

Molecular Design of Transition Metal Alkynyl Complexes as Building Blocks for Luminescent Metal-Based Materials: Structural and Photophysical Aspects

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ABSTRACT

In this Account, the design and successful isolation of a series of soluble di- and polynuclear alkynyl complexes of selected metals with d^8 and d^{10} electronic configurations are described. These organometallic complexes are found to exhibit rich photophysical and photochemical properties that are unique to the presence of the alkynyl ligand. By a systematic variation of the nature of the ligands, the metal centers, and certain structural features, the photophysical properties could be readily varied and their spectroscopic origins elucidated. Some of these complexes have been shown to be ideal building blocks for the design of luminescent organometallic oligomers and metal-based functional materials.

Introduction

Since the past decade, there has been a blooming growth in the development of the chemistry of carbon-rich metal-containing systems, in particular those with long sp carbon chains.^{1–3} Such a rapid growth is partly assisted by the urgent demand for new materials in molecular electronics as a result of the inherent limit of the present semiconductor technology. The alkynyl group, with its linear geometry, structural rigidity, extended π -electron delocalization, and ability to interact with metal centers via $p\pi$ – $d\pi$ overlap, has been an attractive candidate to serve as building blocks for the construction of carbon-rich metal-containing materials that may possess potential applications as nonlinear optical materials, molecular wires, and molecular electronics. Despite the growing

interests and extensive studies in metal alkynyls in the past decade or so, relatively less attention was focused on the exploration and exploitation of this class of compounds as luminescent materials.

Early works on metal alkynyls involve those of polymeric nature, which precluded further purification and characterization. Hagihara and co-workers reported the first soluble platinum and palladium polyynyl complexes.^{4,5} Subsequent reports on metal-containing polyynes provided important contributions in this area.⁶ Despite all these important works, studies on these polymeric systems present difficulties such as the exact arrangement of the structure, molecular weight distribution, heterogeneity of samples, reproducibility, and many others, which would render a direct understanding of the structure–property relationship and the fundamental understanding on the spectroscopic origin of these chromophores less straightforward and less amenable to study.

In addition, the wide diversity of possible bonding motifs of the alkynyl moiety has aroused our interest in investigating their potential in the design and synthesis of di- and polynuclear metal complexes, particularly those of d^8 and d^{10} metal centers exhibiting d^8 – d^8 and d^{10} – d^{10} weak metal···metal interactions. The short metal···metal contacts found in these metal complexes as a consequence of relativistic and correlation effects are believed to play a determinant role in the excited-state properties.^{7–9}

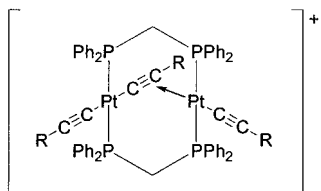
In this regard, we have directed our research efforts specifically to the design and synthesis of soluble molecular metal alkynyls with luminescence properties, which we believe, by a systematic variation of the electronic properties of the ligands and the nature of the metal centers, a fundamental understanding of the spectroscopic origin and the structure–property relationship could be realized. Through a judicious choice of metal and ligand systems, these soluble metal alkynyls might even be employed as versatile building blocks for the design and construction of luminescent organometallic oligomers and molecular metal-based functional materials. The purpose of this Account is to present our recent efforts in the design, synthesis, and photophysical studies of luminescent polynuclear d^8 and d^{10} metal alkynyls, which may give readers a more thorough and fundamental understanding on the structure–property relationship and the spectroscopic origin of these carbon-rich metal-containing materials. The several classes of compounds that we have chosen for illustration in this Account may at first glance appear to be somewhat disconnected and unrelated since they may have very different spectroscopic origins. However, they are in fact interrelated and may serve as good models in providing a thorough understanding on the subtle roles and the interplay of factors, i.e., the nature of the metal centers, the nature of the alkynyl ligands, the nuclearity, and metal–metal interactions, that would govern the spectroscopic origin of the lowest-lying emissive states of these classes of complexes.

Vivian W.-W. Yam was born in Hong Kong in 1963. She obtained her B.Sc.(Hons) degree in 1985 from The University of Hong Kong and her Ph.D. degree in 1988 from the same university under the supervision of Professor Chi-Ming Che on high-valent metal–oxo chemistry. She was a lecturer in the Department of Applied Science at the City Polytechnic of Hong Kong (now City University of Hong Kong) for two years before moving back to The University of Hong Kong in 1990. She is currently the Chair of Chemistry and Head of the Department of Chemistry at The University of Hong Kong. She was awarded the Croucher Senior Research Fellowship (2000–01) and was elected as a Member of the Chinese Academy of Sciences in 2001. Her research interests include the photophysics and photochemistry of polynuclear metal complexes and clusters with special emphasis on metal alkynyls, chalcogenides, and chalcogenolates, supramolecular chemistry, and molecular metal-based functional materials for spectrochemical and luminescent sensing, molecular recognition, optoelectronics, and molecular devices.

Platinum(II) Alkynyls

Dinuclear A-Frame Complexes. We have developed a general synthetic route for the preparation of A-frame dinuclear platinum(II) arylalkynyl complexes, $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CR})(\text{C}\equiv\text{CR})_2]^+$.^{10,11} A related $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{C}'\text{Bu})(\text{C}\equiv\text{C}'\text{Bu})_2]^+$ has been previously prepared using an alternative method,¹⁰ which could not be generally applied to other alkynyls, however.

These complexes exhibit long-lived intense luminescence both in the solid state and in solution.^{10,11} The electronic absorption spectra in solution displayed a low-energy band at 400–450 nm, which was red-shifted with respect to the related mononuclear complexes, *trans*- $[\text{Pt}(\text{C}\equiv\text{CR})_2(\text{dppm-}P)_2]$.



To understand the electronic absorption and emission behavior of these dinuclear platinum(II) complexes, the spectroscopic properties of the mononuclear analogues *trans*- $[\text{Pt}(\text{C}\equiv\text{CR})_2(P^*P-P)_2]$ have been investigated. In collaboration with D. L. Phillips, we were able to establish and confirm the spectral assignment of the low-energy absorption band in *trans*- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{dppm-}P)_2]$ as a metal-to-ligand charge-transfer (MLCT[d(Pt) \rightarrow $\pi^*(\text{C}\equiv\text{CR})$]) transition from resonance Raman (RR) spectroscopic studies.¹¹ Similar assignments have been made on *trans*- $[\text{Pt}(\text{C}\equiv\text{C}'\text{Bu})_2(\text{dppm-}P)_2]$ and *trans*- $[\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PET}_3)_2]$.^{12,13} The occurrence of the absorption band at higher energy in *trans*- $[\text{Pt}(\text{C}\equiv\text{C}'\text{Bu})_2(\text{dppm-}P)_2]$ over *trans*- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{dppm-}P)_2]$ correlates well with the $\pi^*(\text{C}\equiv\text{CR})$ orbital energy and lends further support to a MLCT assignment. In addition, the observation of vibronically structured luminescence in the low-temperature glass of *trans*- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{dppm-}P)_2]$ and extended-Hückel molecular orbital calculations on the model complex *trans*- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{dmpm-}P)_2]$ also supported an emissive state of large ${}^3\text{MLCT}[\text{Pt} \rightarrow \text{C}\equiv\text{CR}]$ character.¹⁷

The extent of possible perturbation of the alkynyl groups on the ${}^1\text{MLCT}$ transition of *trans*- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{dppm-}P)_2]$ and the interplay of various kinds of excited states in governing the nature of the lowest-lying excited state can be further probed by comparing the RR results with that of a related *trans*- $[\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PET}_3)_2]$.¹⁴ It was demonstrated that the initial excited-state vibrational reorganizational energy and displacement is mostly along the nominal C=C stretch, consistent with an assignment of the absorption band to a MLCT[Pt \rightarrow C=C] transition. Besides, the room-temperature ${}^3\text{MLCT}$ emission of *trans*- $[\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PET}_3)_2]$ in solution displays a vibronically resolved progression with $\sim 2000\text{ cm}^{-1}$ spacing, suggesting that the ${}^3\text{MLCT}$ state exhibits a noticeable structural change along the nominal C=C stretch mode. An increased C=C bond lengthening in the initial ${}^1\text{MLCT}$

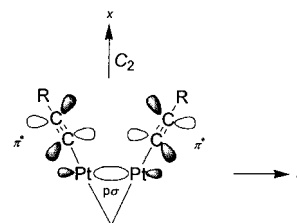


FIGURE 1. Schematic diagram showing $p\sigma(\text{Pt})-\pi^*(\text{C}\equiv\text{CR})$ overlap in $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CR})(\text{C}\equiv\text{CR})_2]^+$.

excited states of *trans*- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{dppm-}P)_2]$ compared to *trans*- $[\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PET}_3)_2]$ relative to their ground states suggests that the presence of phenyl groups could significantly perturb the C=C reaction coordinate and the MLCT[Pt \rightarrow C=C] transition by drawing the charge and associated structural changes further out into the ligands. Such C=C bond length changes are consistent with an expected nominal bond order change from 3 to 2.5 for a Pt \rightarrow $\pi^*(\text{C}\equiv\text{CR})$ charge transfer. These together with the observed Huang–Rhys factor $S < 1$ further support an assignment of a MLCT rather than intraligand ($\text{IL}[\pi-\pi^*(\text{C}\equiv\text{CR})]$) transition. A larger amount of Pt–P character in the MLCT state of *trans*- $[\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PET}_3)_2]$ has been observed, as reflected by the proportionately greater distribution of reorganization in the low-frequency modes associated with the Pt–P and Pt–C groups, relative to *trans*- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{dppm-}P)_2]$. This is consistent with the higher and closer energy of the $\pi^*(\text{C}\equiv\text{CH})$ to the 3d(phosphorus) orbital than $\pi^*(\text{C}\equiv\text{CPh})$, which would give rise to a mixing of MLCT[Pt \rightarrow P] character into the MLCT[Pt \rightarrow C=C] state. The energy separation between the $\pi^*(\text{C}\equiv\text{CR})$ acceptor orbital and the 3d(phosphorus) orbital appears to play an important role in governing the excited-state character of these complexes. In general, the better is the π -acceptor ability of C=C and the larger is the energy separation between the $\pi^*(\text{C}\equiv\text{CR})$ acceptor orbital and the 3d(phosphorus) orbital, the larger and the more predominant will be the MLCT[Pt \rightarrow C=C] character in the lowest-lying excited state.

With reference to previous spectroscopic work on dinuclear d^8-d^8 systems^{7,18} and the understanding of the spectroscopic origin of the mononuclear *trans*- $[\text{Pt}(\text{C}\equiv\text{CR})_2(\text{dppm-}P)_2]$, the low-energy absorption band in the dinuclear A-frame $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CR})(\text{C}\equiv\text{CR})_2]^+$ has been assigned as a metal–metal bond-to-ligand charge-transfer (MMLCT[$d\sigma^* \rightarrow p\sigma/\pi^*$]) transition, which is red-shifted with respect to the MLCT[d(Pt) \rightarrow $\pi^*(\text{C}\equiv\text{CR})$] transition in the mononuclear *trans*- $[\text{Pt}(\text{C}\equiv\text{CR})_2(\text{dppm-}P)_2]$ ($d\sigma^*$ is the antibonding overlap of Pt($5d_z$)-Pt($5d_z$) and $p\sigma$ is the bonding overlap of Pt($6p_z$)-Pt($6p_z$), taking Pt–Pt axis as z axis). In view of the low-lying π^* orbital energies of the alkynyl ligands, it is believed that the LUMO of these dinuclear complexes would have substantial mixing of the $\pi^*(\text{C}\equiv\text{CR})$ character with the $p\sigma$ orbital, assuming a C_{2v} symmetry (Figure 1).¹¹

$[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CR})(\text{C}\equiv\text{CR})_2]^+$ exhibits long-lived intense luminescence both in the solid state and in solution at room temperature,^{10,11} with broad emission bands in the yellow-orange region. The 77 K solid-state

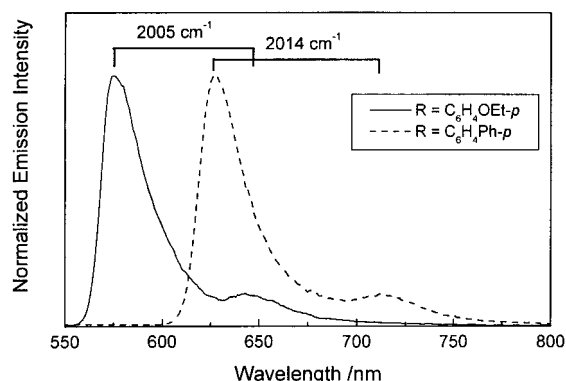


FIGURE 2. 77 K solid-state emission spectra of $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CR})(\text{C}\equiv\text{CR})_2]\text{PF}_6$.

emission spectra show vibronic-structured bands with progressional spacings that are typical of the $\nu(\text{C}\equiv\text{C})$ stretch in the ground state (Figure 2). This, together with the dependence of the emission energy on the alkynyl ligand, is suggestive of the involvement of the alkynyl ligand in the transition. The 298 K solid-state emission energy follows an order $\text{R} = \text{C}_6\text{H}_4\text{Ph-4} < \text{Ph} < \text{C}_6\text{H}_4\text{OMe-4} \leq \text{C}_6\text{H}_4\text{OEt-4} \approx \text{C}_6\text{H}_4\text{Et-4} < \text{tBu}$, in line with the increasing $\pi^*(\text{C}\equiv\text{CR})$ orbital energy. An assignment of the emission origin as a pure metal-centered $^3[(d\sigma^*)(p\sigma)]$ state arising from $\text{Pt}\cdots\text{Pt}$ interaction similar to those of other dinuclear $d^8\text{-}d^8$ systems has therefore not been favored. Further supports come from the observed higher emission energy of $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{C}'\text{Bu})(\text{C}\equiv\text{C}'\text{Bu})_2]^+$ compared to that of $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{C}'\text{Ph})(\text{C}\equiv\text{C}'\text{Ph})_2]^+$, in which the former has shorter $\text{Pt}\cdots\text{Pt}$ distance than the latter.^{10,12} A stronger $\text{Pt}\cdots\text{Pt}$ interaction would have been expected for $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{C}'\text{Bu})(\text{C}\equiv\text{C}'\text{Bu})_2]^+$ on the basis of bond length arguments alone, which should give rise to a lower-lying $^3[(d\sigma^*)(p\sigma)]$ state.

An assignment of a MMLCT origin for the emission in solution has further been supported by RR studies on $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{C}'\text{Ph})(\text{C}\equiv\text{C}'\text{Ph})_2]^+$.¹³ Unlike the RR spectrum of *trans*- $[\text{Pt}(\text{C}\equiv\text{C}'\text{Ph})_2(\text{dppm-}P)_2]$ which shows only one strong $\text{C}\equiv\text{C}$ stretch,¹³ that of $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{C}'\text{Ph})(\text{C}\equiv\text{C}'\text{Ph})_2]^+$ shows three strong $\text{C}\equiv\text{C}$ stretches corresponding to the three different alkynyl environments. An interesting trend in the relative intensities of the three $\text{C}\equiv\text{C}$ stretches has been observed, in that the intensity of the 2027-cm^{-1} peak, which corresponds to the μ -bridging $\text{C}\equiv\text{C}$ vibration, is the smallest upon excitation at the blue edge of the MMLCT band and increases in intensity relative to the 2062- and 2125-cm^{-1} peaks as the excitation line shifts toward the red edge of the MMLCT envelope. This is consistent with the presence of more than one configuration that contributes to the MMLCT absorption, corresponding to the photoinduced charge transfer to the three different but closely lying $\pi^*(\text{C}\equiv\text{C}'\text{Ph})$ orbitals, with the $\pi^*(\mu\text{-C}\equiv\text{C}'\text{Ph})$ orbital lowest lying in energy (Figure 3). Excitation to the red edge of the MMLCT band would selectively excite the MMLCT transition that is more localized on the $\pi^*(\mu\text{-C}\equiv\text{C}'\text{Ph})$ orbital and give rise to preferential resonance enhancement of the 2027-cm^{-1} peak. The close resemblance of the progressional spacings

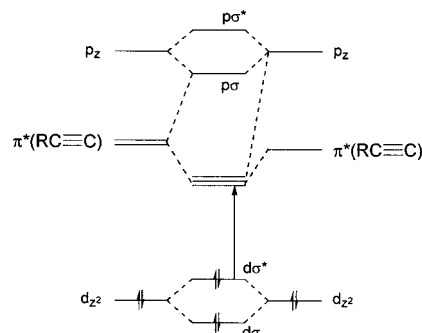
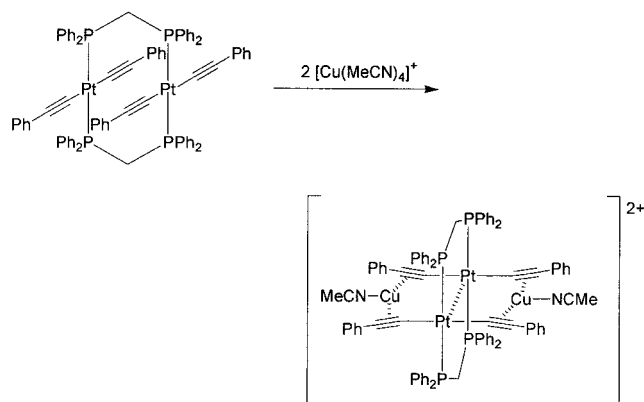


FIGURE 3. Simplified molecular orbital diagram for $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CR})(\text{C}\equiv\text{CR})_2]^+$.

Scheme 1



of $\sim 2000\text{-cm}^{-1}$ observed in the 77 K emission spectra to the 2027-cm^{-1} stretch is consistent with the lowest lying emissive state having predominantly MMLCT [$d\sigma^* \rightarrow \pi^*(\mu\text{-C}\equiv\text{C}'\text{Ph})$] character, as is required by Kasha's rule, although some thermal equilibrations among the various closely lying MMLCT states are possible.

Dinuclear Face-to-Face Complexes. A related class of face-to-face dinuclear platinum(II) alkynyl complexes, $[\text{Pt}_2(\mu\text{-dppm})_2(\text{C}\equiv\text{CR})_4]$, was studied. With this class of complexes, both the $\text{Pt}\cdots\text{Pt}$ distances and the π -acceptor nature of the alkynyl group are expected to play an important role in governing their spectroscopic characteristics. In this regard, we have adopted a novel approach to elucidate the spectroscopic origin of this class of complexes through the employment of $[\text{Pt}_2(\mu\text{-dppm})_2(\text{C}\equiv\text{C}'\text{Ph})_4]$, first synthesized by Pringle and Shaw,¹⁹ as an η^2 -ligand to encapsulate metal ions such as copper(I) in a tweezerlike/sandwich fashion to generate a mixed-metal tetranuclear complex, $[\text{Pt}_2(\mu\text{-dppm})_2(\text{C}\equiv\text{C}'\text{Ph})_4]\text{Cu}(\text{MeCN})_2(\text{PF}_6)_2$ (Scheme 1).²⁰ By doing so, a shortening of the $\text{Pt}\cdots\text{Pt}$ distance together with a change in the π -accepting ability of the alkynyl group could be observed. Systematic comparison studies through the perturbation of the $\text{Pt}\cdots\text{Pt}$ distances as well as the π -accepting ability of the alkynyl group would then allow one to have a better understanding and further insights into the nature of the excited-state origin of this class of compounds.

Similar to the A-frame system, the face-to-face dinuclear $[\text{Pt}_2(\mu\text{-dppm})_2(\text{C}\equiv\text{C}'\text{Ph})_4]$ exhibit intense low-energy absorption bands that involve the $^1[(d\sigma^*)^2] \rightarrow ^1[(d\sigma^*)(p\sigma/\pi^*(\text{C}\equiv\text{C}'\text{Ph}))^1]$ MMLCT transition. The red shift

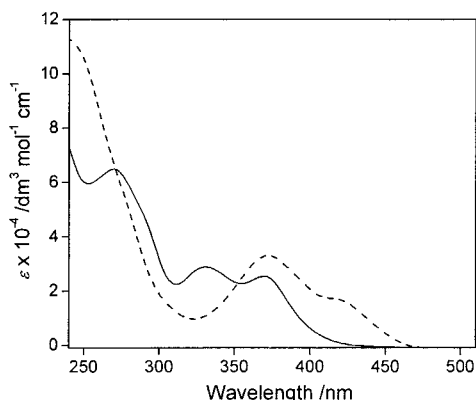


FIGURE 4. Electronic absorption spectra of $[\text{Pt}_2(\mu\text{-dppm})_2(\text{C}\equiv\text{CPh})_4]$ (—) and $[\text{Pt}_2(\mu\text{-dppm})_2(\text{C}\equiv\text{CPh})_4\{\text{Cu}(\text{MeCN})\}_2](\text{PF}_6)_2$ (- - -) in CH_2Cl_2 . Reprinted with permission from ref 20. Copyright 2001 American Chemical Society.

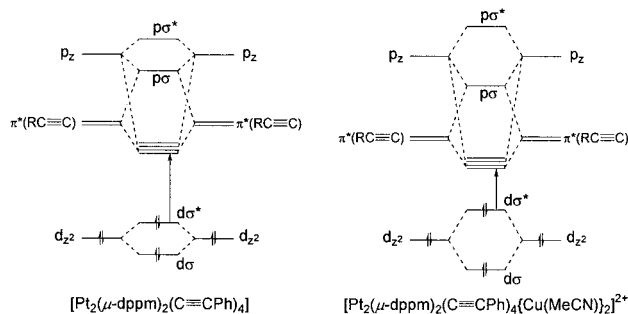


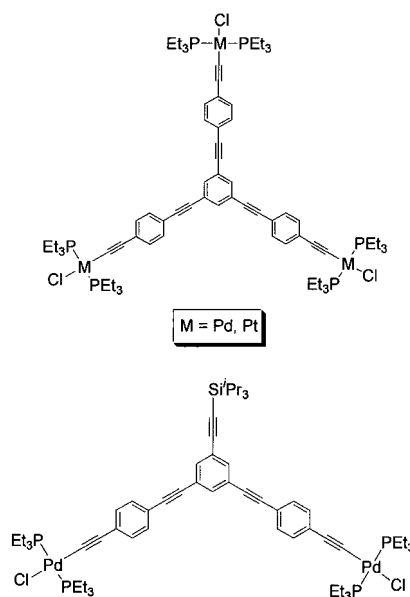
FIGURE 5. Diagram showing the narrowing of HOMO–LUMO energy gap of the face-to-face dinuclear platinum(II) complex upon copper(I) coordination.

of the absorption bands in $[\text{Pt}_2(\mu\text{-dppm})_2(\text{C}\equiv\text{CPh})_4\{\text{Cu}(\text{MeCN})\}_2](\text{PF}_6)_2$ relative to $[\text{Pt}_2(\mu\text{-dppm})_2(\text{C}\equiv\text{CPh})_4]$ (Figure 4) is consistent with such an assignment since a narrowing of the HOMO–LUMO energy gap would occur upon a shortening of the Pt...Pt distance as well as an increase in the π -accepting ability of the $\text{C}\equiv\text{CPh}$ groups upon π -coordination to copper(I) (Figure 5).

Upon photoexcitation of the solid or solution samples at $\lambda > 350$ nm, strong vibronic-structured yellow to orange emission bands with progressional spacings of the ground state $\nu(\text{C}\equiv\text{C})$ stretch are observed, which are suggestive of an involvement of the $\text{C}\equiv\text{CPh}$ moiety in the emissive state and are ascribed to ${}^3\text{MMLCT}$ phosphorescence. Again, the red shift of emission energy upon copper(I) coordination is consistent with the trend observed in the electronic absorption studies, in which the reduced Pt...Pt separation in $[\text{Pt}_2(\mu\text{-dppm})_2(\text{C}\equiv\text{CPh})_4\{\text{Cu}(\text{MeCN})\}_2](\text{PF}_6)_2$ would give rise to a larger $d\sigma-d\sigma^*$ splitting and hence an increase in the $d\sigma^*$ orbital energy, as well as a decrease of the $\pi^*(\text{C}\equiv\text{CPh})$ orbital energy upon coordination to copper(I). The smaller vibrational progressional spacings in $[\text{Pt}_2(\mu\text{-dppm})_2(\text{C}\equiv\text{CPh})_4\{\text{Cu}(\text{MeCN})\}_2](\text{PF}_6)_2$ compared to $[\text{Pt}_2(\mu\text{-dppm})_2(\text{C}\equiv\text{CPh})_4]$ are also consistent with the reduced bond strength of the $\text{C}\equiv\text{C}$ bond upon π -coordination to copper(I). Interestingly, the vibrational progressional spacings in the A-frame $[\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CPh})(\text{C}\equiv\text{CPh})_2]^+$ are similar to that in $[\text{Pt}_2(\mu\text{-dppm})_2(\text{C}\equiv\text{CPh})_4\{\text{Cu}(\text{MeCN})\}_2]^{2+}$ but at a lower frequency than

that of $[\text{Pt}_2(\mu\text{-dppm})_2(\text{C}\equiv\text{CPh})_4]$, probably as a result of the bridging nature of the $\mu\text{-C}\equiv\text{CPh}$ ligand. The ${}^3\text{MMLCT}$ emission energies have been found to follow the trend $[\text{Pt}_2(\mu\text{-dppm})_2(\text{C}\equiv\text{CPh})_4] > [\text{Pt}_2(\mu\text{-dppm})_2(\mu\text{-C}\equiv\text{CPh})(\text{C}\equiv\text{CPh})_2]^+ \approx [\text{Pt}_2(\mu\text{-dppm})_2(\text{C}\equiv\text{CPh})_4\{\text{Cu}(\text{MeCN})\}_2]^{2+}$, in line with the better π -accepting ability of the $\mu\text{-C}\equiv\text{CPh}$ ligand.

Polynuclear Complexes. Recent interest in platinum(II) alkynyl chemistry has been extended toward platinum-containing hyperbranched molecules and organometallic dendrimers.^{21,22} However, the luminescence behavior of such a class of complexes is relatively rare. In this regard, we have explored the luminescence properties of a new series of branched palladium(II) and platinum(II) complexes containing the rigid conjugated aryalkynyl ligand 1,3,5-($\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}$) $_3\text{C}_6\text{H}_3$.^{23,24} Employment of the tris-isopropylsilyl-protected derivative, 1,3-($\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}$) $_2$ -5-[(Pr) $_3\text{SiC}\equiv\text{C}$] C_6H_3 , for the construction of dinuclear palladium(II) dendrimeric precursors has also been achieved.²³



The electronic absorption spectra of these complexes are dominated by high-energy bands typical of the $\text{IL}[\pi-\pi^*(\text{C}\equiv\text{CR})]$ transitions. A red shift in the absorption energies from 1,3,5-($\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}$) $_3\text{C}_6\text{H}_3$ to 1,3,5-[$\text{Cl}(\text{PEt}_3)_2\text{PdC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}$] $_3\text{C}_6\text{H}_3$ to 1,3,5-[$\text{Cl}(\text{PEt}_3)_2\text{PtC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}$] $_3\text{C}_6\text{H}_3$ suggests that the transitions would involve a metal-to-alkynyl MLCT character, best described as an admixture of $\text{IL}[\pi\rightarrow\pi^*(\text{C}\equiv\text{CR})]$ and $\text{MLCT}[d_\pi(\text{M})\rightarrow\pi^*(\text{C}\equiv\text{CR})]$ transitions with predominantly IL character or, alternatively, a metal-perturbed IL transition.

The 77 K solid-state and EtOH–MeOH glass of these complexes show intense green to yellow luminescence upon photoexcitation (Figure 6). Similar to the electronic absorption, the red shift in the emission energy on going from $\text{M} = \text{Pd}$ to Pt is suggestive of an emission origin of mixed $\text{IL}[\pi\rightarrow\pi^*(\text{C}\equiv\text{CR})]/\text{MLCT}[d_\pi(\text{M})\rightarrow\pi^*(\text{C}\equiv\text{CR})]$ triplet state with predominantly IL character.

It appears that an increase in the conjugation of the alkynyl ligand would change the nature of the emission

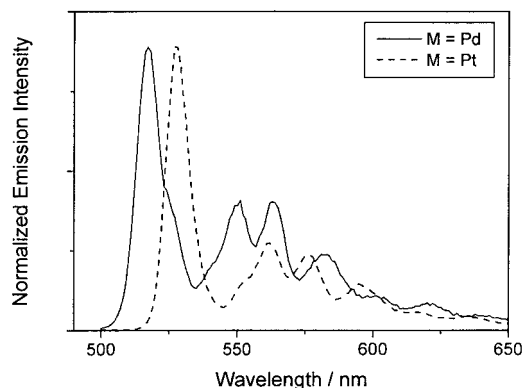
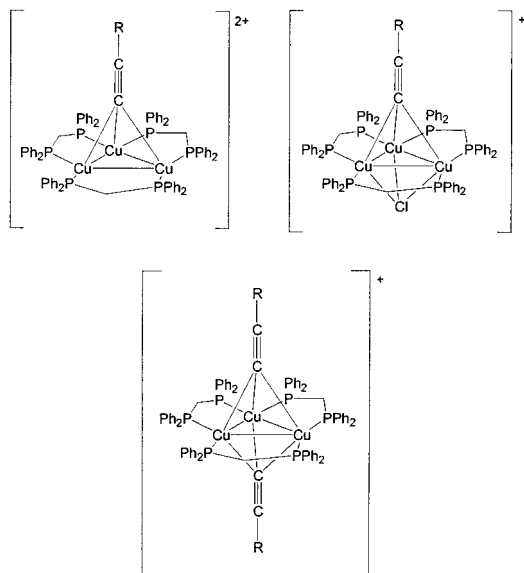


FIGURE 6. Emission spectra of $[\text{Cl}(\text{PEt}_3)_2\text{MC}\equiv\text{C}_6\text{H}_4\text{C}\equiv\text{C}]_3\text{C}_6\text{H}_5$ ($\text{M} = \text{Pd}, \text{Pt}$) in 77 K EtOH–MeOH(4:1 v/v) glass.

from a predominantly ${}^3\text{MLCT}[\text{d}_\pi(\text{M}) \rightarrow \pi^*(\text{C}\equiv\text{CR})]$ origin to one that has an increasing ligand-centered character, i.e., a mixed $\text{IL}[\pi \rightarrow \pi^*(\text{C}\equiv\text{CR})]/{}^3\text{MLCT}[\text{d}_\pi(\text{M}) \rightarrow \pi^*(\text{C}\equiv\text{CR})]$ state with predominantly IL character.

Copper(I) and Silver(I) Alkynyls

Trinuclear Complexes. Since the first report on the synthesis and crystal structures of $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CPh})]^{2+}$ and $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CPh})_2]^+$ by Gimeno and co-workers,²⁵ a number of related luminescent polynuclear copper(I) alkynyl complexes have been synthesized and studied by us.^{26–37} The first series is the trinuclear copper(I) alkynyl complexes, $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CR})_2]^+$ and $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CR})]^{2+}$.^{26–28,35} Related mixed-capped complexes have also been made.^{26,34}



The observed $\text{Cu}\cdots\text{Cu}$ distances usually follow the order $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CR})]^{2+} > [\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CR})(\mu_3\text{-Cl})]^+ > [\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CR})_2]^+$. Some of these distances are shorter than the sum of van der Waals radii for copper (2.8 Å), indicative of the presence of some weak metal \cdots metal interactions.

The electronic absorption spectra are dominated by high-energy bands, typical of $\text{IL}[\pi \rightarrow \pi^*(\text{diphosphine})]$ and $\text{IL}[\pi \rightarrow \pi^*(\text{C}\equiv\text{CR})]$ transitions, and low-energy shoulders

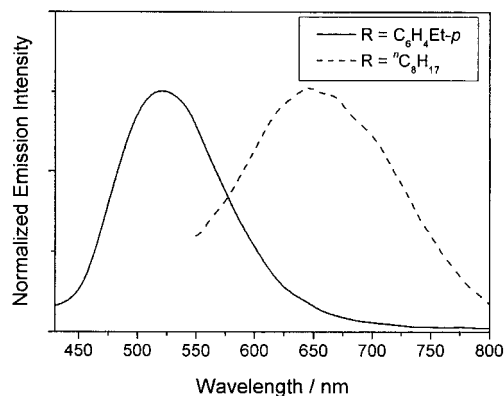


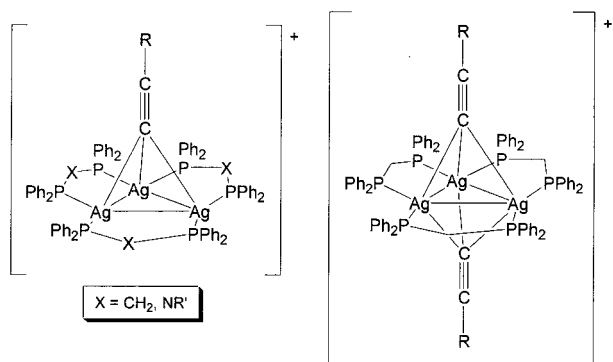
FIGURE 7. Emission spectra of $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CR})](\text{BF}_4)_2$ in degassed acetone solution at 298 K.

tailoring to ~ 400 nm. Rich luminescence behaviors both in the solid state and in solution are observed upon photoexcitation. Vibronic-structured bands with progressional spacings typical of ground-state $\nu(\text{C}\cdots\text{C})$ and $\nu(\text{C}\equiv\text{C})$ stretching frequencies are observed in some of the complexes, suggesting an involvement of alkynyl ligands in the excited states. The lifetimes in the microsecond range are indicative of a spin-forbidden triplet parentage. In general, complexes with electron-rich alkynyl ligands emit at lower energies. For instance, acetone solutions of $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CR})]^{2+}$ show emission maxima in the order $\text{R} = \text{Ph} > \text{C}_6\text{H}_4\text{NH}_2\text{-}4 > \text{C}_6\text{H}_4\text{Et-}4 > \text{tBu} \approx \text{nC}_8\text{H}_{17} \approx \text{nC}_6\text{H}_{13}$,^{28,35} in line with the increasing electron-richness of the alkynyl ligands (Figure 7). Several assignments for the emission origin are possible. One is an emission origin that involves substantial ligand-to-metal charge-transfer $\text{LMCT}[\text{C}\equiv\text{CR} \rightarrow \text{Cu}_3]$ character. The others may involve a ligand-to-ligand charge-transfer $\text{LLCT}[\text{C}\equiv\text{CR} \rightarrow \text{dppm}]$ or a $\text{MLCT}[\text{Cu}_3 \rightarrow \text{dppm}]$ origin. We are inclined toward an assignment of the emission origin as one that is derived from states of substantial $\text{LMCT}[\text{C}\equiv\text{CR} \rightarrow \text{Cu}_3]$ character on the basis of the following observations. The monocapped species have been found to emit at lower energies than the bicapped analogues with the same alkynyl ligands.^{26–28,35} The higher overall positive charge on the monocapped complexes as well as the less electron-rich nature of the copper(I) centers compared to that of the bicapped species would stabilize the essentially metal-centered LUMO, giving rise to a lower-lying $\text{LMCT}[\text{C}\equiv\text{CR} \rightarrow \text{Cu}_3]$ emissive state. On the contrary, a $\text{MLCT}[\text{Cu}_3 \rightarrow \text{C}\equiv\text{CR}]$ origin would predict an opposite trend while a $\text{LLCT}[\text{C}\equiv\text{CR} \rightarrow \text{dppm}]$ origin would show little energy dependence. However, it is reasonable to suggest that the lowest-lying emissive state is mixed with some metal-centered (MC) $3\text{d}^94\text{s}^1$ character, owing to the presence of short $\text{Cu}\cdots\text{Cu}$ distances in these trinuclear copper(I) complexes (especially for the bicapped system). Thus, the lowest-lying emissive state could well be described as an admixture of ${}^3\text{LMCT}$ and ${}^3\text{MC}$ states, modified by $\text{Cu}\cdots\text{Cu}$ interactions. The relative contributions of these two characters depend on both the nature of the alkynyl ligand and the extent of $\text{Cu}\cdots\text{Cu}$ interaction. The only exceptions were observed in complexes with very

electron-deficient alkynyl ligands such as $\text{C}\equiv\text{CC}_6\text{H}_4\text{NO}_2-4$,^{34,36} in which significant involvement of $\text{IL}[\pi-\pi^*(\text{C}\equiv\text{CR})]$ character in the emissive state is observed.

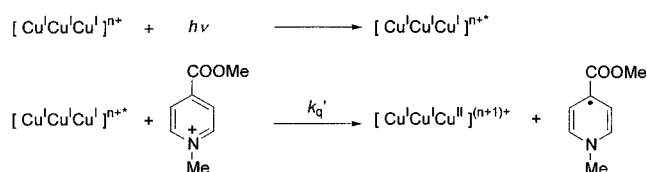
The effects of the bridging diphosphines on the luminescence properties have been probed. Analogous trinuclear complexes with bis(diphenylphosphino)amine ligands $[\text{Cu}_3\{\mu\text{-Ph}_2\text{PN}(\text{R})\text{PPh}_2\}_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CR})_2]^+$ have been synthesized and their luminescence properties examined.³² These complexes also display intense long-lived luminescence upon photoexcitation. The low-energy emission has been suggested to originate from a ${}^3\text{LMCT}[\text{C}\equiv\text{CR}\rightarrow\text{Cu}_3]$ excited state mixed with a ${}^3\text{MC}[\text{d}-\text{s}]$ state on the basis of similar emission energy trends ($-\text{C}\equiv\text{CPh} > -\text{C}\equiv\text{CC}_6\text{H}_4\text{-OEt-4} > -\text{C}\equiv\text{C}^n\text{C}_6\text{H}_{13}$ for the same $\text{Ph}_2\text{PN}(\text{R})\text{PPh}_2$ ligand), which is in line with the increasing electron-donating abilities of the alkynyl ligands. The emission energies for the $[\text{Cu}_3\{\mu\text{-Ph}_2\text{PN}(\text{R})\text{PPh}_2\}_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CC}_6\text{H}_4\text{OEt-4})_2]^+$ complexes with different $\text{Ph}_2\text{PN}(\text{R})\text{PPh}_2$ ligands follow the order $\text{R}' = {}^n\text{Pr} > \text{C}_6\text{H}_4\text{Me-4} > \text{Ph}$. Such a trend parallels the electron richness of the $\text{Ph}_2\text{PN}(\text{R})\text{PPh}_2$ ligands and is in agreement with the assignment of an excited state with substantial $\text{LMCT}[\text{C}\equiv\text{CR}\rightarrow\text{Cu}_3]$ character. A more electron-rich diphosphine ligand would render the predominantly metal-centered acceptor orbital less low-lying in energy and give rise to a higher energy emission. An assignment of an emissive state of ligand-to-ligand charge-transfer ($\text{LLCT}[\text{C}\equiv\text{CR}\rightarrow\text{Ph}_2\text{PN}(\text{R})\text{PPh}_2]$) parentage is, however, not favored in view of the small changes in the energies along the series, whereas an opposite trend would be observed for a $\text{MLCT}[\text{Cu}\rightarrow\text{C}\equiv\text{CR}]$ assignment.

Comparison studies on the luminescence behavior of analogous silver(I) alkynyl complexes should provide insights into the role played by the metal centers in the emission origin. In this regard, a series of related trinuclear silver(I) alkynyl complexes, $[\text{Ag}_3(\mu\text{-Ph}_2\text{PXPPH}_2)_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CR})_2]^{2+}$ (where $\text{X} = \text{CH}_2, \text{N}^n\text{Pr}$) and $[\text{Ag}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CR})_2]^+$, have been successfully synthesized and isolated.²⁵



The $\text{Ag}\cdots\text{Ag}$ distances in the range 2.8–3.4 Å are comparable to the sum of van der Waals' radii of silver (3.44 Å). In general, the silver(I) complexes show a higher energy emission than their copper(I) analogues. For example, the 77 K solid-state emission of $[\text{Ag}_3(\mu\text{-Ph}_2\text{PXPPH}_2)_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CR})_2]^{2+}$ occurs at 0.29–0.33 eV higher in energy than their copper(I) counterparts. The possibility of an emission origin of ${}^3\text{MLCT}[\text{Ag}_3\rightarrow\pi^*(\text{C}\equiv\text{CR})]$ character

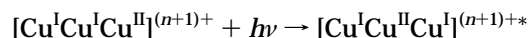
Scheme 2



is not favored due to the large difference (1.19 eV) between the ionization energies of $\text{Cu}^+(\text{g})$ and $\text{Ag}^+(\text{g})$. Instead, the emission has been attributed to originate from a ${}^3\text{LMCT}[\text{C}\equiv\text{CR}\rightarrow\text{Ag}_3]$ state, probably mixed with a ${}^3\text{MC}[\text{ds}/\text{dp}]$ state. However, the mixing of an $\text{IL}[\pi-\pi^*(\text{C}\equiv\text{CR})]$ state is also possible, in view of the highly structured emission spectra, the exceptionally long lifetime, the higher-lying silver-centered acceptor orbitals, and the low-lying π^* orbitals of the less electron-rich alkynyls.

The trinuclear complexes have been shown to exhibit rich photoredox properties, as exemplified by the quenching of the low-energy phosphorescence of copper(I) alkynyls by pyridinium ions through an oxidative electron-transfer mechanism.^{27,28,32,35} For example, the transient absorption difference spectrum of $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CPh})_2]^+$ and 4-(methoxycarbonyl)-*N*-methylpyridinium ion in degassed acetonitrile (0.1 M ${}^n\text{Bu}_4\text{NPF}_6$) shows an intense characteristic pyridinyl radical absorption.²⁷ The proposed mechanism is shown in Scheme 2.

An additional broad NIR absorption band has been observed²⁷ and assigned as an intervalence-transfer (IT) transition of the mixed-valence transient species, $[\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CPh})_2]^{2+}$, i.e., the one-electron oxidized species of $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CPh})_2]^{+*}$.



The IT absorption energies of the mixed-valence species follow the order $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C}^t\text{Bu})_2]^{2+} > [\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CPh})_2]^{2+} > [\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C}^t\text{Bu})(\mu_3\text{-Cl})]^{2+} > [\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C}^t\text{Bu})]^{3+}$,^{27,28,32,35} It is interesting to note that the energy of this NIR absorption band appears to decrease with an increase in the $\text{Cu}\cdots\text{Cu}$ distances observed in the ground-state trinuclear copper(I) complexes. Assuming that the $\text{Cu}\cdots\text{Cu}$ distances in the mixed-valence species would follow the same trend in the metal–metal separation as the ground-state complexes, the observed red shift in absorption energies on going from $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C}^t\text{Bu})_2]^{2+}$ to $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C}^t\text{Bu})(\mu_3\text{-Cl})]^{2+}$ to $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C}^t\text{Bu})]^{3+}$ is in line with a decrease in the $\sigma\rightarrow\sigma^*(\text{Cu}-\text{Cu})$ energy gap as the $\text{Cu}\cdots\text{Cu}$ separation increases. Alternative assignments of the low-energy NIR absorption as $\text{LMCT}[\text{C}\equiv\text{CR}\rightarrow\text{Cu}^{\text{II}}]$ or ligand-field transitions of $\text{Cu}(\text{II})$ were excluded on the basis of the reverse energy trend for $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C}^t\text{Bu})_2]^{2+}$ and $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CPh})_2]^{2+}$ that one would have expected for LMCT transitions and the large extinction coefficients observed.

Incorporation of functional units such as crown ethers to the trinuclear building block has been achieved. For

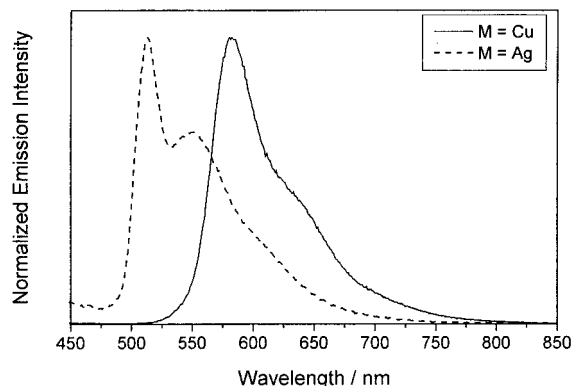
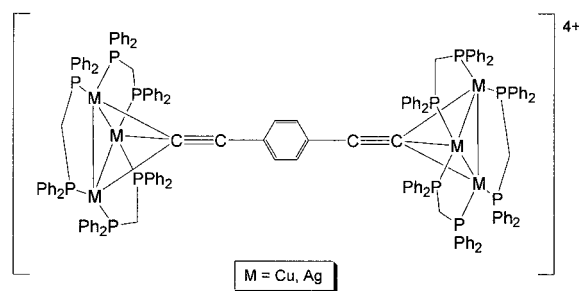


FIGURE 8. Solid-state emission spectra of $[M_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C-}p)M_3(\mu\text{-dppm})_3](\text{BF}_4)_4$ ($M = \text{Cu, Ag}$) at 298 K. Reprinted from ref 34 with permission from Elsevier Science.

example, $[\text{Cu}_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C-B15C5})_2]^+$ (B15C5 = benzo-15-crown-5) has been synthesized and structurally characterized.³⁶ The complex has been shown to serve as a luminescent chemosensor for sodium ion binding.

Hexanuclear Complexes. With our interests in soluble luminescent metal-containing π -conjugated oligomers, attempts have been made to synthesize rigid-rod oligomeric complexes based on the triangulo- M_3 building blocks. Hexanuclear copper(I) and silver(I) alkynyl complexes, $[M_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C-4})M_3(\mu\text{-dppm})_3]^{4+}$ ($M = \text{Cu, Ag}$), were isolated and their photophysical properties studied.³³

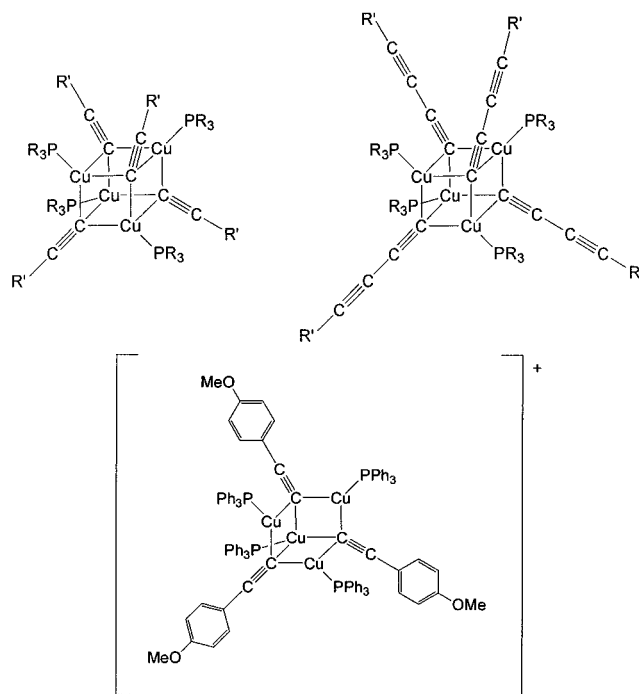


The complex contains two triangulo- $M_3(\text{dppm})_3$ cores bridged by a 1,4-diethynylbenzene unit to give a dumb-bell-shaped structure. The electronic absorption spectra show strong high-energy ligand-centered bands and low-energy vibronic-structured bands with progressional spacings typical of the excited-state $\nu(\text{C}\equiv\text{C})$ stretching frequencies. Long-lived intense orange-yellow and green emissions have been observed for the copper(I) and silver(I) complexes, respectively, upon photoexcitation (Figure 8). The observation of vibronic-structured bands with vibrational progressions typical of $\nu(\text{C}\equiv\text{C})$ stretches in both the excitation and emission spectra indicates the involvement of the highly conjugated arylalkynyl ligand in the excited state. A blue shift in the 77 K solid-state emission energy on going from $M = \text{Cu}$ to Ag is suggestive of the presence of ${}^3\text{LMCT}[\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}\rightarrow M_3]$ character in the excited states, probably mixed with some $\text{MC}[\text{d-s}]$ character. However, owing to the rich vibronic structures, the exceptionally long emission lifetimes, and the extended π -conjugation

of the bridging diynyl unit, an involvement of an $\text{IL}[\pi\text{-}\pi^*(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C})]$ excited state is highly probable. In view of a small difference (0.27 eV) in emission energies from $M = \text{Cu}$ to Ag , a $\text{MLCT}[M_3\rightarrow\pi^*(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C})]$ excited state is not favored although it would give a similar energy trend.

Tetranuclear Copper(I) Alkynyl Complexes. Apart from the luminescent molecular triangles and rods that have been constructed on the basis of the trinuclear alkynyl units, copper(I) alkynyls in the form of molecular cubes, open cubes, and rectangles have also been synthesized and shown to exhibit rich photophysical behavior. In this connection, the close-cuboidal complexes, $[\text{Cu}_4(\text{PR}_3)_4\{\mu_3\text{-}\eta^1\text{-}(\text{C}\equiv\text{C})_n\text{R}'\}_4]$ ($n = 1, 2$), the open-cube complex, $[\text{Cu}_4(\text{PPh}_3)_4(\mu_3\text{-}\eta^1, \eta^1, \eta^2\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-4})_3]^+$, and the rectangular complex, $[\text{Cu}_4(\mu\text{-dppm})_4(\mu_4\text{-}\eta^1, \eta^2\text{-C}\equiv\text{C})]^{2+}$, have been synthesized.

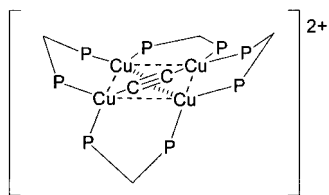
The close-cuboidal tetranuclear copper(I) alkynyl complexes, $[\text{Cu}_4(\text{PR}_3)_4\{\mu_3\text{-}\eta^1\text{-}(\text{C}\equiv\text{C})_n\text{R}'\}_4]$ ($n = 1, 2$), and the related open-cube complex, $[\text{Cu}_4(\text{PPh}_3)_4(\mu_3\text{-}\eta^1, \eta^1, \eta^2\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-4})_3]^+$, are found to exhibit long-lived intense luminescence upon photoexcitation.^{29,30,35,37} Some



of them display vibronic-structured emission bands with progressions typical of ground-state $\nu(\text{C}\equiv\text{C})$ and $\nu(\text{C}\equiv\text{C})$ stretching frequencies. In general, a small red shift in the energy of the low-energy emission in CH_2Cl_2 is observed upon increasing the σ -donating properties of the alkynyl ligands. For example, the emission energies of $[\text{Cu}_4(\text{PPh}_3)_4(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CR}')_4]$ are in the order $\text{R}' = \text{Ph} > \text{C}_6\text{H}_4\text{Et-4} \approx \text{C}_6\text{H}_4\text{OMe-4}$. Therefore, it is likely that the emissive state of these tetranuclear complexes contain some $\text{LMCT}[\text{C}\equiv\text{CR}\rightarrow\text{Cu}_4]$ character. However, on the basis of the short $\text{Cu}\cdots\text{Cu}$ distances observed, the relatively small dependence of the emission energies on the nature of the ligands, and the close resemblance of the emission energy of the cationic open-cube complex to the

related neutral close-cuboidal counterparts in CH_2Cl_2 , the low-energy emissive state should bear a parentage of large MC[d-s] character that is modified by $\text{Cu}\cdots\text{Cu}$ interactions.^{29,30,35,37,39} Similar assignments have been made on the diyanyl close-cuboidal complexes. It is interesting to note that a red shift in the solid-state emission energies is observed on going from the monoyanyl complexes to the diyanyl analogues, which is accompanied by a small increase in the $\text{Cu}\cdots\text{Cu}$ distances. An excited state of solely MC character would predict an opposite emission trend. Thus, it is believed that involvement of an additional $\text{IL}[\pi-\pi^*(\text{C}\equiv\text{CR})]$ character in the excited states of the diyanyl series is present. Similar findings have been found for the monoyanyl complexes that possess strong electron-withdrawing alkynyl ligands such as $\text{R}' = \text{C}_6\text{H}_4\text{Ph-4}$ and $\text{C}_6\text{H}_4\text{NO}_2\text{-4}$, in which the emission bands occur at very low energies and are comparable to those of the free acetylenes. In such cases, the emission has been assigned to arise from an emissive state of essentially $\text{IL}[\pi-\pi^*(\text{C}\equiv\text{CR})]$ origin.

The novel tetranuclear copper(I) alkynyl complex $[\text{Cu}_4(\mu\text{-dppm})_4(\mu_4\text{-}\eta^1, \eta^2\text{-C}\equiv\text{C})]^{2+}$ has its four copper(I) centers arranged in a distorted coplanar rectangular array and the four dppm ligands in a saddle-like arrangement.³¹



The acetylide ligand $(\text{C}\equiv\text{C})^{2-}$ sits in the middle of the distorted rectangle and bridges the four copper(I) centers in both η^1 - and η^2 -bonding modes. The electronic absorption spectrum reveals a high-energy $\text{IL}(\text{dppm})$ absorption band and a low-energy $\text{LMCT}[\text{C}\equiv\text{C}\rightarrow\text{Cu}_4]$ absorption shoulder. Photoexcitation results in long-lived intense greenish-yellow emission. In view of the strong σ -donating properties of the acetylide ligand and the relatively long $\text{Cu}\cdots\text{Cu}$ distances, the origin of the emission, which unlike the close-cuboidal or open-cube complexes described earlier, has been assigned as predominantly ${}^3\text{LMCT}[\text{C}\equiv\text{C}\rightarrow\text{Cu}_4]$ in nature.

Summary and Outlook

Undoubtedly, the search for molecular materials as functional building blocks, especially for applications in molecular machinery and electronics, is a field that has attracted chemists' attention in the past few years. I hope that this Account can, through a direct visualization on the structure-property relationship and some fundamental understanding on the spectroscopic origin of d^8 and d^{10} transition metal alkynyl complexes, provide insights to readers on the development of transition metal alkynyls as luminescent molecular materials. Apparently, by subtle changes and variations of the metal centers, nuclearity, and the alkynyl ligands as well as the ancillary ligands, one can readily manipulate the delicate balance

and interplay of factors that would determine the relative importance of various excited states and the emission energies of the complexes, and hence, the structural, photophysical, and photochemical behaviors of the complexes could be fine-tuned in a systematic manner.

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