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Supramolecular Assemblies

Platinum-Based Phosphorescent Double-Decker Tweezers: A Strategy for Extended Heterologous Metal–Metal Interactions**

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Dedicated to Dr. Claude Lapinte on the occasion of his 65th birthday

Supramolecular assemblies with noncovalent metal–metal interactions have received much attention recently because the interactions may involve changes in optical and electrochemical properties, and may find potential uses in biosensing,[1] chemosensing,[2] and molecular devices.[3] A key factor for the successful development of such functional materials with metal–metal interactions is to find ways to design and to control the aggregation processes of monomeric complexes in a well-defined manner, especially in a one-dimensional array.[4,5] Moreover, transition-metal assemblies with rich photoluminescence properties have been relatively unexplored[6,7] because of the frequently observed emission quenching processes that occur via energy and/or electron transfer between the host and the guest molecules,[8] and also via lower-lying metal d–d ligand-field (LF) excited states.[7]

The square-planar d^8 platinum(II) polypyridine system is one of the fascinating classes of materials that exhibits rich photophysical behavior as well as interesting polymorphism in the solid state, with the association of $Pt^{II}\cdots Pt^{II}$ interactions.[9] In particular, alkynyl platinum(II) terpyridine complexes have been found to exhibit self-assembly in fluid solution, with dramatic color changes and emergence of new emission bands in the near-IR (NIR) region.[9a,10] Although the aggregate formation processes from monomeric species in such system have been fairly well-developed in solution,[9a,10] the formation of well-defined oligomers by intermolecular assembly is relatively unexplored, with difficulties in achieving it in a controllable manner.

Recently, a molecular tweezer-like dinuclear host complex based on alkynyl platinum(II) terpyridine units has been reported to bind various transition-metal guest complexes, including those of d^8 and d^{10} metals (Pt^{II}, Pd^{II}, Au^{III}, and Au^{I})[11a] and polyaromatic hydrocarbons (PAHs)[11b] in a 1:1 sandwich binding mode. Characteristics of new low-energy absorption and emission bands, ascribed to the metal–metal-to-ligand charge transfer (MMLCT) excited states, were observed as a result of the presence of significant metal–metal interactions upon association of the transition-metal guest complexes. Unlike the related double salts in the previously reported literature,[12] no precipitation or oligomerization was observed in the association of such a cationic host molecule with anionic platinum(II) guests. It is envisaged that the extension of the motif for the accommodation of two guest molecules in a "double sandwich" fashion may lead to a fine control in the construction of higher oligomeric assemblies. Herein, we report the design and synthesis of a novel class of phosphorescent double-decker tweezers (or triple-decker complexes) based on the trinuclear alkynyl platinum(II) terpyridine complexes and the study of their host–guest associations with two mononuclear square-planar platinum(II) guest complexes (Scheme 1).

Both double-decker host complexes **1** and **2** with two pockets for guest accommodation have been designed to study the effect of extension of host–guest interaction on the molecular tweezer system. Complex **1** consists of three cationic alkynyl platinum(II) terpyridine units connected by an oligophenylenepyridylene backbone, while complex **2** contains two cationic alkynyl platinum(II) terpyridine units bridged by a neutral bis(alkynyl) platinum(II) bipyridine system. Both were synthesized in good yields by the copper(I)-catalyzed platinum–carbon bond formation (see the Supporting Information). Room-temperature ^1H NMR spectra of the complexes in $CDCl_3$, CD_3CN, and $[D_6]DMSO$ revealed broadened signals in the aromatic region (Supporting Information, Figure S1), suggesting the presence of dynamic behavior in the solution state with rates that are slow on the NMR timescale. This result is in contrast to that observed for the related dinuclear complexes,[11] which showed well-resolved ^1H NMR signals at room temperature in $CDCl_3$. Upon elevation of temperature, relatively well-

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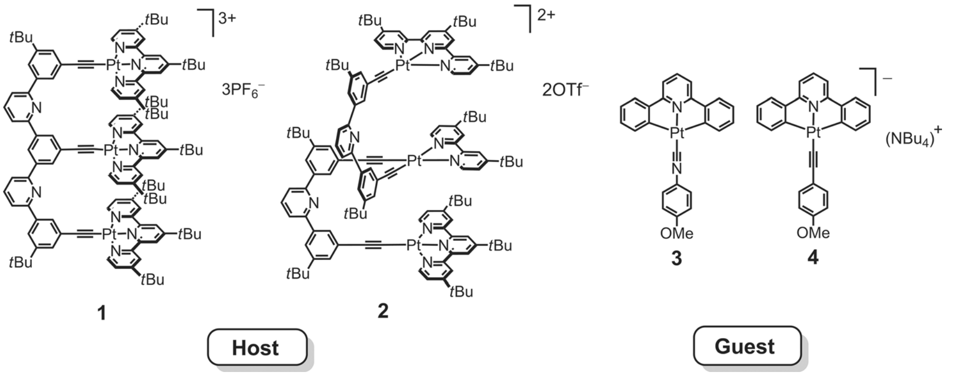

Scheme 1. Structures of host (**1** and **2**) and guest (**3** and **4**) complexes.

resolved signals could be obtained in [D$_6$]DMSO for **1** at 298 K and in CD$_3$CN for **2** at 343 K (Figures S2 and S3). Both complexes gave satisfactory elemental analyses and they were characterized by ESI mass spectroscopy (Figures S4 and S5).

The solid-state structure of **1** has been determined by X-ray crystallography,[13] and it is worth noting that the complex cations were found to exist in a dimeric form in which two symmetrical complexes are mutually intercalated with each other, having a crystallographic inversion center (Figure 1). $\mathrm{Pt^{II}\cdots Pt^{II}}$ and π–π interactions between the peripheral and central interlocked [Pt(terpy)] moieties were suggested by the observation of short $\mathrm{Pt^{II}\cdots Pt^{II}}$ contacts of 3.432 Å and interplanar separations of 3.436 Å. The UV/Vis absorption bands at 400 to 620 nm in the solid state were observed at lower energy than that in the solution state (Figure S6), which is in agreement with the dimerization behavior with extended $\mathrm{Pt^{II}\cdots Pt^{II}}$ and π–π interactions in the solid state. Low-energy absorption bands at around 400-500 nm were observed in the UV/Vis absorption spectra of **1** and **2** in CH$_2$Cl$_2$ (Table 1; Supporting Information, Figure S7), attributed to an admixture of metal-to-ligand charge transfer (MLCT) and ligand-to-ligand charge transfer (LLCT) transitions. Solutions of complexes **1** and **2** (ca. 10^{-5} M)[14] were found to exhibit strong emission at 607 nm and 611 nm, respectively (Table 1; Supporting Information, Figure S8), and the emission origin is assigned as derived from the ^{3}MLCT excited state with some mixing of ^{3}LLCT character. Red-shifted emission bands were observed for both complexes **1** and **2** in the solid state both at room temperature and low temperature, supporting the intermolecular interaction in the solid state (Table 1; Supporting Information, Figure S9).

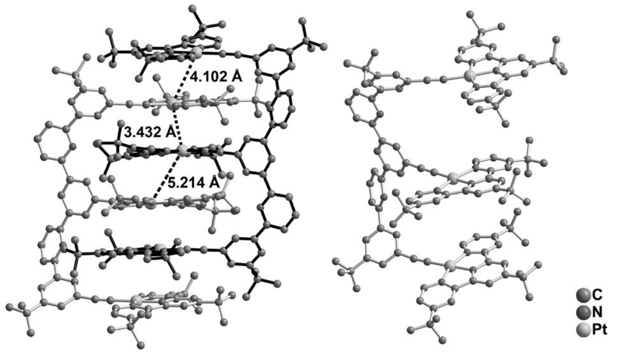

Figure 1. Solid-state structure of the complex cations of **1** in dimeric form (left) and the extracted monomer form (right). Hydrogen atoms, anions, and solvents were omitted for clarity.

Host–guest interactions of **1** and **2** with various guests were studied using UV/Vis absorption and emission spectroscopy (Figure 2; Supporting Information, Figure S10; unnormalized emission spectral changes of **1** are shown in Figure S11). Upon addition of the neutral guest complex **3** to complex **1**, new lower-energy absorptions with peak maximum at around 500–580 nm were observed (Figure 2 (left, top)). With reference to our previous spectroscopic studies on related homo- and heterometallic host–guest systems,[10] such new absorptions could be attributed to metal–metal-to-ligand charge transfer (MMLCT) transitions as a result of the intercalation of guest molecules into the cavity of host **1**, involving significant noncovalent $\mathrm{Pt^{II}\cdots Pt^{II}}$ and π–π interactions. Similarly, upon addition of the anionic guest **4** into complex **1**, a new lower-energy absorption at around 500–750 nm was observed (Figure 2 (right, top)). For the case of complex **2**, less prominent new lower-energy absorptions at around 500–750 nm were observed (Figure S10). All of the the UV/Vis absorption spectral traces show well-defined isosbestic points, suggesting the clean interconversions between the host and the host–guest complex. A stoichiometric 1:2 binding was obtained from the Job's plot of continuous variation, determined by UV/Vis spectroscopic measurements (Figure S12), indicating that two guest complexes are inserted into the cavity of the host complexes, which is in line with the molecular design of the double-decker host. Corresponding emission studies were also performed under similar conditions. Upon addition of the neutral guest **3** to complex **1**, normalized emission spectra

Table 1: UV/Vis absorption and emission properties of complexes **1** and **2**.

Complex	Media (T [K])	UV/Vis λ_{max} [nm] ($\varepsilon \times 10^{-4}$ [dm^3 mol^{-1} cm^{-1}])	Emission λ_{max} [nm] (lifetime [µs])
1	CH$_2$Cl$_2$ (298)	313 (6.58), 338 (3.97), 411 (1.27), 466 (1.09)	607 (1.76)[a]
	solid (298)		630 (<0.1)
	solid (77)		645 (1.8)
2	CH$_2$Cl$_2$ (298)	313 (sh, 6.53), 339 (3.09), 408 (1.44), 467 (0.94)	611 (0.55)[a]
	solid (298)		676 (<0.1)
	solid (77)		680 (<0.1)

[a] [Complex] = ca. 5.0 × 10^{-5} M in deaerated CH$_2$Cl$_2$.

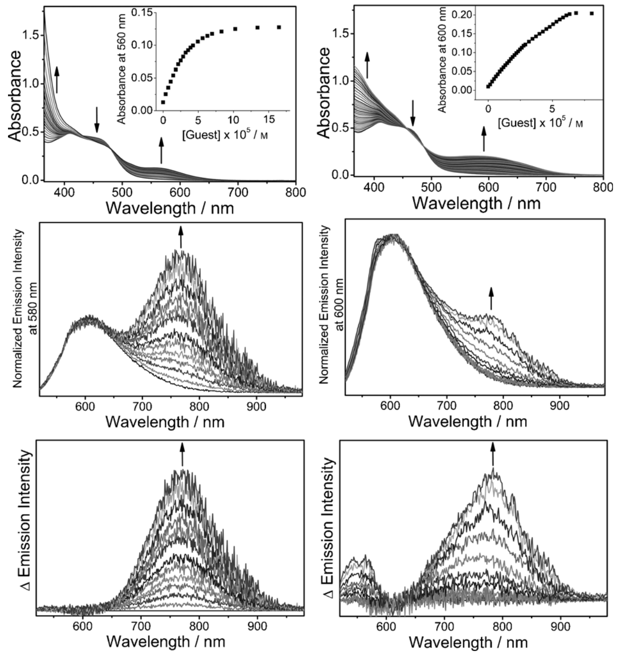

Figure 2. UV/Vis absorption (top) and emission (middle) spectral changes and emission difference spectra (bottom) based on normalized spectra of complex **1** upon addition of [Pt(C^N^C)(C≡N-C_6H_4-OMe-*p*)] (**3**; left) and [Pt(C^N^C)(C≡C-C_6H_4-OMe-*p*)](NBu_4) (**4**; right). The insets show the plot of absorbance at 560 nm (left) and at 600 nm (right).

clearly showed the emergence of a new emission band at about 770 nm (Figure 2 (left, middle)). Similarly, emission enhancement at about 790 nm was observed for complex **1** upon addition of the anionic guest **4** in their normalized spectra (Figure 2 (right, middle)). Similar to the electronic absorption titration studies, the growth of the new emission band is attributed to the formation of noncovalent $Pt^{II}\cdots Pt^{II}$ and π–π interactions upon intercalation of guest molecules into the host cavity and such emission is originated from the ^{3}MMLCT excited sate. The 790 nm-emission is lower in energy than those reported in polypyridine-based trinuclear platinum(II) systems in solution,[11,15] which suggests significant Pt⋯Pt interactions extended over multiple platinum centers. Although the titration studies of complex **2** with the guest complexes **3** and **4** showed less prominent changes with an emission shoulder increasing at around 700–800 nm (Figure S13), a new emission band at 710 nm was observed for a 1:2 mixture of **2** and **4**.

The host–guest binding studies of complex **1** with the neutral guest **3** and the anionic guest **4** were also investigated by ^{1}H NMR spectroscopy in $CDCl_3$. A mixture of complex **1** with the guests **3** (Figure 3) and **4** (Figure S14) in $CDCl_3$ gave well-resolved ^{1}H NMR spectra, indicating that the dynamic behavior of complex **1** has been frozen on the timescale of the ^{1}H NMR experiment.[16] ^{1}H–^{1}H COSY and NOESY NMR spectra of complex **1** with neutral guest gave a reasonable assignment (Figures S15–S19). While most of the proton signals showed significant upfield shift owing to π–π interactions, the signals of the phenyl protons H_e and H_l that are directed toward the inner cavity showed downfield shifts (Figure 3; Supporting Information, Figure S14), suggesting a change in the surroundings. According to the NOE cross peak signals, a plausible host–guest association mode could be proposed (Figure S20). The observation of strong cross peaks between the *tert*-butyl groups on the terpyridine units of host **1** and the diphenylpyridine plane of guest **3** clearly suggests that a head-to-head binding mode is involved in the host–guest interactions, unlike the head-to-tail dimeric arrangement found in the solid-state structure of complex **1**. Similar features were also found with anionic guest **4** from the corresponding ^{1}H–^{1}H COSY and NOESY NMR studies, suggesting the 1:2 sandwich association mode for the host–guest interactions in solution. The ^{1}H NMR spectra of mixtures of complex **2** with the guests **3** and **4** showed ill-resolved broadened signals (Figure S3), which is probably due to the flexible structure of complex **2** and the relatively weak interactions (see below). ESI-TOF-MS measurements of the host–guest mixtures in CH_2Cl_2 further confirmed the presence of the host–guest adducts, as revealed by the observation of the corresponding molecular ion peaks (Figures S21–S24).

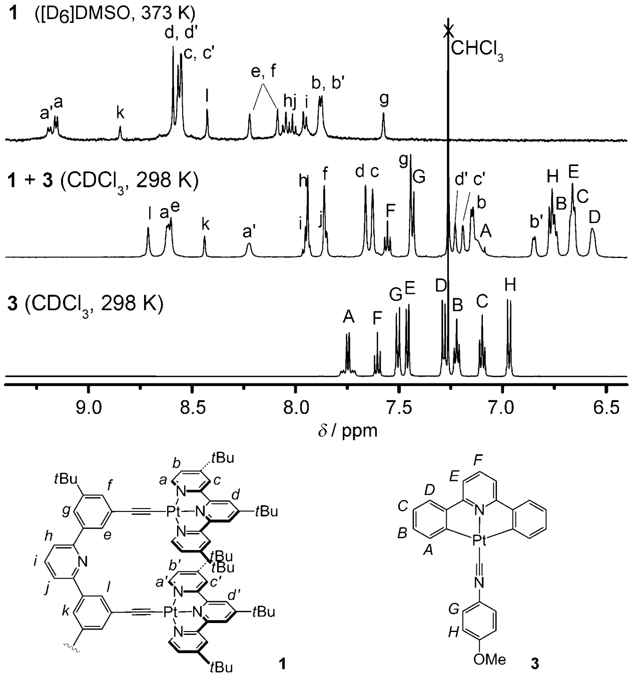

Figure 3. ^{1}H NMR spectra of complex **1** (top, in [D_6]DMSO at 373 K), complex **1** with two equiv of **3** (middle, in $CDCl_3$ at 298 K), and **3** (bottom, in $CDCl_3$ at 298 K).

Binding constants (*K*) of the 1:2 host–guest association and the Hill coefficient (*n*) were determined by the Hill's plot (Figure S25), and the results are summarized in Table 2. Relatively larger binding constants were obtained for complex **1** with the guest complexes than that for complex **2**. The largest binding constant of complex **1** with complex **4** exceeds $10^{13}\ L^2\,mol^{-2}$. Moderate to strong positive cooperative effects ($n = 1.4$–1.7) were found for all of the binding studies. By the consideration of electronic effect alone, the binding of the second guest would be anticipated to be less-favorable than the first insertion, as the electron-rich guest upon complexation would make the electron-deficient host less electron-

Table 2: Binding constants (log *K*) and Hill coefficients (*n*) determined by Hill plots in CH_2Cl_2.[a]

Host	Guest	log *K*	*n*
1	**3**	11.5	1.56
1	**4**	13.5	1.71
2	**3**	6.52	1.40
2	**4**	12.5	1.64

[a] The values were determined by using UV/Vis absorption titration studies at 298 K.

deficient. Thus the positive cooperative effect in such binding processes is attributed to the involvement of structural factors. On the basis of the ^{1}H NMR spectroscopic results, the first guest association would enhance the rigidity of the host molecules, providing a pre-organized structure for the second guest insertion to take place, as revealed by the suppression of dynamic motion upon guest binding (Scheme S1). Such hypothesis is also supported by the result that the order of magnitude of the binding constants has the same tendency as the Hill coefficient $(n(\mathbf{1{\cdot}4}) > n(\mathbf{2{\cdot}4}) > n(\mathbf{1{\cdot}3}) > n(\mathbf{2{\cdot}3}))$. This is a rare example of the strong allosteric effect directed by metal–metal interactions.[17]

In summary, we demonstrated that the unique double-decker tweezers-type host complexes **1** and **2**, based on phosphorescent alkynyl platinum(II) polypyridine systems, could show significant host–guest interactions with interesting spectroscopic changes. The host–guest mixtures include various assemblies of positively, neutral, and negatively charged platinum(II) complexes organized in an unprecedented well-defined and controlled manner, which is in contrast to previous studies where difficulties for the fine control of assembly were reported.[18] The present study shows a rational design for the assembly of planar metal species and would open up a new avenue for the control of "extended" interactions with well-defined host–guest supramolecular assemblies based on metal–metal interactions, and may find applications in the construction of chemosensors and molecular-based devices.

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