DOI: 10.1002/chem.200800276

Polyelectrolyte-Induced Self-Assembly of Positively Charged Alkynylplatinum(II)–Terpyridyl Complexes in Aqueous Media

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Abstract: Polyelectrolytes carrying multiple negative charges were found to induce the aggregation and self-assembly of the positively charged platinum(II)–terpyridyl complexes in aqueous media. The aggregation and self-assembly of the complexes were driven by electrostatic interactions between the polymer and the complex, and by terpyridine ligand π–π stacking and platinum–platinum (metal–metal) interactions. As a result, remarkable UV/Vis and emission spectral changes were observed. The spectroscopic property changes were related to the structural properties of the metal complexes as well as the polyelectrolytes. The induced self-assembly of the platinum complexes was also strongly affected by the solution properties of the aqueous media, for example, the solution pH, ionic strength, and the percentage of organic solvent added.

Keywords: noncovalent interactions · platinum · polyelectrolytes · self-assembly · UV/Vis spectroscopy

Introduction

Polymers containing charged groups, known as polyelectrolytes, are among the most important classes of macromolecules. Common examples of polyelectrolytes include a large number of biopolymers, for example, proteins, nucleic acids, and many types of synthetic polymers. They have been extensively studied over the past several decades, due both to scientific interest in understanding their behavior as well as the enormous potential in various applications, in diverse fields such as chemistry, biology, materials science, medicine, physics, and nanotechnology. Polyelectrolytes have been fabricated into multilayers, self-assemblies, thin films, and nanostructures, and have been used for electronic and photonic applications; for separation and sensor developments; for biomedical applications, including controlled drug delivery, gene therapy; and the development of new biomaterials.[1] Despite growing interest in the use of polyelectrolytes for the supramolecular ionic assembly of moieties containing opposite charges, most of the work reported is confined to the use of inorganic ions or chromophoric ions that are organic in nature. Assembly of metal–ligand chromophoric units from polyelectrolytes is extremely scarce.[1,2]

Platinum(II)–polypyridyl complexes belong to a particularly interesting class of organometallic chromophoric complexes, and they are square planar. These complexes are known for many years to possess a strong tendency to arrange themselves into linear chain or oligomeric structures in the solid state, many of which involve metal–metal interactions and aromatic ligand π–π stacking interactions. Depending on the extent of these interactions, these complexes often exhibit different colors.[3–13]

We recently synthesized a number of platinum(II)–terpyridyl complexes, and interesting solid-state as well as solution spectroscopic properties, including induced aggregation under various conditions, have been observed.[14–18] Herein we present a detailed study of the properties of polyelectrolyte-induced self-assembly of several organometallic platinum(II) complexes in aqueous media. Triflate salts of several water-soluble alkynylplatinum(II)–terpyridine complexes with different cationic charges and ligands of different hydrophobicity have been synthesized (**1**–**4**), and tested for their self-assembly properties in the presence of various anionic polyelectrolytes. The UV/Vis and emission spectral changes were studied and correlated to the nature of the complexes, polymer, and the media. It is envisaged that such

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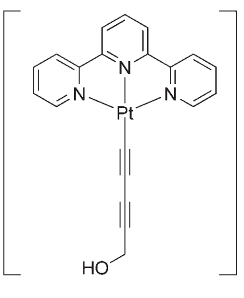
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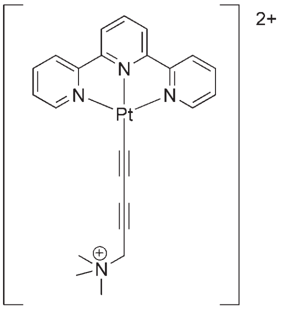
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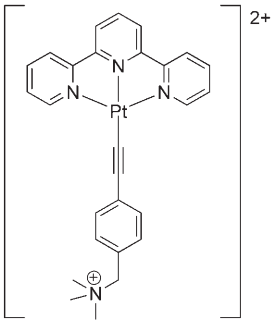
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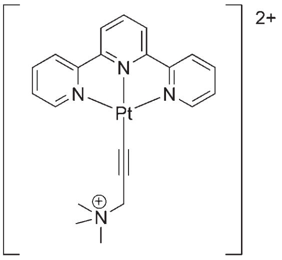
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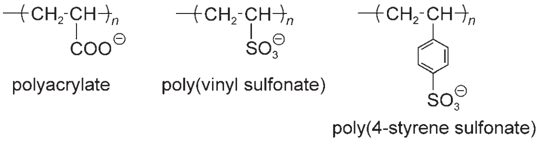
studies would provide a fundamental understanding of the various factors that govern the self-assembly of the metal complexes and the interplay of electrostatic and hydrophobic interactions between the polyelectrolytes and the metal complexes, which may serve as model systems for the understanding of the interactions between the metal complexes and various anionic biomolecules.

Results and Discussion

Four platinum(II)–alkynyl complexes **1**–**4** were synthesized by the reaction of Sonogashira coupling and characterized by ^{1}H NMR and IR spectroscopy, MS, and elemental analyses. Functionalization of the platinum(II)–terpyridyl–alkynyl complexes through the attachment of a hydroxymethyl functional group at the butadiynyl end in **1** and trimethylammonium groups to give dicationic species in **2**–**4** has rendered these complexes soluble in water. These complexes with different charges and degree of hydrophobicity were designed and employed for the present study. Of the four complexes, complex **3**, which contains an extra phenyl ring, is the most hydrophobic. For complexes **2**–**4**, the positively charged trimethylammonium group is furthest away from the platinum metal center and the terpyridine ligand in **3**, while complex **4**, which contains only one alkynyl unit, has the positively charged trimethylammonium group closest in distance from the platinum metal center and the terpyridine ligand.

Three polymers of different nature were also selected for the present investigation, namely polyacrylate, poly(vinyl sulfonate), and poly(4-styrene sulfonate). Poly(vinyl sulfonate) and poly(4-styrene sulfonate) in their acid forms carry the strongly acidic sulfonic acid groups, whereas polyacrylate in its acid form carries the mildly acidic carboxylic acid functions. Poly(4-styrene sulfonate), which contains a phenyl ring, is more hydrophobic than the other two polymers.



Electronic absorption and emission properties: The UV/Vis spectra of complexes **1**–**4** (30 μм) in a water–acetonitrile mixture (5 mм Tris-HCl, 10 mм NaCl, pH 7.5, 40 % CH_3CN) showed an intense band at 300–360 nm and a less intense band at 360–500 nm, typical of that found for alkynylplatinum(II)–terpyridine complexes (Figure 1). The electronic absorption spectral data are summarized in Table 1. Based on our previous work[14–18] and other related studies,[3–13] the high-energy bands of complexes **1**–**4** are tentatively assigned as intraligand π→π* transitions of the terpyridine and alkynyl ligand, while the lower energy bands are assigned as

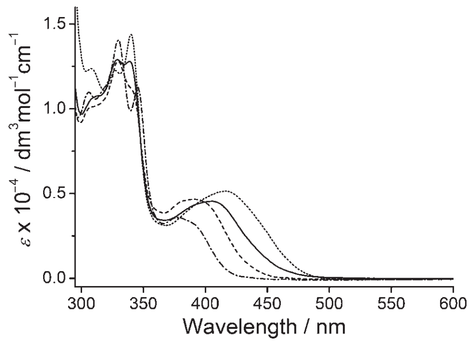


Figure 1. UV/Vis spectra of 30 μм of complexes **1** (——), **2** (– – –), **3** (•••••) and **4** (–•–•) in buffer–CH_3CN solvent mixture (Medium: 5 mм Tris-HCl, 10 mм NaCl, pH 7.5, 40 % CH_3CN).

Table 1. Photophysical data of complexes **1**–**4** in solution state.

	Absorption, λ_{max} [nm] (ε [$dm^3 mol^{-1} cm^{-1}$])[a]	Emission λ_{max} [nm][b]
1	238 (33665), 267 (19315), 278 (18090), 287 (22540), 313 (10765), 329 (12905), 339 (12805), 405 (4550)	788
2	237 (31240), 256 (22190), 277 (17940), 286 (24725), 308 (10110), 330 (12805), 340 (11225), 391 (4665)	742
3	242 (32720), 274 (40235), 285 (40480), 308 (12380), 327 (12270), 340 (14385), 417 (5145)	796
4	233 (27975), 254 (23725), 274 (21055), 283 (31930), 306 (10980), 330 (14070), 346 (11255), 378 (3590)	–[c]

[a] Measured in water–acetonitrile mixture (5 mм Tris-HCl, 10 mм NaCl, pH 7.5, 40 % CH_3CN) with 30 mм complexes. [b] Measured in buffer (5 mм Tris-HCl, 10 mм NaCl, pH 7.5) with 0.15 mм complexes. [c] Non-emissive

admixtures of metal-to-ligand charge-transfer (MLCT; $d\pi(Pt)\rightarrow\pi^*(tpy)$) and alkynyl-to-terpyridine ligand-to-ligand charge-transfer (LLCT) transitions. The observed shift of the energy of the absorption bands at 360–500 nm in the order: **4**(λ_{max}=378 nm; E=26455 cm^{-1}) > **2**(λ_{max}=391 nm; E=25575 cm^{-1}) > **1**(λ_{max}=405 nm; E=24691 cm^{-1}) > **3**(λ_{max}=417 nm; E=23981 cm^{-1}) is in line with the order of the increasing electron-richness of the alkynyl ligands. Complex **4**, which contains a positively charged electron-withdrawing trimethylammonium group closest to the platinum(II)–terpyridyl unit, possesses the least electron-rich alkynyl ligand, giving rise to the highest energy MLCT/LLCT transition. The lower electronic absorption energies of **2** than **4** and of **3** than **2** are also consistent with the increasing distance of the trimethylammonium moiety on going from **4** to **2** to **3**, which gave rise to the decreasing electron-withdrawing inductive effect of the $^{+}NMe_3$ group. A better π-donating ability of **3** is also anticipated with the presence of the phenyl moiety. Complex **1**, with the absence of the positively charged trimethylammonium unit on the alkynyl ligand, showed a lower energy MLCT/LLCT transition than **2**, as the neutral non-cationic hydroxymethylbutadiynyl ligand should behave as a better donor ligand.

When the percentage of acetonitrile in the solvent mixture was reduced, the UV/Vis spectra of complexes **1**–**4** (30 μM) all showed a decrease in the intensity of the low-energy MLCT/LLCT band and the emergence of a new lower energy absorption shoulder in the region of approximately 480–550 nm. Concentration-dependence studies of complexes **1**–**4** indicate that Beer's law is not obeyed in the low-energy absorption region at high complex concentrations. With reference to our previous studies,[14–18] the emergence of the low-energy absorption shoulder or tail originates from a metal–metal-to-ligand charge-transfer (MMLCT) transition as a result of close Pt–Pt contacts and π–π interactions in solution. The UV/Vis studies thus strongly suggest that these complexes show a tendency to exhibit ground-state complex aggregation in aqueous solution. This is not surprising; since the aromatic terpyridine ligand is relatively hydrophobic, and in addition, the planar structure of the complexes also facilitates their intermolecular stacking interactions. Since complex **1** has only one positive charge and thus is a monocationic complex, the electrostatic repulsive force between the complex molecules is the smallest, and so it has the strongest tendency of showing a background self-aggregation. The significantly tailed UV/Vis spectrum with noticeable absorption spanning all the way to about 600 nm is a strong indication of the background aggregation. Complex **4**, on the other hand, is dicationic and, in addition, the trimethylammonium charged group is positioned closest to the hydrophobic terpyridine moiety; hence there exists the strongest electrostatic repulsive force among the complex molecules that gives rise to the weakest tendency for background self-association to occur.

Corresponding emission studies of complex **1** (30 μM) in a water–acetonitrile mixture (5 mM Tris, 10 mM NaCl, pH 7.5, 0–40 % CH_3CN) showed the appearance of a weak emission band at around 800 nm, with the intensity becoming stronger with decreasing CH_3CN percentage. In pure buffer, besides complex **1**, complex **3** (30 μM) also showed a very weak emission band at around 800 nm. In addition, when a more concentrated complex solution was tested (0.15 mM), complexes **1**–**3** clearly showed emission bands at 788, 742, and 796 nm, respectively, while complex **4** remained non-emissive (Table 1). Based on the UV/Vis absorption studies, the emission bands, which appear in the NIR region, are tentatively assigned as triplet MMLCT emission,[14–18] resulting from the background self-aggregation of the platinum(II) complexes.

The influence of the solution ionic strength on the complex background self-aggregation in a pure aqueous buffer solution was also studied. The metal complex concentration was kept at 30 μM and the NaCl concentration was varied. For all four complexes, upon increasing the NaCl concentration, the UV/Vis spectra showed an increase in the intensity of the complex MMLCT bands, indicating an enhancement of background aggregation of the complexes (complex **1** precipitated at around 0.5 M NaCl concentration, while solutions of complexes **2**–**4** remained clear at 1 M NaCl concentration). Figure 2 shows the UV/Vis absorption spectra of **2** and **3** in the absence and in the presence of 1 M NaCl in buffer solution. Emission studies also revealed that with the increase of the NaCl concentration, complex **3** showed quite clear MMLCT band intensity enhancement, while complex **1** showed small MMLCT band intensity enhancement; complexes **2** and **4** did not show the appearance of the MMLCT emission band. These results indicate that the addition of NaCl increased the tendency of complex π–π hydrophobic stacking interactions, causing an increase in the background aggregation. Thus the effect of NaCl is exactly opposite to that of adding acetonitrile. The tendency for the complex to undergo background self-aggregation is also consistent with the nature and properties of the complexes as discussed earlier (vide supra).

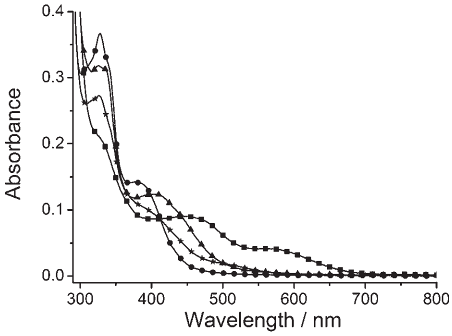


Figure 2. UV/Vis absorption spectra of **2** in the absence (●) and in the presence (⋆) of 1 M NaCl, and **3** in the absence (▲) and in the presence (■) of 1 M NaCl in buffer (5 mM Tris, 10 mM NaCl, pH 7.5) solution.

Polyelectrolyte-induced aggregation studies: When 30 μM of complex **1** was mixed with 180 μM of the polymers in a pure aqueous buffer solution (5 mM Tris-HCl, 10 mM NaCl, pH 7.5), drastic UV/Vis spectral changes were observed (see Figure 3). With polyacrylate and poly(vinyl sulfonate), new UV/Vis bands with peak maxima appeared at 550 nm ($E = 18181\ \text{cm}^{-1}$) and 552 nm ($E = 18116\ \text{cm}^{-1}$), respectively, in the electronic absorption spectra of **1**. With poly(4-styrene sulfonate), a weak broad absorption shoulder at longer wavelength (ca. 522 nm; $E = 19157\ \text{cm}^{-1}$) with no clear band maximum was observed. Similar UV/Vis spectral changes were generally observed with complexes **2** and **3** in the presence of the polymers, while complex **4** also gave similar changes in the UV/Vis absorption patterns, albeit considerably smaller changes were observed. The UV/Vis spectral changes of complex **2** in the presence of various polymers are shown in Figure 3.

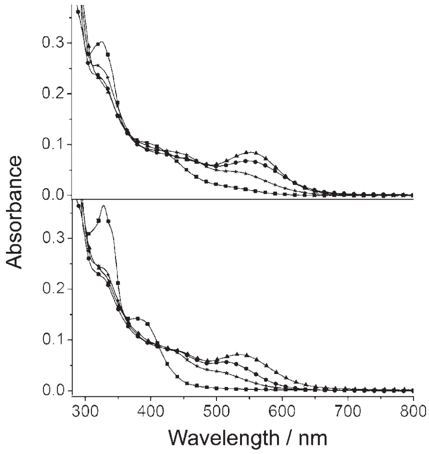


Figure 3. UV/Vis absorption spectra of 30 μM of **1** (top) and **2** (bottom) in the absence of polymers (■) and in the presence of the 180 μM of polyacrylate (●), poly(vinyl sulfonate) (▲), and poly(4-styrene sulfonate) (⋆) in buffer (5 mM Tris, 10 mM NaCl, pH 7.5) solution.

With reference to our previous work and other related studies, the new UV/Vis bands are assigned as MMLCT transitions.[14–18] The results clearly show that upon mixing of the complex with the polymer, electrostatic interactions between the complex and the polymer induced the self-assembly of the complex molecules through metal–metal and π–π stacking interactions. The properties of the complex self-assembly are apparently related to the properties of the complex molecules and the nature of the polymers. In general, more evident UV/Vis spectral changes typical of the formation of self-assembled aggregates were observed in complexes **1**–**3**, whereas for complex **4**, the UV/Vis changes were far less significant. For example, when the complexes were mixed with polyacrylate, the shifts in energy to the red from the complex monomer MLCT/LLCT absorption band to the corresponding complex aggregate absorption band were 6509, 6120, 6858, and 2005 cm^{-1} for complexes **1**–**4**, respectively.[19] For the same complex, poly(vinyl sulfonate) gave better performance than polyacrylate in inducing the self-assembly of the complex molecules, while poly(4-styrene sulfonate) was the least effective. For example, when poly(vinyl sulfonate) was mixed with complexes **1**–**3**, pronounced aggregate formation was observed, as reflected by the growth of the aggregate MMLCT absorption, with UV/Vis absorption energy changes between the monomer and the aggregate species of 6575, 6883, and 7118 cm^{-1}, whereas for poly(4-styrene sulfonate), the corresponding values were 5534, 5575, and 5930 cm^{-1} for complexes **1**–**3**, respectively. The larger spectral shifts of the aggregate MMLCT absorption from the corresponding monomeric MLCT/LLCT absorption in poly(vinyl sulfonate) than poly(4-styrene sulfonate) are indicative of a stronger metal–metal and π–π stacking interactions in the complex aggregates of the former, as the difference in the energy of the monomer and aggregate/oligomer absorption is a measure of the strength of these metal–metal and π–π interactions. It is likely that the stronger hydrophobic interactions between the more hydrophobic poly(4-styrene sulfonate) and the complex would reduce the tendency of the complex to undergo self-assembly. It is also interesting to note that in all cases complex **3** gave the largest UV/Vis band energy changes between the monomer and the aggregates regardless of the polymer used (6858, 7118, and 5930 cm^{-1} for polyacrylate, poly(vinyl sulfonate), and poly(4-styrene sulfonate), respectively), presumably because of its stronger hydrophobic characters.

The appearance of new emission bands upon mixing of complexes with various polyelectrolytes was observed. For the mixtures of 30 μM of complexes **1**–**4** with 180 μM of polyacrylate, new emission bands with peak maxima at 795, 764, 812, and 668 nm, respectively, were found (Figure 4). Similar observations were also identified by using poly(vinyl sulfonate) and poly(4-styrene sulfonate), and the corresponding emission spectra of **1** and **3** in the presence of the polymers, together with the emission spectra of their monomeric forms are depicted in Figure 5. As described earlier, these newly appeared emission bands are assigned as MMLCT triplet emission.[14–18] It is interesting to note that the relative positions of the emission bands appear to be related to the properties of the complex molecules. For the mixtures of the polymers with complexes **2**–**4**, complex **3** in all cases studied

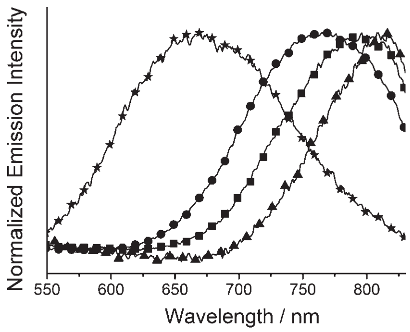


Figure 4. Normalized emission spectra of 30 μM of **1** (■), **2** (●), **3** (▲) and **4** (⋆) mixed with 180 μM of polyacrylate in buffer (5 mM Tris, 10 mM NaCl, pH 7.5) solution.

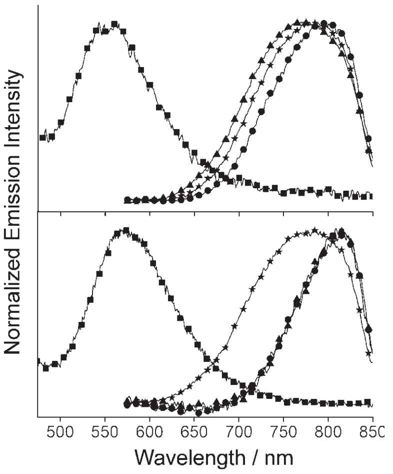


Figure 5. Normalized emission spectra of 30 μм of **1** (top) and **3** (bottom) in the absence of polymers (■) in buffer–CH_3CN solvent mixture and in the presence of the 180 μм of polyacrylate (●), poly(vinyl sulfonate) (▲), and poly(4-styrene sulfonate) (⋆) in buffer (5 mм Tris, 10 mм NaCl, pH 7.5) solution.

gave an emission band at the longest wavelength (with peak maxima at 812 (12315), 815 (12270), and 777 nm (12870 cm^{-1}) for polyacrylate, poly(vinyl sulfonate), and poly(4-styrene sulfonate) respectively), whereas complex **4** gave an emission band at the shortest wavelength (with peak maxima at ca. 668 (14970), 663 (15083), 639 nm (15649 cm^{-1}) for polyacrylate, poly(vinyl sulfonate), and poly(4-styrene sulfonate) respectively), which is consistent with the relative MLCT/LLCT UV/Vis absorption trends of these complex assemblies. As mentioned above, the degree of conjugation of the electron-donating alkynyl group and the strength of the electron-withdrawing positively charged trimethylammonium group determine the emission energy and consequently their relative band positions. Complex **4**, which has a trimethylammonium group separated by only one alkynyl attached to platinum, is the least electron-rich complex, whereas complex **3**, with an aryl-substituted alkynyl group, is the most electron-rich complex. In addition, as the electron-withdrawing trimethylammonium group moves further away from complexes **4** to **2** to **3**, the electron-withdrawing effect becomes less important. As a result, complex **4** gave an emission band of the highest energy, while complex **3** gave an emission band of the lowest energy. It is also interesting to note that complex **3** gave the highest energy MMLCT emission (780 nm) arising from aggregate formation upon addition of poly(4-styrene sulfonate) when compared with the other anionic polymers, polyacrylate (812 nm) and poly(vinyl sulfonate) (816 nm), as shown in Figure 5 (bottom). The occurrence of the MMLCT emission band at higher energy is indicative of a weaker tendency for the complex cations to stack with each other to form self-assembly. The reduced tendency of complex stacking is ascribed to the hydrophobic interactions between the relatively hydrophobic planar styryl groups and the more hydrophobic complex **3** bearing an aryl group on the alkynyl unit.

Effect of organic solvent: As mentioned above, the addition of acetonitrile can reduce hydrophobic π–π stacking interactions between the complex molecules and help to minimize the complex background self-aggregation. Our results show that the addition of acetonitrile can also effectively reduce the nonspecific hydrophobic interactions between the complex molecules and the polymer. For complex binding to poly(4-styrene sulfonate), in a pure aqueous buffer solution, only weak complex self-assembly was observed as shown in Figure 3. With the addition of 40% of acetonitrile, the background aggregation was suppressed, and more importantly, the performance of poly(4-styrene sulfonate)-induced complex self-assembly was found to improve significantly for complexes **1**–**3** as a result of the reduced nonspecific hydrophobic interactions. Much increased MLCT/LLCT UV/Vis absorption band intensity and clear band maximum were both observed. It is also interesting to note that since the hydrophobic interactions were largely suppressed, unlike in the pure aqueous buffer solution, in which complex **3** gave the largest UV/Vis band-energy changes between the monomer and the aggregates, complexes **1**–**3** all gave similar performance (energy difference: 6866, 6778, and 6590 cm^{-1} for complexes **1**–**3**, respectively).

Effect of polyelectrolyte concentration: The influence of the ratio of polymer to complex on the self-assembly properties of the complexes was studied. It was observed that addition of 0.5–1.5 times the amount of polyacrylate (based on carboxylate unit concentration) to a solution of complex **1** at a concentration of 30 μм gave rise to a slightly turbid solution, with strong light-scattering in both the UV/Vis and emission spectra. It is likely that with such relatively small amounts of polymer added, the negative charges on the polymer were largely neutralized upon binding to the metal complex, and since there would not be enough electrostatic repulsive forces between the polymer molecules for their dispersion, aggregation and precipitation resulted. In contrast, with a larger excess (3–48 times) of polyacrylate added, both the UV/Vis and emission spectra showed the formation of low-energy MMLCT absorption and emission bands, indicative of excellent complex self-assembly. It is interesting to note that the spectral changes are relatively insensitive to a variation in the amount of polymer added, indicating that in this polyacrylate concentration range the self-assembly of complex **1** took place to a significant extent and was not sensitive to the amount of polymer added. Similar results were obtained for complexes **2** and **3**. For complex **4**, the ^{3}MMLCT emission of complex aggregates gave the best results under the conditions of 3–6 times the amount of polyacrylate added, with a significant decrease of the ^{3}MMLCT emission intensity upon further increase of the polymer concentration, and the almost complete disappearance of the emission band when 24 times the amount of polyacrylate were added.

As shown in our previous study, in an organic solvent mixture, when the amount of base added was kept constant, addition of large excess of poly(acrylic acid) resulted in a significant decrease of the complex self-assembly, as a result of the "diluted" average number of negatively charged carboxylate functional groups on each polymer chain.[17] In an aqueous buffer solution, the situation is quite different. Since the solution pH was kept at a constant value of 7.5, addition of uncharged poly(acrylic acid) is equivalent to the addition of negatively charged polyacrylate, and the "dilution" effect is largely reduced. However, for complex **4**, since it has the weakest tendency to aggregate and self-assemble among the four complexes studied as a result of the strong repulsive forces that exist between the positively charged complex molecules, addition of a large excess of polyacrylate results in a stronger tendency to "dilute" the average number of complex molecules that would bind to each polymer chain, leading to a reduced ^{3}MMLCT emission.

Effect of solution buffer pH: The influence of the solution buffer pH on the self-assembly properties of the metal complexes was also investigated. For polyacrylate, since the carboxylic acid functionality is only mildly acidic, a large decrease of the buffer pH reduces the percentage of the ionized functional groups on each polymer chain, and thus influences the electrostatic binding of the positively charged complexes to the polymer chain and their self-assembly. It was found that for the mixture of 30 μM of complex **1** and 180 μM of polyacrylate, a decrease of the buffer pH from 7.5 to 6.0 and 5.0 caused only small UV/Vis spectral changes, suggesting that the assembly properties of the complex were little influenced in this pH region. Further decrease of the buffer pH to 4.0 and 3.0 caused the solution to turn turbid, indicating precipitation of the metal-complex-bound polymer, probably as a result of the reduced net negative charges on each polymer chain. At pH 2.0, the negative charges on the polymer were largely removed, and the solution appeared turbid, because of the decreased solubility of the polymer. However, with the addition of 20% acetonitrile, a clear yellow solution was obtained, with little complex aggregation observed. Upon bringing the solution back to basic conditions, both the UV/Vis and emission spectra showed the revival of complex assembly, as indicated by the observation of the low-energy MMLCT absorption and emission bands. Poly(vinyl sulfonate), on the other hand, was less susceptible to a change in pH since the sulfonic acid moiety is strongly acidic. The polymer-induced complex assembly was found to be little influenced by the buffer pH. At pH 2.0, a mixture of 30 μM of complex **1** and 180 μM of poly(vinyl sulfonate) still showed excellent complex self-assembly.

Effect of solution ionic strength: The effect of the ionic strength of the buffered solution on the polyelectrolyte-induced complex self-assembly was also studied. For a mixture of 30 μM of complex **2** and 180 μM of polyacrylate, UV/Vis spectral studies showed an increased background light-scattering as the concentration of NaCl was increased, indicating that the complex-bound polymer started to gradually aggregate, as a result of the increased strength of the hydrophobic interactions. Interestingly, a concomitant decrease in the MMLCT emission band intensity occurred (Figure 6), which indicates that the bound complex molecules were gradually replaced by sodium ions. With 0.34 M NaCl added, the complex molecules were completely replaced by sodium ions, and a clear yellow solution was obtained. Our results also show that because of the weaker tendency of complex **4** to aggregate, upon mixing of it with polyacrylate, the MMLCT emission band was completely gone with a total of only 0.1 M NaCl added.

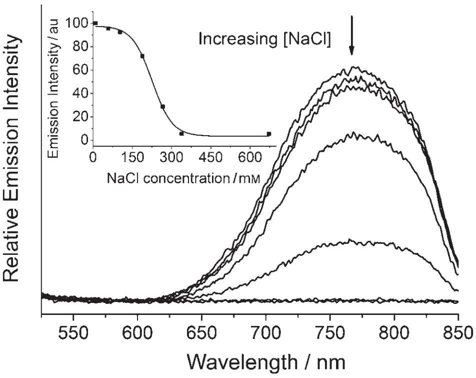


Figure 6. Emission spectra of 30 μM of complex **2** + 180 μM of polyacrylate, 5 mM Tris-HCl, 10 mM NaCl, pH 7.5, with increasing concentration of NaCl added. Inset: plot of emission intensity at 771 nm as a function of NaCl concentration.

Conclusions

In the present study, several polymers carrying multiple negatively charged functional groups have been shown to induce the aggregation and self-assembly of the positively charged water-soluble alkynylplatinum(II)–terpyridyl complexes in an aqueous medium. The driving forces for the induced aggregation and self-assembly were the result of electrostatic binding of the complex molecules to the polymer, metal–metal and ligand π–π stacking interactions, which gave rise to remarkable UV/Vis and emission spectral changes. The spectral changes were found to be related to the properties of the complexes as well as the polymers. The induced complex self-assembly was also influenced by the properties of the aqueous medium, for example, ionic strength, buffer pH, and the percentage of organic solvent added. The current approach could be potentially utilized to detect and characterize various charged polymers, as demonstrated by our parallel research work on single-stranded nucleic acids.[20] Similar to pyrene, which has been utilized to probe polymer conformational changes,[1] it is envisaged that our complex molecules could also be used for probing conformational changes in polymers through the observation of the ^{3}MMLCT emission. An additional advantage lies in the fact that besides the appearance of new emission bands, the significant UV/Vis spectral changes that give rise to visual color changes could also be utilized for the probing of polymer conformation studies.

Experimental Section

Materials and characterization: All reagents were used as received. Poly(acrylic acid) was synthesized as previously described with M_w of 10971.[17] Poly(vinylsulfonic acid sodium salt) with M_w of 4000–6000, poly(sodium 4-styrenesulfonate) with M_w of 70000, propargyl bromide, and propargyl alcohol were obtained from Aldrich.

^{1}H NMR spectra were recorded with a Bruker DPX-300 (300 MHz) or Bruker AVANCE 400 (400 MHz) Fourier transform NMR spectrometer at ambient temperature, with chemical shifts reported relative to tetramethylsilane. Positive FAB mass spectra were obtained by using a Finnigan MAT95 mass spectrometer. IR spectra were obtained as Nujol mulls on KBr disks on a Bio-Rad FTS-7 Fourier transform infrared spectrophotometer (4000–400 cm^{-1}). Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences. UV/Vis absorption spectra were recorded on a Cary 50 (Varian) spectrophotometer equipped with a Xenon flash lamp. Steady-state emission spectra were recorded using a Spex Fluorolog-2 Model F111 spectrofluorometer. The emission spectra were obtained with an excitation wavelength of 400 nm and were not corrected for PMT (photomultiplier tube) response. Standard quartz cuvettes with 1 cm path length were used for all spectral measurements. Unless specified otherwise, a buffer solution containing 5 mM Tris-HCl and 10 mM NaCl at pH 7.5 at ambient temperature was used throughout the current investigation.

Synthesis of the metal complexes: $[Pt(tpy)(C\equiv C\text{-}C\equiv CCH_2OH)][OTf]$ (**1**) was synthesized as reported previously.[20] The compounds $Me_3Si\text{-}C\equiv CC_6H_4CH_2Br$,[21] $Me_3SiC\equiv C\text{-}C\equiv CCH_2Br$,[22] $[Pt(tpy)Cl][OTf]$,[23] and $[Pt(tpy)(CH_3CN)][OTf]_2$[14,24] were synthesized according to literature methods.

Synthesis of functionalized alkynes

$[HC\equiv CC_6H_4CH_2NMe_3\text{-}4][OTf]$: A mixture of $Me_3SiC\equiv CC_6H_4CH_2Br$ (72 mg, 0.27 mmol) and trimethylamine (5 mL) was stirred in diethyl ether (5 mL) for 30 min, during which precipitates of the bromide salt were obtained. This was filtered and washed with diethyl ether, and was then dissolved in methanol and metathesized to the trifluoromethanesulfonic (triflate) salt with a saturated methanolic solution of silver triflate. During the metathesis reaction, the protecting group of the acetylene was also removed. Removal of the AgBr precipitate gave a colorless filtrate and the solvent was evaporated to dryness under reduced pressure. Extraction of the residue with chloroform, followed by solvent removal gave the desired product as a white solid. Yield: 70 mg (80 %); ^{1}H NMR (CD_3OD): $\delta = 3.10$ (s, 9H; $\text{-}NMe_3$), 3.70 (s, 1H; $\text{-}C\equiv CH$), 4.52 (s, 2H; $\text{-}CH_2\text{-}$), 7.55 (d, $J = 8.3$ Hz, 2H; $\text{-}C_6H_4\text{-}$), 7.62 ppm (d, $J = 8.3$ Hz, 2H; $\text{-}C_6H_4\text{-}$).

$[HC\equiv CCH_2NMe_3][OTf]$: The procedure was similar to that for $[HC\equiv CC_6H_4CH_2NMe_3\text{-}4][OTf]$ except that propargyl bromide (80 % in toluene; 1.25 g, 8.41 mmol) was used instead of $Me_3SiC\equiv CC_6H_4CH_2Br$ to give $[HC\equiv CCH_2NMe_3][OTf]$ as a pale yellow solid. Yield: 1.64 g (79 %); ^{1}H NMR (CD_3OD): $\delta = 3.26$ (s, 9H; $\text{-}NMe_3$), 3.55 (t, $J = 2.5$ Hz, 1H; -CH-), 4.39 (d, $J = 2.5$ Hz, 2H; $\text{-}CH_2\text{-}$).

$[Me_3SiC\equiv C\text{-}C\equiv CCH_2NMe_3][OTf]$: The procedure was similar to that for $[HC\equiv CC_6H_4CH_2NMe_3\text{-}4][OTf]$ except that $Me_3SiC\equiv C\text{-}C\equiv CCH_2Br$ (100 mg, 0.465 mmol) was used instead of $Me_3SiC\equiv CC_6H_4CH_2Br$ to give $[Me_3SiC\equiv C\text{-}C\equiv CCH_2NMe_3][OTf]$ as a white solid. Yield: 128 mg (86 %); ^{1}H NMR ($CDCl_3$): $\delta = 0.23$ (s, 9H; $Me_3Si\text{-}$), 3.36 (s, 9H; $\text{-}NMe_3$), 4.59 ppm (s, 2H; $\text{-}CH_2\text{-}$).

The freshly prepared functionalized alkynes were immediately used for the synthesis of the platinum(II) complexes as they were not very stable upon prolonged storage.

Synthesis of platinum(II) complexes

$[Pt(tpy)(C\equiv C\text{-}C\equiv CCH_2NMe_3)][OTf]_2$ (2): The complex was synthesized according to modification of a literature procedure.[14] A mixture of $[Me_3SiC\equiv C\text{-}C\equiv CCH_2NMe_3][OTf]$ (38 mg, 0.11 mmol) and potassium fluoride (13 mg, 0.22 mmol) in methanol (30 mL) was heated to 50 °C for 30 min, after which $[Pt(tpy)(CH_3CN)][OTf]_2$ (71 mg, 0.09 mmol) was added, and the resultant orange solution was stirred at 50 °C overnight. Solvent was then removed under reduced pressure, and the residue washed with a small amount of methanol and was then dissolved in acetonitrile. Subsequent recrystallization by diffusion of diethyl ether vapor into an acetonitrile solution of the product gave complex **2** as an orange red solid. Yield: 45 mg (57 %); ^{1}H NMR (CD_3CN): $\delta = 3.16$ (d, $J =$ 2.4 Hz, 9H; $\text{-}NMe_3$), 4.30 (d, $J = 2.4$ Hz, 2H; $\text{-}CH_2\text{-}$), 7.77–7.82 (m, 2H; tpy), 8.25–8.49 (m, 7H; tpy), 9.03 ppm (d, $J = 5.6$ Hz, 2H; tpy); IR (Nujol): $\tilde{\nu} = 2217$ (m; $C\equiv C$), 2083 (m; $C\equiv C$), 1157 cm^{-1} (m; $S{=}O$); positive-ion FAB-MS: m/z: 698 $[M{+}OTf]^+$; elemental analysis calcd (%) for $C_{25}H_{22}N_4F_6O_6PtS_2\cdot 2H_2O$: C 34.00, H 2.96, N 6.34; found: C 33.89, H 2.68, N 6.24.

$[Pt(tpy)(C\equiv CC_6H_4CH_2NMe_3\text{–}4)][OTf]_2$ (3): Complex **3** was synthesized by a modified procedure of the Cu^I-catalyzed reaction for platinum(II)–alkynyl complexes.[25] The chloroplatinum(II) precursor complex, $[Pt(tpy)Cl][OTf]$ (160 mg, 0.26 mmol) was dissolved in degassed DMF (10 mL) containing triethylamine (4 mL), followed by the addition of $[HC\equiv C\text{-}C_6H_4CH_2NMe_3\text{-}4][OTf]$ (215 mg, 0.67 mmol) and a catalytic amount of copper(I) iodide. The reaction mixture was stirred overnight at room temperature, after which diethyl ether (100 mL) was added and stirred for 10 min. The product was isolated by filtration, washed with diethyl ether, and dried. Subsequent recrystallization by diffusion of diethyl ether vapor into a solution of the product in acetonitrile gave complex **3** as a red solid. Yield: 146 mg (62 %); ^{1}H NMR (CD_3CN): $\delta = 3.05$ (s, 9H; $\text{-}NMe_3$), 4.43 (s, 2H; $\text{-}CH_2\text{-}$), 7.49 (d, $J = 8.2$ Hz, 2H; $\text{-}C_6H_4\text{-}$), 7.60 (d, $J =$ 8.2 Hz, 2H; $\text{-}C_6H_4\text{-}$), 7.75 (t, $J = 5.8$ Hz, 2H; tpy), 8.22–8.41 (m, 7H; tpy), 9.09 ppm (d, $J = 5.8$ Hz, 2H; tpy); IR (Nujol): $\tilde{\nu} = 2120$ (m; $C\equiv C$), 1153 cm^{-1} (m; $S{=}O$); positive-ion FAB-MS: m/z: 750 $[M{+}OTf]^+$; elemental analysis calcd (%) for $C_{29}H_{26}N_4F_6O_6PtS_2\cdot H_2O$: C 37.95, H 3.08, N 6.10; found: C 37.76, H 3.09, N 5.95.

$[Pt(tpy)(C\equiv C\text{-}CH_2NMe_3)][OTf]_2$ (4): The synthetic procedure for complex **4** was similar to that for complex **3**, except that $[HC\equiv CCH_2NMe_3]$-$[OTf]$ (103 mg, 0.415 mmol) was used instead of $[HC\equiv CC_6H_4\{CH_2NMe_3\}\text{-}4][OTf]$ to give complex **4** as a yellow solid. Yield: 106 mg (62 %); ^{1}H NMR ($[D_6]$DMSO): $\delta = 3.19$ (s, 9H; $\text{-}NMe_3$), 4.54 (s, 2H; $\text{-}CH_2\text{-}$), 7.90 (t, $J = 5.6$ Hz, 2H; tpy), 8.52 (t, $J = 7.8$ Hz, 2H; tpy), 8.58–8.70 (m, 5H; tpy), 9.04 ppm (d, $J = 5.6$ Hz, 2H; tpy); IR (Nujol): $\tilde{\nu} = 2145$ (m; $C\equiv C$), 1160 cm^{-1} (m; $S{=}O$); positive-ion ESI: m/z 262.6 $[M]^{2+}$; elemental analysis calcd (%) for $C_{23}H_{22}N_4F_6O_6PtS_2\cdot 0.5\,CH_3CN$: C 34.15, H 2.81, N 7.47; found: C 34.33, H 3.02, N 7.49.

Acknowledgements

V.W.-W.Y. acknowledges receipt of the Distinguished Research Achievement Award from The University of Hong Kong. This work has been supported by a Central Allocation Vote (CAV) Grant (Project No. HKU 2/05C) and a National Natural Science Foundation of China and the Research Grants Council of Hong Kong Joint Research Scheme (NSFC-RGC Project No. N HKU 737/06) from the Research Grants Council of Hong Kong Special Administrative Region, P. R. China.

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Received: February 14, 2008