\mu\text{-dppm})_3\{\mu_3\text{-}\eta^1\text{-C}\equiv\text{C}\equiv\text{C-Re}(\text{Me}_2\text{bpy})(\text{CO})_3\}_2]^+$  (688 nm) to  $[\text{Cu}_3(\mu\text{-dppa})_3\{\mu_3\text{-}\eta^1\text{-C}\equiv\text{C}\equiv\text{C-Re}(\text{Me}_2\text{bpy})(\text{CO})_3\}_2]^+$  (677 nm) [ $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ,  $\text{dppa} = \text{Ph}_2\text{PNHPPH}_2$ ], consistent with the stronger electron-donating ability of  $\text{dppm}$  than  $\text{dppa}$ , which would render the Cu(I)-coordinated alkynyl more electron-rich, and in turn would render the Re(I) centre more electron-rich, raising the energy of the  $\text{d}\pi(\text{Re})$  orbitals, causing a lower energy  ${}^3\text{MLCT}$  emission. It is interesting to note that the complexes emitted at lower energy than their respective precursor complexes, for example,  $[\text{Ag}_6(\mu\text{-dppm})_4\{\mu_3\text{-C}\equiv\text{C}\equiv\text{C-Re}({}^t\text{Bu}_2\text{bpy})(\text{CO})_3\}_4](\text{PF}_6)_2$  (604 nm)  $<$   $[\text{Re}({}^t\text{Bu}_2\text{bpy})(\text{CO})_3(\text{C}\equiv\text{C}\equiv\text{CH})]$  (580 nm). The observation of a red shift in emission energy of the mixed-metal complexes relative to their precursor complexes may suggest that the emissive states could best be described as having predominantly  ${}^3\text{MLCT} [\text{d}\pi(\text{Re}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})]$  character, but probably mixed with some  ${}^3\text{LLCT} [\pi(\text{C}\equiv\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})]$  character that has been perturbed by the  $\text{M}_3$  or  $\text{Ag}_6$  core.

3.1. Mixed-metal dinuclear rhenium(I)–iron(II) alkynyl complex and a related gold(I) alkynyl luminescence switch

### 3.1. Mixed-metal dinuclear rhenium(I)–iron(II) alkynyl complex and a related gold(I) alkynyl luminescence switch

In addition to the mixed-metal rhenium(I)–copper(I) and –silver(I) alkynyl complexes, a mixed-metal dinuclear rhenium(I)–iron(II) alkynyl complex,  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{C}\equiv\text{C-C}_6\text{H}_4\text{-C}\equiv\text{C})\text{Fe}(\text{C}_5\text{Me}_5)(\text{dppe})]$  [ $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ], has been obtained from the reaction of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{C}\equiv\text{C-C}_6\text{H}_4\text{-C}\equiv\text{C-H})]$  and  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{dppe})\text{Cl}]$  in the presence of  $\text{KPF}_6$  and  ${}^t\text{BuOK}$  in methanol [48]. Oxidation of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{C}\equiv\text{C-C}_6\text{H}_4\text{-C}\equiv\text{C})\text{Fe}(\text{C}_5\text{Me}_5)(\text{dppe})]$  with  $[\text{Cp}_2\text{Fe}]\text{PF}_6$  produced the oxidized species,  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{C}\equiv\text{C-C}_6\text{H}_4\text{-C}\equiv\text{C})\text{Fe}(\text{C}_5\text{Me}_5)(\text{dppe})]\text{PF}_6$ , in good yield. Unlike the related luminescent rhenium(I)-alkynyl precursor  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{C}\equiv\text{C-C}_6\text{H}_4\text{-C}\equiv\text{C-H})]$ ,  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{C}\equiv\text{C-C}_6\text{H}_4\text{-C}\equiv\text{C})\text{Fe}(\text{C}_5\text{Me}_5)(\text{dppe})]$  was found to be non-emissive, probably as a result of the respective intramolecular reductive electron transfer and energy transfer quenching of the emissive  $\text{d}\pi(\text{Re}) \rightarrow \pi^*(\text{bpy})$   ${}^3\text{MLCT}$  state by the low-lying MLCT and ligand-field (LF) excited states of the iron moiety. Thus the presence of low-lying MLCT and LF excited states of the iron moiety would readily quench the  ${}^3\text{MLCT}$  emission of the rhenium bipyridyl core, either by non-radiative interstate crossing, energy transfer or electron transfer processes. Interestingly, switching “ON” of the luminescence property derived from the  $\text{d}\pi(\text{Re}) \rightarrow \pi^*(\text{bpy})$   ${}^3\text{MLCT}$  state can be demonstrated upon oxidation of  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{C}\equiv\text{C-C}_6\text{H}_4\text{-C}\equiv\text{C})\text{Fe}(\text{C}_5\text{Me}_5)(\text{dppe})]$  to  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{C}\equiv\text{C-C}_6\text{H}_4\text{-C}\equiv\text{C})\text{Fe}(\text{C}_5\text{Me}_5)(\text{dppe})]\text{PF}_6$  (Scheme 6). The recovery of emission

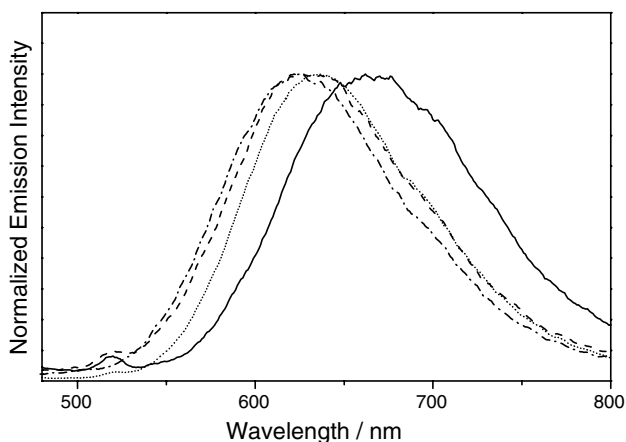
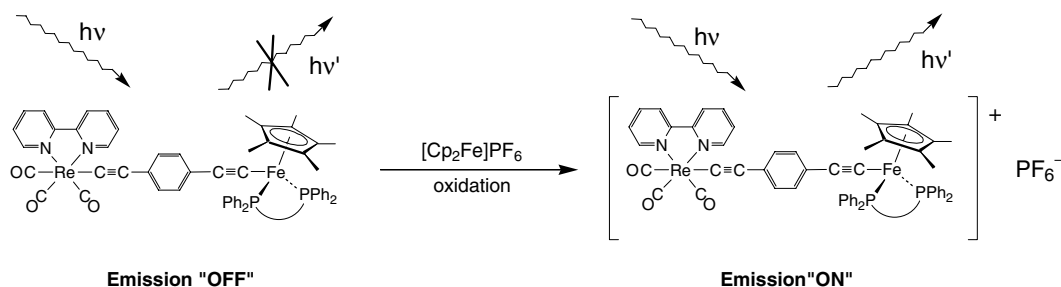


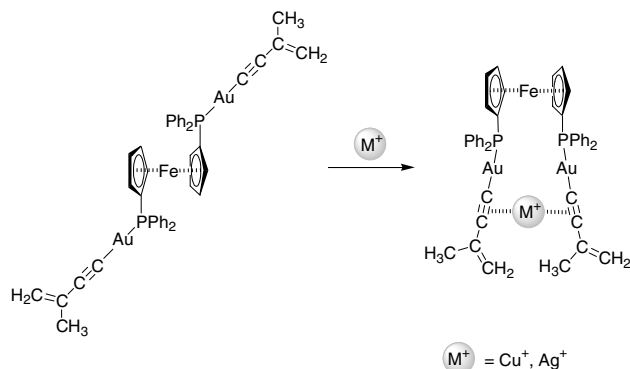
Fig. 1. Normalized emission spectra of  $[\text{Ag}_6(\mu\text{-dppm})_4\{\mu_3\text{-C}\equiv\text{C}\equiv\text{C-Re}(\text{N}^{\wedge}\text{N})(\text{CO})_3\}_4](\text{PF}_6)_2$  [ $\text{N}^{\wedge}\text{N} = \text{Br}_2\text{phen}$  (—),  $\text{phen}$  (···),  $\text{Me}_2\text{bpy}$  (---) and  ${}^t\text{Bu}_2\text{bpy}$  (-·-·)] in  $\text{CH}_2\text{Cl}_2$  at 298 K.



Scheme 6.

behaviour in the oxidized species may be ascribed to the fact that the Fe(III) centre is electron-deficient and is not a good electron donor, and thus no reductive electron transfer quenching can occur. This can also be reflected by the blue shift of the  $^3\text{MLCT}$  emission bands in  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C})\text{Fe}(\text{C}_5\text{Me}_5)(\text{dppe})]\text{PF}_6$  (590 nm) relative to the related mononuclear complex,  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{CH})]$  which exhibits an emission band at ca. 650 nm. Since the iron(III) metal center with an overall positive charge of +1 can be regarded as an electron-withdrawing substituent on the 1,4-diethynylbenzene unit, the alkynyl group would behave as a poorer  $\sigma$ - as well as  $\pi$ -donor, lowering the energy level of the  $d\pi(\text{Re})$  orbital, and resulted in a shift of the  $^3\text{MLCT}$  energy to higher energy. Such a blue shift in emission energy is consistent with the assignment of a  $^3\text{MLCT}$  emission origin. Similarly, one can visualize this as the stabilization of the  $d\pi(\text{Fe})$  orbital in the Fe(III) state, which would lead to the absence of low-lying LF and MLCT states that would quench the emission. Thus, the system could be considered as a molecular redox “switch” capable of the switching on and off of the triplet photoluminescence of the rhenium(I) diimine moiety via the formation of a heterobimetallic complex system.

A related luminescence switch based on gold(I) alkynyls has also been synthesized [49]. Switching of the behaviour has also accomplished via metal ion-binding (Scheme 7).



Scheme 7.

### 3.2. Platinum(II) terpyridyl alkynyl system

Apart from the rhenium(I) diimine system, another interesting class of compounds that show intense  $^3\text{MLCT}$  emission is the platinum(II) terpyridine system. Despite platinum(II) alkynyls being known, most of them are confined to that of platinum phosphines, with corresponding studies on the nitrogen donor analogues unexplored. Functionalization of the platinum(II) terpyridyl system using a strategy similar for the preparation of the rhenium(I) alkynyl system by reacting  $[\text{Pt}(\text{tpy})(\text{MeCN})](\text{OTf})_2$  [ $\text{tpy} = 2,2':6',2''$ -terpyridine] with  $\text{HC}\equiv\text{CR}$  in the presence of a base afforded the platinum(II) alkynyl complexes,  $[\text{Pt}(\text{tpy})(\text{C}\equiv\text{CR})]^+$  (Scheme 8) [50]. The electronic absorption spectra of the platinum(II) alkynyl complexes in acetonitrile solution exhibited in addition to the intense intraligand (IL) absorptions at 300–350 nm, a less intense low-energy band at ca. 456–480 nm with  $\epsilon$  in the order of  $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . The low-energy absorption band at 456–480 nm, which is sensitive to the nature of the alkynyl ligand, is tentatively assigned to the  $d\pi(\text{Pt}) \rightarrow \pi^*(\text{tpy})$  MLCT transition. In general, the stronger is the electron-donating ability of the alkynyl ligand, the lower will be the energy of the low-energy absorption. This observation is in line with a MLCT assignment of the low-energy absorption band, since electron-rich substituents on the phenyl ring of the alkynyl ligand would render the platinum metal center more electron-rich and hence raise the  $d\pi(\text{Pt})$  orbital energy, leading to a lower energy MLCT absorption. Excitation of the complexes gave rise to long-lived low-energy emissions at 510–830 nm. The emission energies of the complexes in solution were also found to depend on the nature of the substituents on the phenyl ring of the alkynyl ligands (Fig. 2), a trend consistent with a  $^3\text{MLCT}$  emission assignment, probably mixed with some alkynyl-to-terpyridine LLCT character.

As an extension of our work on platinum(II) alkynyl systems and the growing interest in the chemistry of carbon-rich metal-containing poly-yenes, an investigation on the luminescence properties of the  $[\text{Pt}](\text{C}\equiv\text{C})_n$ -[Pt] system of various alkynyl chain lengths

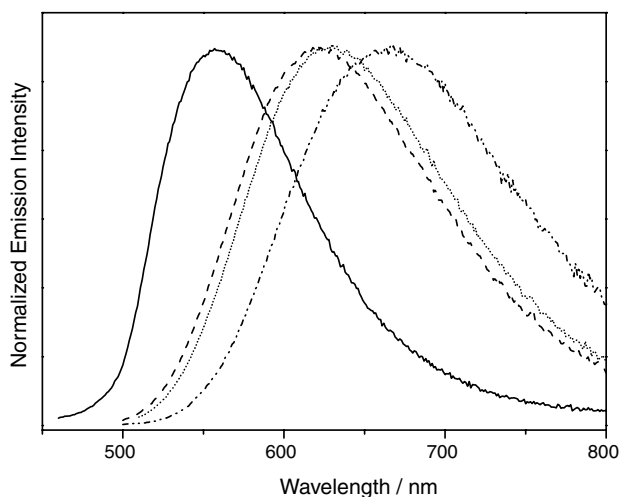
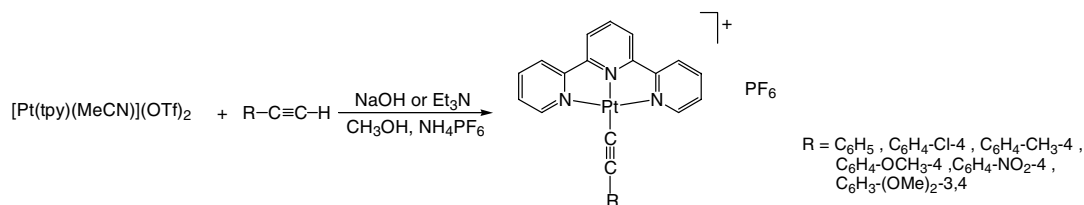


Fig. 2. Normalized emission spectra of  $[\text{Pt}(\text{tpy})(\text{C}\equiv\text{CR})]\text{PF}_6$  [ $\text{R}=\text{C}_6\text{H}_5$  ( $\cdots$ ),  $\text{C}_6\text{H}_4\text{-Cl-4}$  (---),  $\text{C}_6\text{H}_4\text{-CH}_3\text{-4}$  (-·-·-) and  $\text{C}_6\text{H}_4\text{-NO}_2\text{-4}$  (—)] in acetonitrile at 298 K.

with platinum(II)-terpyridyl groups as the transition metal end-capped termini was initiated. A series of alkynyl-bridged dinuclear platinum(II)-terpyridyl complexes,  $[\text{Pt}(\text{tBu}_3\text{tpy})(\text{C}\equiv\text{C})_n\text{Pt}(\text{tBu}_3\text{tpy})](\text{X})_2$  ( $n=1$ ,  $\text{X}=\text{OTf}$ ;  $n=2$ ,  $\text{X}=\text{OTf}$ ;  $n=4$ ,  $\text{X}=\text{PF}_6$ ;  $\text{tBu}_3\text{tpy}=4,4',4''$ -tri-*tert*-butyl-2,2':6',2''-terpyridine) was designed and synthesized [51]. The choice of the bulky tri-substituted terpyridine ligand is to eliminate the influence of Pt··Pt and  $\pi$ - $\pi$  interactions on the luminescence behaviour. The luminescence behaviour together with the structure-property relationships of the complexes were studied. The platinum(II) metal center in these complexes adopts an essentially square-planar geometry with slight distortion due to the coordination constraints imposed by the terpyridyl ligand. The two platinum(II)-terpyridyl ends are connected by the alkynyl chain in a linear  $[\text{Pt}-(\text{C}\equiv\text{C})_n-\text{Pt}]$  fashion. Similar to the mononuclear platinum(II) terpyridyl alkynyl complexes, these diplatinum terpyridyl end-capped oligoynes showed intense high-energy intraligand absorptions at ca. 308–342 nm and low-energy absorption bands at ca. 428–522 nm in acetonitrile solution (Fig. 3). The low-energy bands in the visible region were assigned to  $[\text{d}\pi(\text{Pt}) \rightarrow \pi^*(\text{terpyridine})]$  MLCT transition, probably mixed with an alkynyl-to-terpyridine LLCT character. It is interesting to

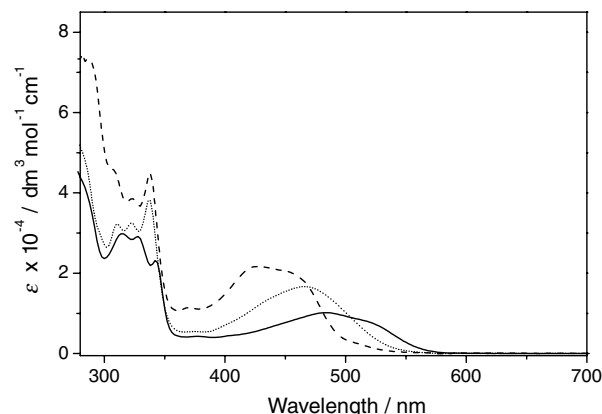


Fig. 3. Electronic absorption spectra of  $[\text{Pt}(\text{tBu}_3\text{tpy})(\text{C}\equiv\text{C})_n\text{Pt}(\text{tBu}_3\text{tpy})](\text{X})_2$  [ $n=1$  (—),  $\text{X}=\text{OTf}$ ;  $n=2$  ( $\cdots$ ),  $\text{X}=\text{OTf}$ ;  $n=4$  (---),  $\text{X}=\text{PF}_6$ ] in acetonitrile at 298 K.

note that the low-energy absorption band of  $[\text{Pt}(\text{tBu}_3\text{tpy})(\text{C}\equiv\text{C})_2\text{Pt}(\text{tBu}_3\text{tpy})](\text{OTf})_2$  showed an extinction coefficient that was almost double that of the 382–400 nm band of the related mononuclear complex,  $[\text{Pt}(\text{tBu}_3\text{tpy})(\text{C}\equiv\text{C})]\text{OTf}$ . The low-energy absorption band was found to shift to higher energy with an increasing number of  $\text{C}\equiv\text{C}$  units. This is rather unusual as one would have expected a shift to lower energy with increasing  $\text{C}\equiv\text{C}$  units as is commonly found in organic poly-yne and in other metal-alkynyl systems. Similar to the rhenium(I) alkynyl system [42], the blue shift observed upon increasing the number of  $\text{C}\equiv\text{C}$  units has been attributed to be a result of the greater stabilization of the  $\text{d}\pi$  orbital on platinum(II) upon increasing the length of the conjugated alkynyl chain. Two effects may account for the observed trend. One is the  $\pi$ -donor ability exhibited by the alkynyl chain, giving rise to a filled-filled  $\text{p}\pi\text{-d}\pi$  overlap. The other is the  $\pi$ -accepting ability of the alkynyl chain, resulting in a  $\text{d}\pi\text{-}\pi^*$  interaction. Given the similar  $\sigma$ -donating ability of the monoyne, diyne and tetrayne bridges, the  $\pi$ -donor orbital energy of the  $(\text{C}\equiv\text{C})_n$  bridge should follow the order:  $n=4 > 2 > 1$ . Despite the fact that a better energy match between the  $\text{d}\pi(\text{Pt})$  and the  $\pi(\text{C}\equiv\text{C})_n$  orbitals upon increasing the  $\text{C}\equiv\text{C}$  chain length is expected to raise the  $\text{d}\pi(\text{Pt})$  orbital energy, the decreased overlap integral between the  $\text{d}\pi(\text{Pt})$  and the  $\pi(\text{C}\equiv\text{C})_n$  orbitals resulting from the delocalization of electron density

across the  $C\equiv C$  unit would, on the other hand, lead to a net overall decrease in the  $d\pi(\text{Pt})$  orbital energy, rendering the  $d\pi(\text{Pt})$  orbital on the complex with the longest  $(C\equiv C)_n$  unit lowest-lying in energy, and hence giving rise to the highest MLCT absorption energy. An alternative rationale arises from the increased  $\pi$ -accepting ability of the alkynyl unit upon increasing the  $(C\equiv C)_n$  chain, i.e. the  $\pi^*(C\equiv C)_n$  orbital energy follows the order:  $n = 4 < 2 < 1$ , which would stabilize the  $d\pi(\text{Pt})$  orbital via  $d\pi-\pi^*$  overlap. Similar findings have been observed in the related rhenium(I)-alkynyl system [42].

Upon excitation at  $\lambda > 400$  nm, the diplatinum alkynyl-bridged complexes exhibited intense luminescence at ca. 550–625 nm. The luminescence is derived from states of a predominantly  $^3\text{MLCT}$  [ $d\pi(\text{Pt}) \rightarrow \pi^*(\text{Bu}_3\text{tpy})$ ] character, probably mixed with some intraligand  $^3\text{IL}$  [ $\pi \rightarrow \pi^*(C\equiv C)_n$ ] and ligand-to-ligand charge transfer  $^3\text{LLCT}$  [ $\pi(C\equiv C)_n \rightarrow \pi^*(\text{Bu}_3\text{tpy})$ ] character. Rich vibronic structures were observed in the emission spectrum of  $[\text{Pt}(\text{Bu}_3\text{tpy})(C\equiv C)_4\text{Pt}(\text{Bu}_3\text{tpy})](\text{PF}_6)_2$ , with vibrational progressional spacings typical of  $\nu(C\equiv C)$  stretch in the ground state, indicating involvement of the alkynyl bridge and the possible mixing of a  $^3\text{LLCT}$  [ $\pi(C\equiv C)_n \rightarrow \pi^*(\text{Bu}_3\text{tpy})$ ] state and an  $^3\text{IL}$  [ $\pi \rightarrow \pi^*(C\equiv C)_n$ ] state into the  $^3\text{MLCT}$  [ $d\pi(\text{Pt}) \rightarrow \pi^*(\text{Bu}_3\text{tpy})$ ] state. It is likely that the emission origin has in addition to a  $^3\text{MLCT}$  origin, mixing of a  $^3\text{LLCT}$  and  $^3\text{IL}$  character, with the mixing being more important with the increasing  $\pi$ -conjugation in the  $C_8$  chain (Fig. 4). The observation of a Huang–Rhys factor of less than 1 in the 77 K glass emission spectra of the  $C_2$  and  $C_4$  bridged species is in line with an assignment of predominantly  $^3\text{MLCT}$  character. It is likely that upon increasing the  $\pi$ -conjugation of the  $C_n$  chain, the emission origin changes in character, with an increasing contribution from the  $^3\text{IL}$  [ $\pi \rightarrow \pi^*(C\equiv C)_n$ ] excited state,

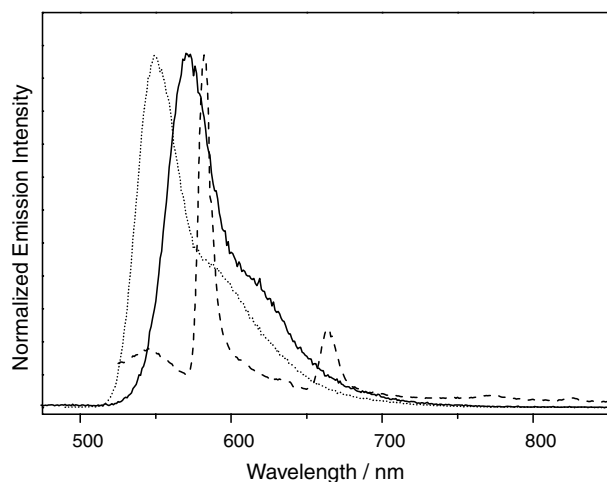
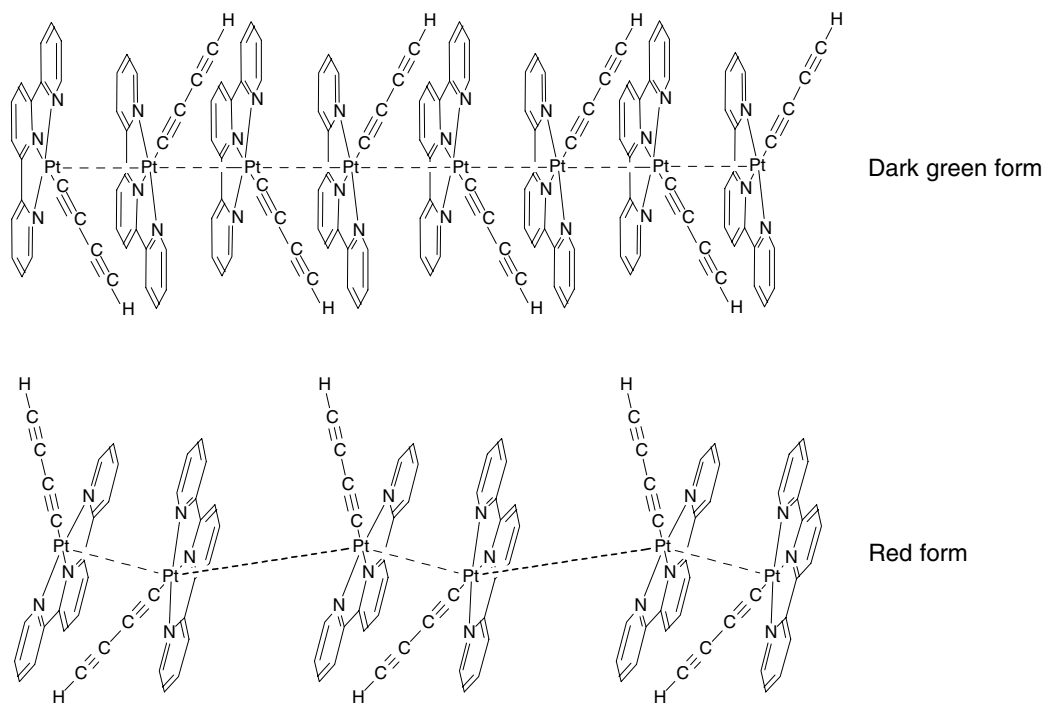


Fig. 4. Normalized emission spectra of  $[\text{Pt}(\text{Bu}_3\text{tpy})(C\equiv C)_n\text{Pt}(\text{Bu}_3\text{tpy})](X)_2$  [ $n = 1$  (—),  $X = \text{OTf}$ ;  $n = 2$  (···),  $X = \text{OTf}$ ;  $n = 4$  (---),  $X = \text{PF}_6$ ] in butyronitrile glass at 77 K.

leading to an emission that is predominantly  $^3\text{IL}$  in character.

Square planar platinum(II) polypyridine complexes are well known to exhibit rich polymorphism in the solid-state, with their solid-state colours dependent on the extent of metal–metal interactions and  $\pi-\pi$  stacking of the polypyridyl ligands. During the course of these studies, interesting and rich polymorphic behaviour was also observed in some of the platinum(II) terpyridine alkynyl complexes. The platinum(II)-butadiynyl complex of terpyridine,  $[\text{Pt}(\text{tpy})(C\equiv C\equiv C\text{H})]\text{OTf}$  was found to exist in two forms, a dark green form and a red form (Scheme 9); both of which have been structurally characterized and shown to exhibit different crystal packing arrangements [52]. The dark green form exists as a linear-chain with the platinum atoms equally spaced, with short intermolecular  $\text{Pt}\cdots\text{Pt}$  contacts of 3.388 Å. When viewed along the metal–metal axis, the platinum atoms are almost superimposable to give a nearly perfect linear  $[\text{Pt}]_n$  chain. The individual molecules are rotated with respect to their neighbors, with a partial stacking of the aromatic terpyridyl units. The red form, on the other hand, shows dimeric structure with alternating  $\text{Pt}\cdots\text{Pt}$  distances of 3.394 and 3.648 Å. The “short” and “long”  $\text{Pt}\cdots\text{Pt}$  bonds exhibit a zigzag arrangement. On the other hand, a related  $[\text{Pt}(\text{Bu}_3\text{tpy})(C\equiv C\equiv C\text{H})]\text{OTf}$  exists as discrete monomeric units with no evidence of short  $\text{Pt}\cdots\text{Pt}$  contacts, as is required by the steric demand of the bulky 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine ligand.

Dissolution of either of the two forms of  $[\text{Pt}(\text{tpy})(C\equiv C\equiv C\text{H})]\text{OTf}$  in acetonitrile or acetone gave a yellow solution with the same UV–vis absorption spectrum, which is dominated by high-energy intraligand absorptions and a low-energy MLCT absorption at 416 nm in the visible region, typical of monomeric platinum(II) terpyridyl complexes. Upon increasing the diethyl ether content in solution, the colour of the solution changed dramatically from yellow to green to blue, with a new absorption band formed at 615 nm concomitant with a drop in absorbance at 416 nm (Fig. 5), and a tremendous emission enhancement at 785 nm in the near-infrared region was observed (Fig. 6). In contrast, the related  $[\text{Pt}(\text{Bu}_3\text{tpy})(C\equiv C\equiv C\text{H})]\text{OTf}$  complex with a bulky tri-*tert*-butyl-2,2':6',2''-terpyridine ligand shows no observable colour changes in various solvent mixtures. The drastic colour changes displayed by the solutions of  $[\text{Pt}(\text{tpy})(C\equiv C\equiv C\text{H})]\text{OTf}$  are believed to arise from the formation of aggregates in solution as a result of the reduced solvation upon increasing the diethyl ether composition. The intense emission at 785 nm that only becomes switched on and enhanced with increasing diethyl ether content has also been ascribed to an origin that arises as a result of aggregate formation, probably facilitated by the propensity to form metal–metal interactions and  $\pi-\pi$  stacking.



Scheme 9.

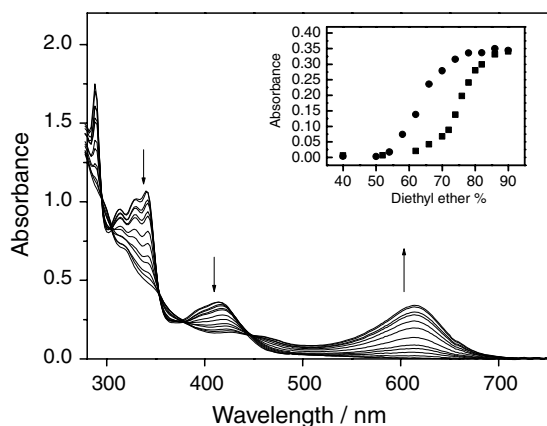


Fig. 5. UV-vis absorption changes of  $[\text{Pt}(\text{tpy})(\text{C}\equiv\text{CC}\equiv\text{CH})]\text{OTf}$  in acetonitrile with increasing diethyl ether composition. Inset: Plot of absorbance vs. diethyl ether composition in acetonitrile at 615 nm (■) and in acetone at 610 nm (●).

Thus the 615-nm band in the electronic absorption spectrum was assigned as a metal-metal-to-ligand charge-transfer (MMLCT) transition, and the 785-nm phosphorescence as derived from states of a  $^3\text{MMLCT}$  character. The remarkable change of colour as well as emission characteristics induced by changes in the solvent composition may be regarded as a special type of solvatochromism. It is anticipated that such drastic solvent-induced sensitive changes in colour and on-off switching of emission via aggregation of metal-metal bonded and  $\pi$ -stacked species would serve as versatile reporters and probes of environmental changes and may

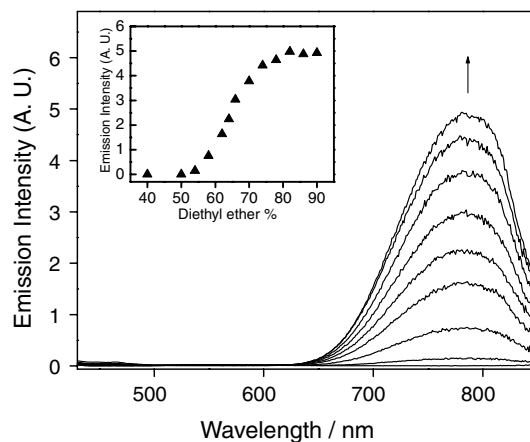


Fig. 6. Emission changes of  $[\text{Pt}(\text{tpy})(\text{C}\equiv\text{CC}\equiv\text{CH})]\text{OTf}$  in acetone upon increasing diethyl ether content. Inset: Plot of corrected emission intensity as a function of diethyl ether composition (▲).

find potential applications in materials science and sensor technology.

#### Acknowledgements

Financial support from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project no. HKU 7123/00P) and The University of Hong Kong Foundation for Educational Development and Research Limited are gratefully acknowledged.



The author is also indebted to her students whose names appear in the references.

## References

- [1] R. Faust, *Angew. Chem., Int. Ed.* 37 (1998) 2825.
- [2] U.H.F. Bunz, Y. Rubin, Y. Tobe, *Chem. Soc. Rev.* 28 (1999) 107.
- [3] A. de Meijre (Ed.), *Carbon Rich Compounds II: Macrocyclic Oligoacetylenes and Other Linearly Conjugated Systems*, Topics in Current Chemistry 201, Springer-Verlag, Berlin, 1999.
- [4] R. Eastmond, T.R. Johnson, D.R.M. Walton, *Tetrahedron* 28 (1972) 4601.
- [5] T.R. Johnson, D.R.M. Walton, *Tetrahedron* 28 (1972) 5221.
- [6] G. Schermann, T. Grösser, F. Hampel, A. Hirsch, *Chem. Eur. J.* 3 (1997) 1105.
- [7] T. Gbntner, F. Hampel, J. Gisselbrecht, A. Hirsch, *Chem. Eur. J.* 8 (2002) 408.
- [8] T. Skotheim, in: T. Skotheim (Ed.), *Handbook of Conducting Polymers*, vols. 1 and 2, Marcel Dekker, New York, 1986.
- [9] D.W. Bruce, D. O'Hare (Eds.), *Inorganic Materials*, Wiley, London, 1992.
- [10] U.H.F. Bunz, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 969.
- [11] H. Lang, *Angew. Chem., Int. Ed. Engl.* 33 (1994) 547.
- [12] J. Manna, K.D. John, M.D. Hopkins, *Adv. Organomet. Chem.* 38 (1998) 79.
- [13] M.I. Bruce, *Coord. Chem. Rev.* 166 (1997) 91.
- [14] N.J. Long, C.K. Williams, *Angew. Chem., Int. Ed.* 42 (2003) 2586.
- [15] J. Stahl, J.C. Bohling, E.B. Bauer, T.B. Peters, W. Mohr, J.M. Martin-Alvarez, F. Hampel, J.A. Gladysz, *Angew. Chem., Int. Ed.* 41 (2002) 1872.
- [16] R. Dembinski, T. Bartik, B. Bartik, M. Jaeger, J.A. Gladysz, *J. Am. Chem. Soc.* 1222 (2000) 810.
- [17] V.W.W. Yam, *Acc. Chem. Res.* 35 (2002) 555.
- [18] V.W.W. Yam, *Chem. Commun.* (2001) 789.
- [19] S. Rigaut, J. Perruchon, L. Le Pichon, D. Touchard, P.H. Dixneuf, *J. Organomet. Chem.* 670 (2003) 37.
- [20] A. La Groia, A. Ricci, M. Bassetti, D. Masi, C. Bianchini, C. Lo Sterzo, *J. Organomet. Chem.* 683 (2003) 406.
- [21] K. Sonogashira, K. Ohga, S. Takahashi, N. Hagihara, *J. Organomet. Chem.* 188 (1980) 237.
- [22] N. Chawdhury, A. Köhler, R.H. Friend, M. Younus, N.J. Long, P.R. Raithby, J. Lewis, *Macromolecules* 31 (1998) 722.
- [23] H.B. Fyfe, M. Mlekuz, G. Stringer, N.J. Taylor, T.B. Marder, *Inorganic and Organometallic Polymers with Special Properties*, in: R.M. Laine (Ed.), NATO ASI Series, 206, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992, p. 331.
- [24] S.K. Hurst, M.O. Cifuentes, A.M. McDonagh, M.G. Humphrey, M. Samoc, B. Luther-Davies, I. Asselberghs, A. Persoons, *J. Organomet. Chem.* 642 (2002) 259.
- [25] S.K. Hurst, M.G. Humphrey, J.P. Morrall, M.P. Cifuentes, M. Samoc, B. Luther-Davies, G.A. Heath, A.C. Willis, *J. Organomet. Chem.* 670 (2003) 56.
- [26] P.N. Prasad, D.J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley-Interscience, New York, 1991.
- [27] M.H. Chisholm, *Angew. Chem., Int. Ed. Engl.* 30 (1991) 673.
- [28] T.L. Schull, J.G. Kuchmerick, C.H. Patterson, C. George, M.H. Moore, S.K. Pollack, R. Shashidhar, *J. Am. Chem. Soc.* 125 (2003) 3202.
- [29] M. Mayor, C. von Hänisch, H.B. Weber, J. Reichert, D. Beckmann, *Angew. Chem., Int. Ed.* 41 (2002) 1183.
- [30] A. Abe, N. Kimura, S. Tabata, *Macromolecules* 24 (1991) 6238.
- [31] T. Kaharu, H. Matsubara, S. Takahashi, *J. Mater. Chem.* 1 (1991) 145.
- [32] V.W.W. Yam, *Acc. Chem. Res.* 35 (2002) 555.
- [33] V.W.W. Yam, *Chem. Commun.* (2001) 789.
- [34] V.W.W. Yam, W.K. Lee, K.K. Cheung, B. Crystall, D. Phillips, *J. Chem. Soc., Dalton Trans.* (1996) 3283.
- [35] V.W.W. Yam, W.K.M. Fung, M.T. Wong, *Organometallics* 16 (1997) 1772.
- [36] V.W.W. Yam, W.K.M. Fung, K.K. Cheung, *Chem. Commun.* (1997) 963.
- [37] V.W.W. Yam, W.K.M. Fung, K.K. Cheung, *Organometallics* 17 (1998) 3293.
- [38] V.W.W. Yam, W.K.M. Fung, K.K. Cheung, *J. Cluster Sci.* 10 (1999) 37.
- [39] V.W.W. Yam, V.C.Y. Lau, K.K. Cheung, *Organometallics* 14 (1995) 2749.
- [40] V.W.W. Yam, V.C.Y. Lau, K.K. Cheung, *Organometallics* 15 (1996) 1740.
- [41] V.W.W. Yam, S.H.F. Chong, K.K. Cheung, *Chem. Commun.* (1998) 121.
- [42] V.W.W. Yam, S.H.F. Chong, C.C. Ko, K.K. Cheung, *Organometallics* 19 (2000) 5092.
- [43] V.W.W. Yam, K.M.C. Wong, S.H.F. Chong, V.C.Y. Lau, S.C.F. Lam, L. Zhang, K.K. Cheung, *J. Organomet. Chem.* 670 (2003) 205.
- [44] S.H.F. Chong, Ph. D. Thesis, The University of Hong Kong, 2001.
- [45] V.W.W. Yam, W.K.M. Fung, K.M.C. Wong, V.C.Y. Lau, K.K. Cheung, *Chem. Commun.* (1998) 777.
- [46] V.W.W. Yam, W.Y. Lo, C.H. Lam, W.K.M. Fung, K.M.C. Wong, V.C.Y. Lau, N. Zhu, *Coord. Chem. Rev.*, 245 (2003) 39.
- [47] V.W.W. Yam, W.Y. Lo, N. Zhu, *Chem. Commun.* (2003) 2446.
- [48] K.M.C. Wong, S.C.F. Lam, C.C. Ko, N. Zhu, V.W.W. Yam, S. Roué, C. Lapinte, S. Fathallah, K. Costuas, S. Kahlal, J.F. Halet, *Inorg. Chem.* 42 (2003) 7086.
- [49] V.W.W. Yam, K.L. Cheung, E.C.C. Cheng, N. Zhu, K.K. Cheung, *J. Chem. Soc., Dalton Trans.* (2003) 1830.
- [50] V.W.W. Yam, R.P.L. Tang, K.M.C. Wong, K.K. Cheung, *Organometallics* 20 (2001) 4476.
- [51] V.W.W. Yam, K.M.C. Wong, N. Zhu, *Angew. Chem., Int. Ed.* 42 (2003) 1400.
- [52] V.W.W. Yam, K.M.C. Wong, N. Zhu, *J. Am. Chem. Soc.* 124 (2002) 6506.