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Self-Assembly of Luminescent Alkynylplatinum(II) Terpyridyl Complexes: Modulation of Photophysical Properties through Aggregation Behavior

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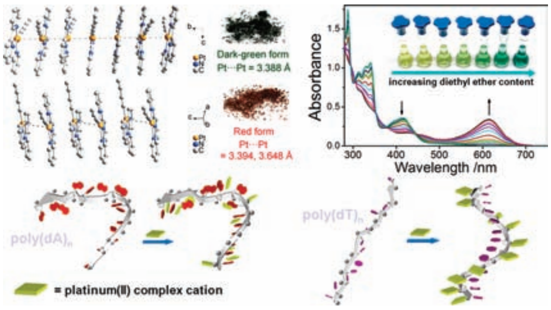

Complexes of platinum(II) with polypyridine (that is, the multidentate ligands related to pyridine, such as bipyridine or terpyridine) have rich photophysical properties. These compounds are able to give different crystal forms in the solid state: this polymorphism is evident in the broad range of colors that can be observed in solid samples. Because of the square-planar coordination geometry of the metal center, Pt···Pt as well as $\pi-\pi$ interactions between the chromophoric polypyridyl platinum(II) moieties are thought to contribute to the polymorphism. Owing to limited solubility, metal···metal interactions in platinum(II) polypyridyl systems had been mainly studied in the solid state, but our preparation of more soluble complexes has enabled detailed spectroscopic examinations in solution. In this Account, we describe our development of these alkynylplatinum(II) terpyridyl complexes and their unique spectral properties.

A series of square-planar platinum(II) terpyridyl complexes with enhanced solubility due to the presence of the alkynyl group exhibited intense emission in solution. The lowest energy absorption and emission bands are suggested to originate from the $d\pi(Pt) \rightarrow \pi^*(terpy)$ metal-to-ligand charge transfer (MLCT) and $\pi(C{\equiv}C-C_6H_4-R) \rightarrow \pi^*(terpy)$ ligand-to-ligand charge transfer (LLCT) transitions. In addition to polymorphism and a wide range of spectral properties, these complexes also exhibit "solvatochromism" and "solvatoluminescence". They show remarkable color changes and luminescence enhancement when the diethyl ether content in a solvent mixture is varied, even as the concentration of the platinum(II) complex is held constant. The dramatic color changes and luminescence enhancement are tentatively suggested to originate from a metal–metal-to-ligand charge transfer (MMLCT) transition: reduced solvation (caused by an increase in the fraction of diethyl ether, which is the nonsolvating component of the liquid) is thought to increase Pt···Pt and $\pi-\pi$ stacking interactions that arise from ground-state self-assembly or aggregate formation. The absorbance and luminescence wavelengths in these solvent-induced self-assemblies are also found to be dependent on the nature of the anions. Thus, counterions play an important role in governing the degree of self-assembly and the extent of interactions within these aggregates.

Several polymers carrying multiple negatively charged functional groups (under basic conditions) as well as oligonucleotides have been shown to induce the aggregation and self-assembly of the positively charged water-soluble alkynylplatinum(II) terpyridyl complexes. The driving force for the induced aggregation and self-assembly is electrostatic binding of the complex molecules to the polymer, which brings the cations into a close proximity that induces Pt···Pt and $\pi-\pi$ interactions and gives rise to remarkable color changes and luminescence enhancement. The spectral changes are shown to be related to the properties of both the complexes and the polymers. Upon electrostatic interaction, the platinum(II) complex cations are also found to stabilize the polymers and biopolymers in a helical conformation through Pt···Pt and $\pi-\pi$ interactions. The influence on their secondary structure is revealed by significant circular dichroism (CD) signal enhancement.

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Introduction

The spectroscopic and photophysical behaviors of d^8 platinum(II) complexes with coordinate-unsaturation and square-planar geometry have attracted great attention in the past few decades, in particular related to their intriguing spectroscopic and luminescence properties associated with their propensity to exhibit metal···metal interactions.[1−19] The platinum(II) polypyridyl system has been receiving a great deal of attention due to its rich photophysical behaviors and interesting spectroscopic features, as well as the intriguing colors associated with the rich solid-state polymorphism of this class of compounds, which are thought to be related to the presence of Pt···Pt or $\pi-\pi$ interactions or both.[4−7] A representative class of the platinum(II) polypyridyl system is the chloroplatinum(II) terpyridyl complex [Pt(terpy)Cl]X (terpy = 2,2′:6′,2′′-terpyridine; X = counteranion),[15] which displays rich polymorphism in the solid state, with its luminescence properties highly dependent on the temperature, type of counteranions, including PF_6^-, ClO_4^-, Cl^-, and $CF_3SO_3^-$, and the solvents used for crystallization.[15] Such solid-state polymorphic phenomena as well as the different absorption and luminescence colors have been suggested to be associated with the different extent of Pt···Pt and $\pi-\pi$ interactions of the terpyridyl ligands in the variations of the stacking arrangement.

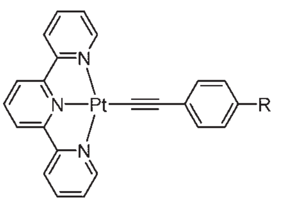
Although the aggregation properties of platinum(II) polypyridyl complexes are known,[11,13−15] most platinum(II) polypyridyl systems are confined to studies of their structures and crystal packings in the solid state showing Pt···Pt interactions and $\pi-\pi$ stacking,[11,13−15] with corresponding studies on aggregate formation in solution relatively less explored.[13] In view of the relatively small association constants found for these systems, compounds of high solubility would be a prerequisite to preparing solutions of high concentrations for the related aggregation studies in solution. However, the solubility problem of the platinum(II) polypyridyl system commonly observed in solution limits an extensive study of their aggregation behaviors in solution.

As an extension of our previous work on transition metal alkynyl complexes,[20−23] efforts have been made to prepare a luminescent alkynylplatinum(II) terpyridyl system, [Pt(terpy)(C≡CR)]$^+$,[24] with enhanced solubility due to the presence of the alkynyl group. Apart from the rich photophysical and luminescence properties, as well as interesting solid-state polymorphism, more importantly, such complexes exhibit remarkable color change and luminescence enhancement ascribed to the presence of Pt···Pt and $\pi-\pi$ stacking interactions resulting from solvent-induced aggregation.[25,26] The sensitivity of the electronic absorption and luminescence properties to the degree of aggregation induced may offer an attractive option for the exploitation of such systems as reporters of solvent environment and microenvironment properties. In this regard, we have directed one of our research efforts specifically to the studies of such aggregation behavior of square-planar platinum(II) complexes in solution. In addition to the basic photophysical properties and interesting polymorphism, the purpose of this Account is to present our recent efforts on the "proof-of-principle" demonstration in the utilization of an alkynylplatinum(II) terpyridyl system as potential colorimetric and luminescent probe of solvent environmental changes and the microenvironments, with the main focus on the intriguing electronic absorption and luminescence variations arising from the presence of Pt···Pt and $\pi-\pi$ stacking interactions due to aggregation.

Basic Photophysical Properties

Unlike the rich luminescence properties exhibited in the solid state or in low-temperature glass media, the chloroplatinum(II) terpyridyl complex, [Pt(terpy)Cl]X, was found to be nonemissive in its solution state at room temperature because of the presence of a lower-lying or thermally accessible ^{3}d−d excited state.[16] Through the replacement of the chloro auxiliary ligand with a strong σ-donor and strong π-acceptor alkynyl group, a series of alkynylplatinum(II) terpyridyl complexes, [Pt(terpy)C≡C−C_6H_4−R-*p*]$^+$ (R = H, Cl, NO_2, CH_3, OCH_3, NH_2, $N(CH_3)_2$, $N(CH_2CH_2OCH_3)_2$)

CHART 1



R = H, Cl, NO_2, CH_3, OCH_3, NH_2, $N(CH_3)_2$, $N(CH_2CH_2OCH_3)_2$

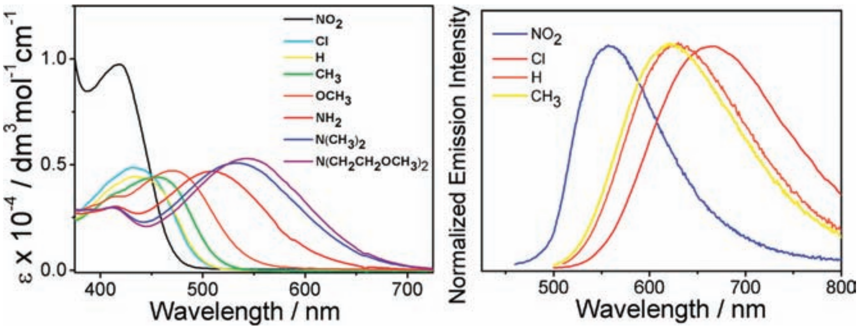


FIGURE 1. (left) Electronic absorption and (right) luminescence spectra of [Pt(terpy)(C≡C$-$C$_6$H$_4-$R-*p*)]$^+$ with various substituents R in acetonitrile at room temperature.

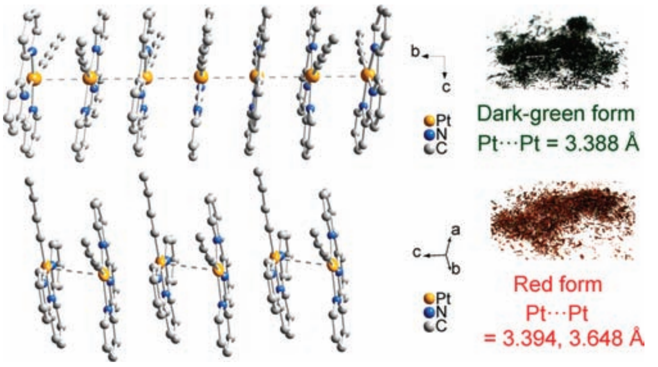


FIGURE 2. Crystal packing diagrams of the complex cations of [Pt(terpy)(C≡C$-$C≡CH)]OTf and photographs in dark green form (upper) and red form (bottom).

FIGURE 3. Solution of [Pt(terpy)(C≡C$-$C≡CH)]OTf (concentration = 1.47 × 10^{-4} M) in acetonitrile$-$diethyl ether mixture demonstrating the remarkable color changes. Diethyl ether composition (from left to right): 64%, 68%, 72%, 74%, 76%, 78%, 80%.

(Chart 1), has been successfully synthesized with enhanced luminescence properties.[24,27]

In addition to the intense intraligand (IL) absorptions at 286$-$350 nm, the electronic absorption spectra of such alkynylplatinum(II) terpyridyl complexes in acetonitrile solution showed a less intense low-energy absorption band at 432$-$546 nm. This low-energy absorption band has been assigned to an admixture of the dπ(Pt) $\rightarrow$ π^*(terpy) metal-to-ligand charge transfer (MLCT) and π(C≡C$-$C$_6$H$_4-$R) $\rightarrow$ π^*-(terpy) ligand-to-ligand charge transfer (LLCT) transitions.[24,27$-$29] In general, the complexes with more electron-rich arylalkynyl ligands exhibited a red shift in such low-energy absorption band (Figure 1 (left)). Upon excitation at $\lambda > 400$ nm, the alkynylplatinum(II) terpyridyl complexes, with the exception of those with $-$OCH$_3$ and $-$NR$_2$ substituents, were found to exhibit luminescence at 560$-$665 nm in acetonitrile solution at 298 K. Parallel to the electronic absorption studies, the luminescence energies were also found to depend on the nature of the arylalkynyl ligands (Figure 1 (right)). On the basis of this observed trend as well as the previous spectroscopic studies of other related platinum(II) terpyridyl complexes,[13$-$16,24,27$-$29] the luminescence has been suggested to originate from the [dπ(Pt) $\rightarrow$ π^*(terpy)] ^{3}MLCT excited state, with some mixing of a [π(C≡CR) $\rightarrow$ π^*(terpy)] ^{3}LLCT character.

Solid-State Polymorphism

Recrystallization of a butadiynyl analogue of the alkynylplatinum(II) terpyridyl complexes, [Pt(terpy)(C≡C$-$C≡CH)]OTf (OTf = trifluoromethanesulfonate), under different conditions afforded two crystal forms, a dark green form and a red form.[25] From X-ray crystallographic study (Figure 2), their crystal packing arrangements revealed that the complex cations are equally separated with short intermolecular Pt···Pt contacts of 3.388 Å in the dark green crystal form, while in the red crystal form, a zigzag arrangement of pairs of complex cations showing dimeric structure with alternating "short" and "long" Pt···Pt distances of 3.394 and 3.648 Å, respectively, was observed. The difference in the crystal colors has been attributed to the variations of the intermolecular arrangement as well as the different extent of Pt···Pt and $\pi$$-$$\pi$ stacking interactions.[25]

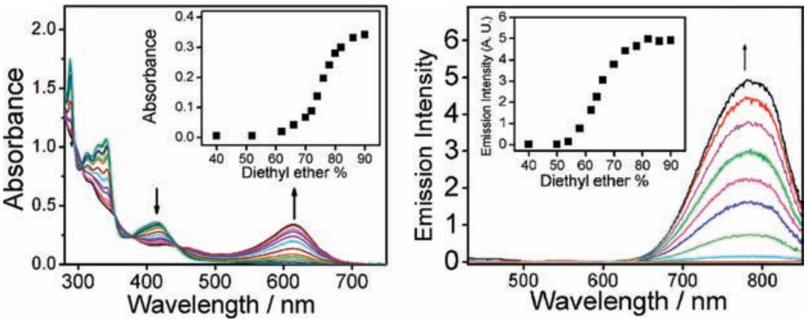


FIGURE 4. (left) Electronic absorption and (right) emission spectral changes of [Pt(terpy)(C≡C−C≡CH)]OTf in acetonitrile with increasing diethyl ether composition. Insets: (left) plot of absorbance at 615 nm and (right) plot of corrected emission intensity vs diethyl ether composition (■).

Solvent-Induced Aggregation

Dissolution of either of the two forms of [Pt(terpy)(C≡C−C≡CH)]OTf gave a yellow solution in acetonitrile with the same electronic absorption spectra that showed a MLCT absorption band at 416 nm, suggestive of the existence of monomeric species in solution. Upon increase of the diethyl ether content in the solution mixture of acetonitrile−diethyl ether while the concentration of the platinum(II) complex is kept the same, the solution color of [Pt(terpy)(C≡C−C≡CH)]OTf changed dramatically from yellow to green to blue (Figure 3).[25] The corresponding electronic absorption spectral trace showed a growth of a new absorption band at 615 nm and a drop in intensity of the absorption band at 416 nm, with well-defined isosbestic points (Figure 4 (left)). Such drastic color changes were ascribed to ground-state self-assembly or aggregate formation in the solution mixture as a result of reduced solvation, arising from an increase in the nonsolvent content of diethyl ether. The new absorption band at 615 nm that imparted the dramatic color change has been tentatively assigned as a metal−metal-to-ligand charge transfer (MMLCT) transition, due to the presence of Pt···Pt and π−π stacking interactions arising from the ground-state oligomerization or aggregate formation.

Upon excitation at the isosbestic point in the electronic absorption studies, a tremendous enhancement of NIR luminescence at 785 nm was observed with increasing diethyl ether content in the solution mixture of acetonitrile−diethyl ether (Figure 4 (right)).[25] The solvent compositions required for the switching on and variations of luminescence intensity are consistent with those for the absorbance changes at 615 nm. Based on this finding, together with the close resemblance of the new absorption bands in the electronic absorption spectra and the excitation bands in the excitation spectra monitored at 785 nm, such new luminescence band in the NIR region was accordingly assigned to be derived from the same MMLCT transition origin, resulting from solvent-induced self-assembly of the alkynylplatinum(II) terpyridyl complexes that has been facilitated by the propensity to form Pt···Pt and π−π stacking interactions.[25]

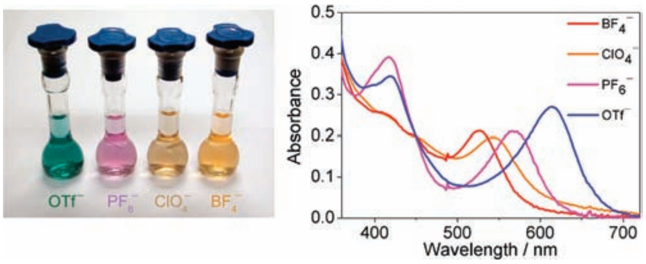


FIGURE 5. (left) Photographs of [Pt(terpy)(C≡C−C≡CH)]X (X = OTf$^-$, PF$_6^-$, ClO$_4^-$, BF$_4^-$) (concentration = 7×10^{-5} M) in a solution of acetonitrile−diethyl ether mixture upon solvent-induced aggregation. The diethyl ether content from left to right: 86%, 86%, 82%, 82%. (right) Corresponding electronic absorption spectra of solutions at room temperature.

In view of the fact that the solid-state color of chloroplatinum(II) terpyridyl complexes has been found to be dependent on the counteranions, similar spectroscopic studies of other salts of [Pt(terpy)(C≡C−C≡CH)]X (X = PF$_6^-$, ClO$_4^-$, BF$_4^-$, and BPh$_4^-$) were also performed to investigate the effect of the nature of the counteranions on the self-assembly of the alkynylplatinum(II) terpyridyl complexes in solution.[26] Upon increase of the diethyl ether content in the solution mixture of acetonitrile−diethyl ether, remarkable color changes from yellow to magenta (PF$_6^-$), pink (ClO$_4^-$), and orange (BF$_4^-$) were also observed (Figure 5 (left)). Including the OTf$^-$ salt, strong dependences of the color and the new absorption bands of the aggregates of [Pt(terpy)(C≡C−C≡CH)]$^+$ on the nature of the counteranions were observed upon self-assembly or aggregate formation with increasing diethyl ether content (Figure 5 (right)). Similarly, the occurrence of the new intense NIR luminescence upon self-assembly or aggregate formation has also been found to be dependent on the nature of the associated

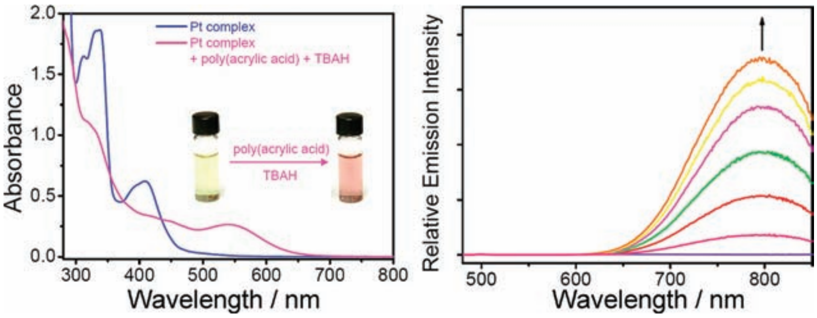
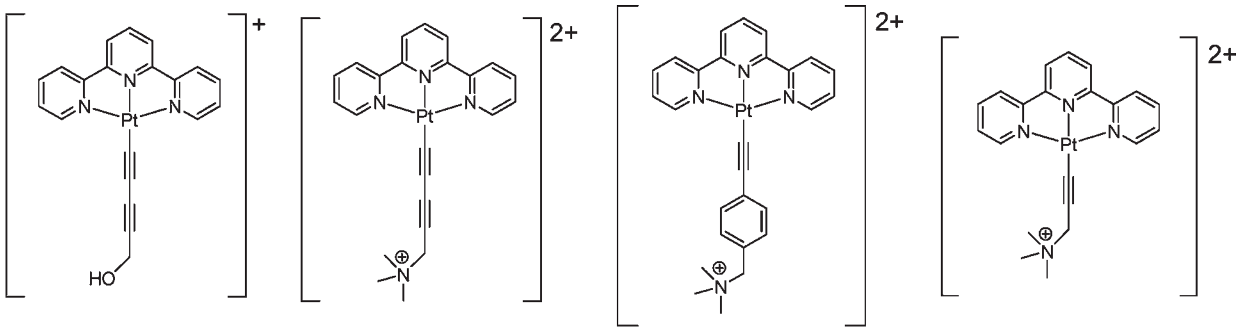


FIGURE 6. (left) Electronic absorption spectral changes of [Pt(terpy)(C≡C−C≡CH)]OTf (0.15 mM) in a mixture of MeOH and CH_3CN (2:1, v/v) upon addition of poly(acrylic acid) (0.45 mM carboxylic acid unit) and TBAH (0.45 mM). Inset: photographs showing the corresponding color change. (right) NIR luminescence enhancement of [Pt(terpy)(C≡C−C≡CH)]OTf upon addition of polyacrylate with equimolar amounts of carboxylic acid and base.

CHART 2

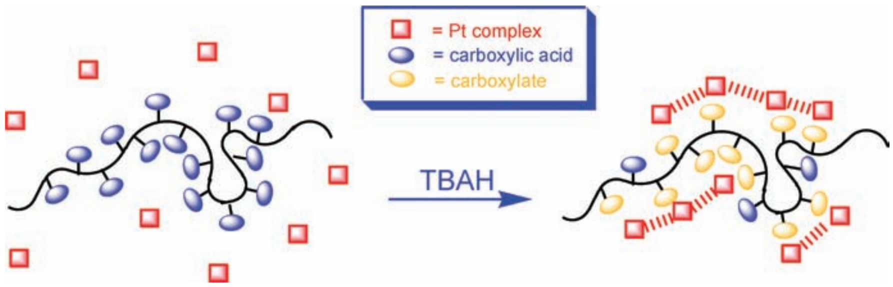


counteranions.[26] Such variations in the absorption and luminescence energies of the new bands indicated that counteranions with different size and shape, as well as the ability to interact with the acetylenic proton, probably play an important role in governing the degree of aggregation and the extent of interactions within these aggregates. No observable color or spectral changes were found for [Pt(terpy)(C≡C−C≡CH)]BPh_4, with the larger size and noncoordinating BPh_4^- anion, further supporting such a hypothesis.

Polyelectrotyle-Induced Aggregation

In light of the fact that the counteranions have been shown to play an important role in governing the assembly of the positively charged alkynylplatinum(II) terpyridyl complex cations in the studies of solvent-induced self-assembly or aggregate formation, one could visualize that the self-assembly of the alkynylplatinum(II) complex cations would also be able to induce a reorganization of the counteranions in order to maintain a charge balance in a local environment. Inspired by the reverse of this concept, the use of an ordered assembly of counteranions arranged in a preorganized fashion as in the polyelectrolyte has been envisaged to induce the self-assembly or aggregation of the positively charged alkynylplatinum(II) terpyridyl units, without the need to change the solvent composition. Addition of polyacrylate, generated from the mixture of poly(acrylic acid) and tetra-*n*-butylammonium hydroxide (TBAH) as the base, into the solution of [Pt(terpy)(C≡C−C≡CH)]OTf in a mixture of MeOH and CH_3CN resulted in a remarkable solution color change from light-yellow to reddish-pink, with an emergence of a new absorption band at about 543 nm (Figure 6 (left)), as well as a new luminescence band at about 800 nm (Figure 6 (right)).[30] The positively charged alkynylplatinum(II) terpyridyl units were believed to assemble together into close proximity to from aggregates via the electrostatic binding to the negatively charged anionic sites on polyacrylate (Scheme 1). Accordingly, the new low-energy absorption and NIR luminescence bands have been assigned as originating from the MMLCT transition due to the presence of Pt···Pt and $\pi-\pi$ stacking interactions, resulting from aggregate formation. In contrast, no similar spectral changes have been observed upon addition of the tri-*tert*-butyl-substituted analogue, [Pt(^{t}Bu$_3$-terpy)(C≡C−C≡CH)]OTf, into the solution of poly(acrylic acid) in the presence of TBAH. It was suggested that the bulky *tert*-butyl

SCHEME 1



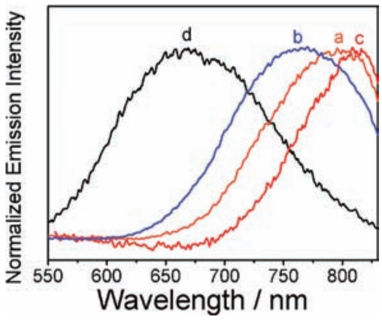
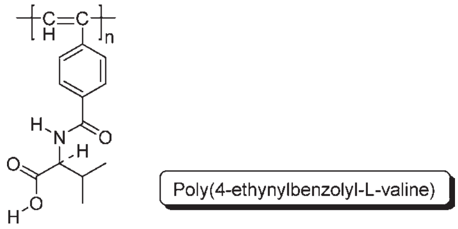


FIGURE 7. Emission spectra of 30 μM (a) $[Pt(terpy)(C{\equiv}C{-}C{\equiv}C{-}CH_2{-}OH)]OTf$, (b) $[Pt(terpy)(C{\equiv}C{-}C{\equiv}C{-}CH_2{-}N(CH_3)_3)](OTf)_2$, (c) $Pt(terpy)(C{\equiv}C{-}C_6H_4{-}CH_2N(CH_3)_3)](OTf)_2$, and (d) $[Pt(terpy)(C{\equiv}C{-}CH_2{-}N(CH_3)_3)](OTf)_2$ mixed with 180 μM polyacrylate in buffer (5 mM Tris, 10 mM NaCl, pH 7.5) solution.

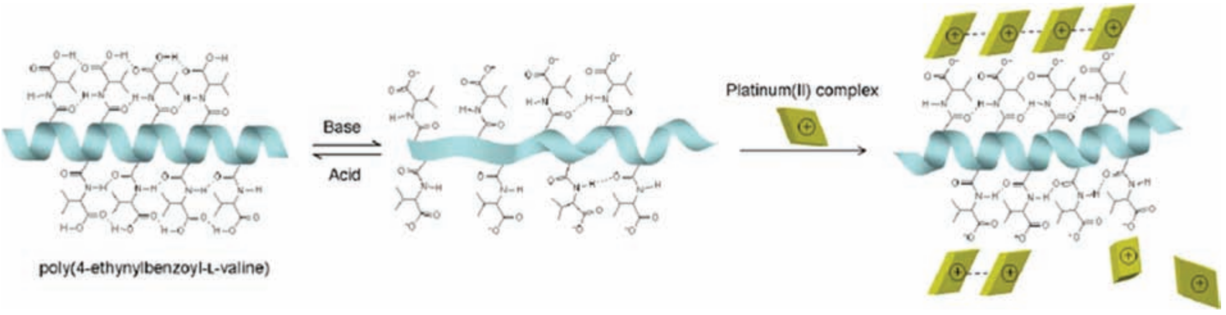
CHART 3



groups would prevent the alkynylplatinum(II) terpyridyl units to assemble together into close proximity.

A detailed study of the properties of polyelectrolyte-induced self-assembly of several water-soluble alkynylplatinum(II) terpyridyl complexes, $[Pt(terpy)(C{\equiv}C{-}C{\equiv}C{-}CH_2{-}OH)]OTf$, $[Pt(terpy)(C{\equiv}C{-}C{\equiv}C{-}CH_2{-}N(CH_3)_3)](OTf)_2$, $[Pt(terpy)(C{\equiv}C{-}C_6H_4{-}CH_2N(CH_3)_3)](OTf)_2$, and $[Pt(terpy)(C{\equiv}C{-}CH_2{-}N(CH_3)_3)](OTf)_2$ (Chart 2), with different cationic charges and ligands of different hydrophobicity in aqueous media upon mixing with various anionic polyelectrolytes, such as polyacrylate, poly(vinyl sulfonate), and poly(4-styrene sulfonate), has also been investigated and correlated with the nature of the complexes and polymers.[31] Similar to the study of polyelectrolyte-induced self-assembly of $[Pt(terpy)(C{\equiv}C{-}C{\equiv}CH)]OTf$ in organic solvent, drastic electronic absorption spectral changes with the emergence of new absorption bands at 538−550 nm were observed upon mixing of any one of the complexes, $[Pt(terpy)(C{\equiv}C{-}C{\equiv}C{-}CH_2{-}OH)]OTf$, $[Pt(terpy)(C{\equiv}C{-}C{\equiv}C{-}CH_2{-}N(CH_3)_3)](OTf)_2$, or $[Pt(terpy)(C{\equiv}C{-}C_6H_4{-}CH_2N(CH_3)_3)](OTf)_2$, with polyelectrolytes in a pure aqueous buffer solution (5 mM Tris-HCl, 10 mM NaCl, pH 7.5).[31] For inducing the self-assembly of the complexes, poly(vinyl sulfonate) was found to have better performance than polyacrylate. On the other hand, poly(4-styrene sulfonate) showed the least effect on the self-assembly and gave rise to a reduced tendency of complex stacking, which has been ascribed to the stronger hydrophobic interactions between the relatively hydrophobic planar styryl groups and the complexes. In order to compare the degree of self-assembly among the complexes, the difference in the energy of the monomeric MLCT/LLCT absorption and the aggregate MMLCT absorption was employed as a measure of the extent of Pt···Pt and π−π stacking interactions.[31] Interestingly, $[Pt(terpy)(C{\equiv}C{-}C_6H_4{-}CH_2N(CH_3)_3)](OTf)_2$ has been found to exhibit the largest electronic absorption spectral shift relative to the other two complexes regardless of the polyelectrolyte used. This has been attributed to the fact that $[Pt(terpy)(C{\equiv}C{-}C_6H_4{-}CH_2N(CH_3)_3)](OTf)_2$, containing an extra phenyl ring among the four complexes studied, has the largest hydrophobicity, which would facilitate the self-assembly of the complexes through the hydrophobic−hydrophobic interaction that acts as an additional driving force, resulting in the largest electronic absorption spectral shift.[31] The absorption spectral changes were found to be far less significant in the dicationic $[Pt(terpy)(C{\equiv}C{-}CH_2{-}N(CH_3)_3)](OTf)_2$, which has been ascribed to the strongest electrostatic repulsive force, in view of the fact that the trimethylammonium charged group was positioned closest to the hydrophobic terpyridine moiety.

SCHEME 2. Proposed Poly(4-ethynylbenzoly-L-valine) Chain Helicity Modulation and Aggregation of Cationic Platinum(II) Complex Ions upon pH Adjustment and Metal Complex Addition



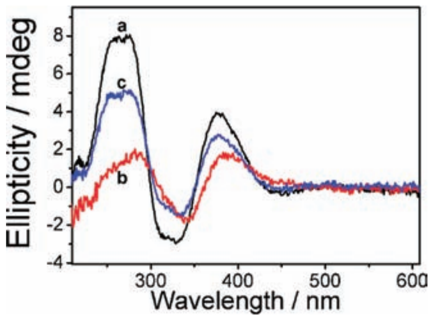


FIGURE 8. CD spectra in methanol of 0.15 mM poly(4-ethynylbenzoly-L-valine) (line a), and upon addition of 0.15 mM KOH (line b), 0.15 mM $[Pt(terpy)(C{\equiv}C{-}C{\equiv}C{-}CH_2{-}OH)]OTf$, and 0.15 mM KOH (line c).

Upon mixing of the alkynylplatinum(II) terpyridyl complexes with various polyelectrolytes, new luminescence bands originating from the MMLCT transition were observed, which indicated the occurrence of self-assembly of the metal complexes (Figure 7).[31] In line with the electronic absorption studies, $[Pt(terpy)(C{\equiv}C{-}C_6H_4{-}CH_2N(CH_3)_3)](OTf)_2$ in all cases showed the lowest-energy luminescence, suggesting the largest extent of aggregate formation attributed to its strongly hydrophobic nature. On the other hand, mixture of poly(4-styrene sulfonate) with any of the complexes showed the weakest tendency to self-assemble as revealed from their MMLCT luminescence energies. This was because the poly(4-styrene sulfonate) with higher hydrophobicity would compete with the complex molecules to form the hydrophobic–hydrophobic interactions.

Since poly(4-ethynylbenzoly-L-valine) (Chart 3) has been found to be capable of forming intrastrand and interstrand hydrogen bonds within and between the polymer chains to assume a helical conformation, with its helicity found to vary with solvent, pH, and temperature,[32] this amphiphilic polymer has been used to induce the self-assembly of $[Pt(terpy)(C{\equiv}C{-}C{\equiv}C{-}CH_2{-}OH)]OTf$.[33] Addition of $[Pt(terpy)(C{\equiv}C{-}C{\equiv}C{-}CH_2{-}OH)]OTf$ to an equimolar solution of poly(4-ethynylbenzoly-L-valine) in the presence of a base in methanol at room temperature gave rise to a new absorption shoulder at 500–600 nm in the electronic absorption spectrum. Similarly, a new NIR emission band at about 800 nm was observed in the methanol solution of $[Pt(terpy)(C{\equiv}C{-}C{\equiv}C{-}CH_2{-}OH)]OTf$ and poly(4-ethynylbenzoly-L-valine) in equimolar ratio in the presence of a base. On the basis of our related spectroscopic studies on other related anionic polyelectroyles, the newly formed electronic absorption shoulder and NIR emission band have been attributed to MMLCT transition, a result of the aggregation of the platinum(II) complexes by the electrostatic attraction from the anionic polyelectrolyte. According to previous studies,[30,31] the anionic form of the amino acid moiety of poly(4-ethynylbenzoly-L-valine) in basic condition has been found to disrupt the hydrogen bonds to result in random polymer chains (Scheme 2), due to the electrostatic repulsion between the negative charges. The absorbance of such new absorption shoulder and the intensity of the low-energy NIR emission band were found to decrease or diminished upon addition of an acid. The reversibility of this aggregation process was confirmed by the on/off switching of these MMLCT absorption shoulder and NIR emission band upon alternate addition of acids and bases with at least eight repeating cycles under constant ionic strength. A drop of circular dichroism (CD) spectral signals of poly(4-ethynylbenzoly-L-valine) has been found upon addition of base, and therefore the organizational structures of the amphiphilic polyacetylenes can be modulated by changing the pH. It is interesting to note that an enhancement of CD signal has been observed when $[Pt(terpy)(C{\equiv}C{-}C{\equiv}C{-}CH_2{-}OH)]OTf$ was added into the basic mixture of poly(4-ethynylbenzoly-L-valine) under constant ionic strength (Figure 8). In view of the fact that no new band formation was found in the CD spectra, the spectral changes have been suggested to

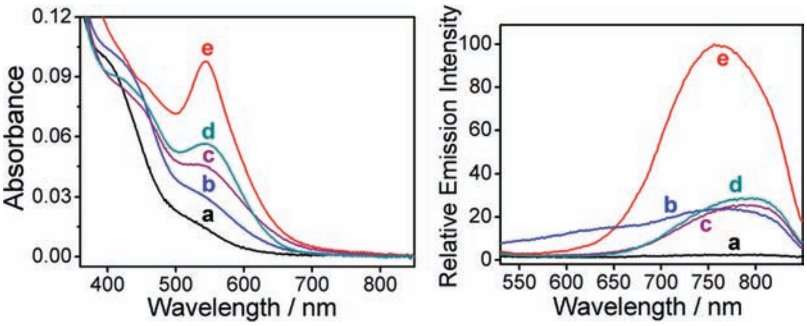


FIGURE 9. Electronic absorption (left) and luminescence (right) spectra of 30 μM of [Pt(terpy)(C≡C−C≡C−CH$_2$−OH)]OTf (line a) and their binding to 90 μM (base concentration) of poly(dA)$_{25}$ (line b), poly(dC)$_{25}$ (line c), poly(dG)$_{25}$ (line d), and poly(dT)$_{25}$ (line e). Medium: 5 mM Tris-HCl, 10 mM NaCl, pH 7.5. Spectra were not corrected for PMT response.

mainly originate from the electronic transitions characteristic of the polyacetylene. It is believed that the electrostatic assembly of the cationic platinum(II) complexes to the anionic sites of the polyacetylene would cause the charge neutralization of the polymer, and at the same time the induced self-assembly of the complexes via metal···metal and $\pi-\pi$ interactions would provide the additional driving force for the stabilization of the polymer chain into helical structures (Scheme 2), leading to the revival of the helical chirality, similar to the stabilization brought about by hydrogen bonding in its acidic form.

Nucleic Acid-Induced Self-Assembly

In view of the fact that single-stranded nucleic acids are polyanionic in nature, biomolecules of single-stranded nucleic acids were explored for inducing the self-assembly of alkynylplatinum(II) terpyridyl complexes in an aqueous environment. [Pt(terpy)(C≡C−C≡C−CH$_2$−OH)]OTf and [Pt(terpy)(C≡C−C≡CH)]OTf have been employed and their self-assembly in the presence of various oligonucleotides, such as poly(dT)$_{25}$, poly(dC)$_{25}$, poly(dG)$_{25}$, and poly(dA)$_{25}$, have been investigated by various spectroscopic techniques.[34] In a buffer solution with constant pH and ionic strength, both complexes showed electronic absorption and luminescence spectral changes upon addition of various oligonucleotides (Figure 9). Concomitant with the growth of the absorption bands or shoulders at $\lambda_{abs} > 520$ nm, new NIR luminescence at about 760−800 nm was also observed. On the basis of our previous work and other related studies,[25,26,30,31,33] the newly formed absorption and luminescence bands at longer wavelength have been attributed to aggregate formation through metal···metal and $\pi-\pi$ interactions and have been tentatively assigned as transitions of MMLCT origin. The self-assembly of the complexes has been suggested to be induced by the electrostatic interactions between the positively charged platinum(II) complexes and the polyanionic oligonucleotides carrying multiple negative charges at near neutral pH. The intensities of the new electronic absorption band for poly(dT)$_{25}$ were found to be the highest, while moderate intensity for poly(dC)$_{25}$ and poly(dG)$_{25}$, and only weak absorbance changes for poly(dA)$_{25}$ were observed. Similary, the new NIR luminescence bands for the mixtures of poly(dT)$_{25}$ with the platinum(II) complexes have been found to be the most intense.[34] On the other hand, the NIR luminescence bands with moderate intensity for poly(dC)$_{25}$ and poly(dG)$_{25}$ also appeared, whereas very broad luminescence bands with no clear band maximum were observed with poly(dA)$_{25}$.

More importantly, mixtures of different oligonucleotides and complexes exhibited drastic changes of CD signals in their CD spectra.[34] For example, addition of [Pt(terpy)(C≡C−C≡C−CH$_2$−OH)]OTf to the buffer solution of poly(dT)$_{25}$ gave a large CD signal enhancement (Figure 10 (left)). Interestingly, a large CD signal was also observed for poly(dC)$_{25}$ but with a mirror image relationship with respect to that of poly(dT)$_{25}$ (Figure 10 (left, inset)). Relatively smaller CD spectral changes were observed for poly(dA)$_{25}$, but the spectra with higher complex concentration were found to be similar in shape to the corresponding CD spectra mixed with poly(dC)$_{25}$ (Figure 10 (right)). In view of the fact that [Pt(terpy)(C≡C−C≡C−CH$_2$−OH)]OTf but not the nucleic acids absorb intensely at wavelengths longer than 300 nm,[35] the strong CD spectral changes observed have been ascribed mainly to the electronic transitions characteristic of the alkynylplatinum(II) terpyridyl complex.[24,27−29] The strong induced CD signal changes were believed to mainly originate from electronic transitions of the metal complexes because only weak CD signals were observed in the solution of nucleic acids alone, which could not account for the strong CD signals induced. On the other hand, addition of

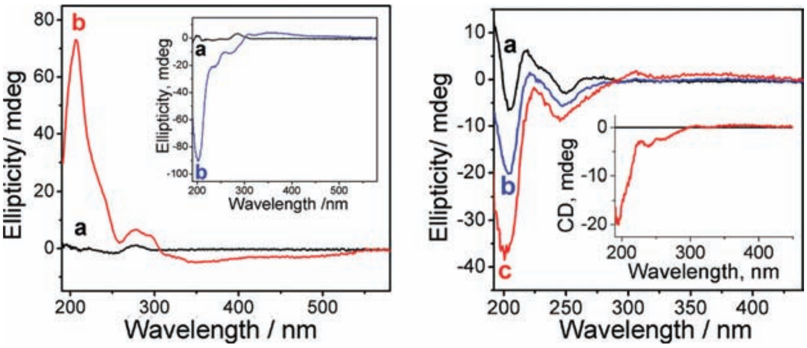
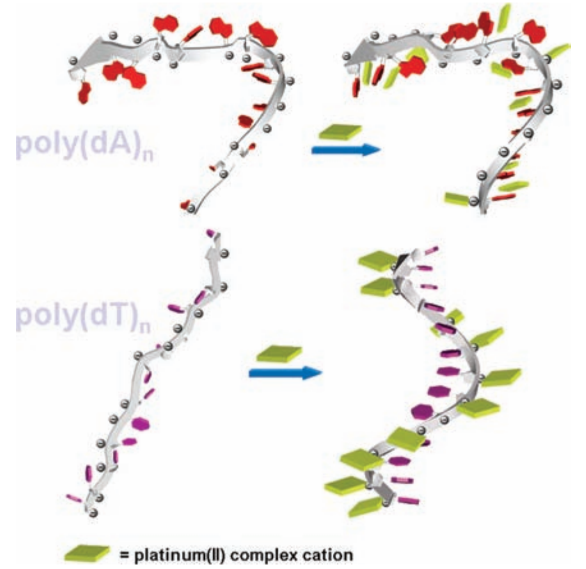


FIGURE 10. (left) CD spectra of 90 μM of poly(dT)$_{25}$ (line a) and its binding with 30 μM [Pt(terpy)(C≡C−C≡C−CH$_2$−OH)]OTf (line b); (inset) CD spectra of 90 μM of poly(dC)$_{25}$ (line a) and its binding with 45 μM [Pt(terpy)(C≡C−C≡C−CH$_2$−OH)]OTf (line b). (right) CD spectra of 90 μM of poly(dA)$_{25}$ (line a) and its binding with 30 and 60 μM [Pt(terpy)(C≡C−C≡C−CH$_2$−OH)]OTf (lines b and c, respectively); (inset) spectrum equals line b minus line a. Medium: 5 mM Tris-HCl, 10 mM NaCl, pH 7.5.

[Pt(terpy)(C≡C−C≡C−CH$_2$−OH)]OTf to the buffer solution of poly(dG)$_{25}$ did not give any observable CD changes, which suggested that the binding of the complexes to nucleic acids does not always induce chirality although the nucleic acids are inherently chiral. The chirality induced has been believed to be associated with the arrangement of the achiral complex molecules into a helical assembly upon electrostatic binding to the anionic phosphate sites, induced by the propensity of these square-planar d^8 platinum(II) terpyridyl units to stack via Pt···Pt and π−π interactions. When [Pt(terpy)(C≡C−C≡C−CH$_2$−OH)]OTf was mixed with poly(L-glutamate) or poly(L-aspartate), MMLCT absorption bands at about 550 nm and MMLCT emission bands at about 798 nm were observed, which was indicative of formation of the complex aggregation,[34] with the observation of large induced CD signals, relative to the very weak CD signals observed in poly(L-glutamate) and poly(L-aspartate) alone. Interestingly, with poly(D-glutamate), a mirror image of the CD signal to that of [Pt(terpy)(C≡C−C≡C−CH$_2$−OH)]OTf and poly(L-glutamate) was obtained. More importantly, the general shape of the CD spectra was found to match quite well with that obtained with the oligonucleotides, suggesting that the induced CD changes were primarily coming from electronic transitions of the metal complexes.

It is interesting to note that the changes in the new electronic absorption, emission, and CD spectra have been found to be dependent on the sequence of the oligonucleotide, which has been suggested to be apparently associated with their primary and secondary structures. Upon addition of the platinum(II) complexes, the oligonucleotide poly(dT)$_{25}$ was found to exhibit strong aggregation of the platinum(II) complexes as revealed by the formation of the more intense MMLCT absorption and emission bands, while the CD signal enhancement was suggestive of the self-assembly of the platinum(II) complexes into a helical array. On the contrary, only less pronounced electronic absorption and emission spectral changes, with a very broad structureless emission spanning in the range of 500−850 nm, and relatively small CD changes were observed upon binding of platinum(II) complexes to poly(dA)$_{25}$. In view of the same number of negative charges carried in poly(dT)$_{25}$ and poly(dA)$_{25}$, there was no obvious reason to assume that the positively charged complex cations would interact electrostatically with poly(dA)$_{25}$ in a much weaker fashion than with poly(dT)$_{25}$. The very broad emission has been attributed to a mixture of complex monomer emission and MMLCT triplet emission resulting from complex aggregation (at around 800 nm). Since poly(dA)$_{25}$ has been reported to exhibit a helical structure by stabilization through adenine base

SCHEME 3. Proposed Interaction between Platinum(II) Complex Cations and Poly(dA)$_n$ (upper) and Poly(dT)$_n$ (bottom)



stacking interactions,[36,37] the hydrophobic interactions between the relatively hydrophobic planar adenine base and the square-planar platinum(II) complex cations have been suggested to reduce the tendency for the complex cations to stack with each other to form a helical self-assembly (Scheme 3). As a result, emission from the mononuclear platinum(II) species has been observed and CD signals from the chirality induced was reduced. Thus broad featureless bands comprising monomer and aggregate emission of the platinum(II) complexes were observed with poly(dA)$_{25}$. This has been further supported by the study in the presence of acetonitrile or trifluoroethanol, which are known to suppress hydrophobic−hydrophobic interactions, in which the monomer emission band resulting from hydrophobic−hydrophobic interaction between the platinum(II) complexes and the adenine bases was suppressed, leading to a more obvious MMLCT emission band in the NIR region. For poly(dT), which was known to have a nonhelical structure with little long-range order and very little base stacking interactions between the thymine bases,[36,37] the relatively more hydrophilic structure together with the bulky methyl group of thymine were envisaged to greatly reduce its hydrophobic interactions with the complex cations, thus favoring the self-assembly of the metal complexes to form helical assembly (Scheme 3).

Concluding Remarks

A series of square-planar platinum(II) terpyridyl complexes, upon incorporation of a strong σ-donor alkynyl ligand into the platinum(II) metal center, have been reported to exhibit intense emission in the solution state at room temperature. These complexes were found to show rich polymorphism with different extent of Pt···Pt and $\pi-\pi$ stacking interactions in the solid state. Apart from this, intermolecular Pt···Pt and $\pi-\pi$ stacking interactions have been observed in the solution state through the self-assembly of these complex cations, caused by solvent-induced or polymer-induced aggregate formation, leading to interesting spectral features with drastic color changes and near-infrared (NIR) emission enhancement, which have been assigned as derived from MMLCT transitions. Since such solution state Pt···Pt and $\pi-\pi$ interactions, responsible for the remarkable spectroscopic changes, were found to be sensitive to the changes in the microenvironment, switching on and off of the Pt···Pt and $\pi-\pi$ interactions could be achieved upon variations of solvent compositions, counteranion, and pH. Upon electrostatic interaction with anionic synthetic polymers or biopolymers, the complex cations have also been found to stabilize polymers and biopolymers in a helical conformation through Pt···Pt and $\pi-\pi$ interactions, influencing their secondary structures, as revealed by the significant circular dichroism (CD) signal enhancement.

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FOOTNOTES

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