Noncovalent Interactions

Polymer-Induced Self-Assembly of Alkynylplatinum(II) Terpyridyl Complexes by Metal···Metal/π···π Interactions**

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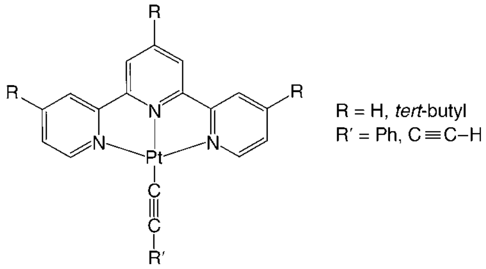
The intriguing structures and bonding properties of square-planar platinum(II) complexes have attracted long-standing interest,[1] and more-so recently with the growing interest in the spectroscopic properties associated with this class of compounds.[2–9] These complexes are known to display a strong tendency towards the formation of highly ordered extended linear chains or oligomeric structures in the solid state.[1e,2,4,5a] A particularly interesting class of platinum(II) complexes is the polypyridyl complexes. The extent of the d^8–d^8 metal–metal interaction and the π–π stacking of the polypyridyl ligand have led to the observation of interesting spectroscopic and luminescence properties,[2–5] and recent reports based on the utilization of these observations for molecular recognition, chemosensing, and optoelectronic applications have also been published.[5,6c,10]

Recently, we reported the synthesis of a butadiynylplatinum(II)–terpyridyl complex and showed that changing the solvent composition from pure acetonitrile to an acetonitrile/diethyl ether mixture resulted in the complex changing from its monomeric state to an aggregated state in solution, and drastic changes in the solution color were observed.[5] Since the platinum(II) complex ion carries a positive charge, to maintain a charge balance and a neutral environment, its aggregation may also induce a reorganization of the counter-anion. Similarly, assembly of the counteranions in an orderly manner may also influence the self-assembly of the positively charged platinum(II) units by an aggregation process. An example of an ordered array of counteranions is the class of polyelectrolyte anions, where negatively charged functional groups are connected to a polymer chain.[11] Polyelectrolyte anions include important macromolecules such as nucleic acids and many types of synthetic polymers, and herein we report the use of a polycarboxylate in the self-assembly of platinum(II) complexes. We found that the polymer itself could, upon deprotonation, induce the self-assembly of the terpyridylplatinum(II) complexes, without the need to change the solvent composition, thus giving rise to remarkable UV/Vis and luminescence changes.

Poly(acrylic acid) was obtained by acid hydrolysis of poly[1-(ethoxy)ethyl acrylate], which was prepared by atom-transfer radical polymerization (ATRP) of the corresponding monomer.[12] Three alkynylplatinum(II) complexes, [Pt(tpy)(C≡C−C≡CH)]OTf (**1**),[5] [Pt(tpy)(C≡C−Ph)]OTf (**2**),[6c] and [Pt(tBu$_3$-tpy)(C≡C−C≡CH)]OTf (**3**)[5] (tpy = 2,2′:6′,2″-terpyridine; OTf = trifluoromethanesulfonate; tBu$_3$-tpy = 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine), were tested in this investigation (Scheme 1). Addition of complex **1** or **2** to a solution of poly(acrylic acid) in the presence of tetrabutylammonium hydroxide (TBAH) as a base in an organic medium resulted in a remarkable change in the color and the UV/Vis absorption spectra (Figure 1). A color change of the solution of complex **1**, from light-yellow to pink/red occurred, and, along with a decrease in the intensity of the absorbance bands at 338 and 408 nm, a new band appeared at 543 nm. Similar observations were found for complex **2**, with a decrease in the intensity of the absorbance bands at about 330 and 430 nm and the formation of new bands at about 480 and 580 nm. The solutions were found to be very stable, with



Scheme 1. Structure of the platinum(II) complexes.

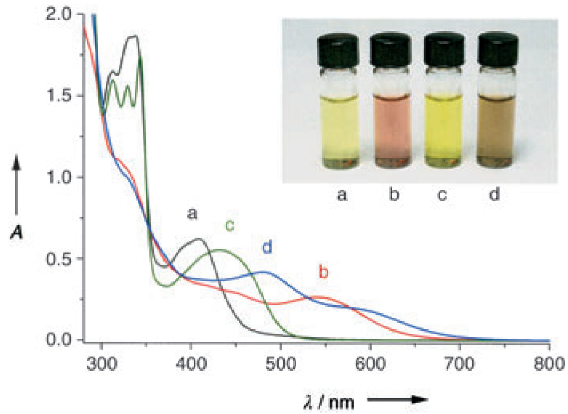


Figure 1. UV/Vis absorbance changes of the complex (0.15 mM) in a mixture of MeOH and CH$_3$CN (2:1, v/v) upon addition of poly(acrylic acid) (0.45 mM carboxylic acid unit) and TBAH (0.45 mM): a) **1**; b) **1** + poly(acrylic acid) + TBAH; c) **2**; d) **2** + poly(acrylic acid) + TBAH. Inset: photographs of the solution mixtures (a)–(d).

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no precipitate formation after standing at ambient temperature for several days. Addition of a solution of complexes **1** or **2** in acetonitrile to either a methanolic solution of poly(acrylic acid) or TBAH alone did not yield any observable changes in the UV/Vis absorption spectra, thereby indicating that the changes are associated with the presence of both poly(acrylic acid) and a base, that is, the deprotonation of poly(acrylic acid) to the anionic polyacrylate.

On the basis of our previous work[5] and other related studies,[3,4] the newly formed bands of complexes **1** and **2** at longer wavelength were assigned as metal-metal-to-ligand charge-transfer (MMLCT) transitions resulting from the aggregation of these complexes, presumably through metal⋯metal and/or π⋯π interactions. These results suggest that the electrostatic binding of the positively charged platinum(II) complex ions to the negatively charged polymer chain brings the platinum(II) complex ions into close proximity with each other and thus induces their aggregation (Figure 2). The decrease in the absorbance intensity in the 330–430 nm region, which is typical of a metal-to-ligand charge transfer (MLCT) transition of a monomeric terpyridylplatinum(II) complex, further supports the conversion of the monomeric complex into an aggregated form.

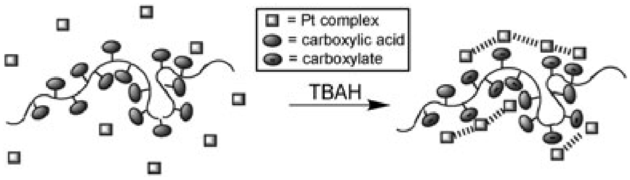

Figure 2. Aggregation of the platinum(II) complex ions in the presence of a base and a polycarboxylic acid.

Addition of complex **3** to a solution of poly(acrylic acid) in the presence of TBAH did not yield any observable color change. Apparently, the bulky *tert*-butyl groups on the terpyridine ring in **3** prevent aggregation of the complex from taking place. A number of small carboxylic acids were also tested, including monocarboxylic acids (acetic acid, acrylic acid, isobutyric acid), dicarboxylic acids (fumaric acid, maleic acid, oxalic acid, malonic acid, succinic acid, glutaric acid), and a tricarboxylic acid (citric acid). No observable color change was observed upon mixing complex **1** or **2** (0.15 mM) with such small mono-, di-, or tricarboxylic acids in the presence of TBAH at different complex/carboxylic acid group/base molar ratios (1/3/3, 2/3/3, and 3/3/3). This result strongly suggests that the aggregation of the metal complex is induced only by the polyacrylate and not by the smaller carboxylates. The observed differences in behavior between poly(acrylic acid) and the smaller carboxylic acids are presumably a result of the high density of negative charge.

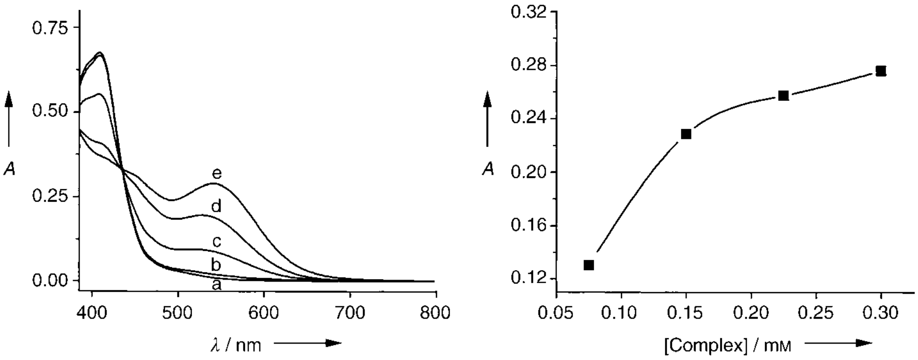

Figure 3. Left: Curve a: complex **1** (0.15 mM) in MeOH/CH$_3$CN (2:1, v/v); curves b–e: complex **1** (0.15 mM) + poly(acrylic acid) (22.5, 15, 7.5, 0.45 mM carboxylic acid unit, respectively) + TBAH (0.45 mM) in MeOH/CH$_3$CN (2:1, v/v). Right: complex **1** + poly(acrylic acid) (0.225 mM carboxylic acid unit) + TBAH (0.225 mM) in MeOH/CH$_3$CN (2:1, v/v).

The aggregation process was found to be fully reversible. Thus, addition of HCl to a solution of **1** in the aggregated state converted the red solution back into the yellow solution characteristic of the original monomeric state, by protonation of the polyanion to form the polyacid. Addition of TBAH to the yellow solution caused the solution to become red again. The corresponding changes in the UV/Vis absorption spectra confirmed the reversible interconversion between the aggregated state and the monomeric state upon repeated addition of acid and base. In addition, positive-ion ESI-MS experiments confirmed that no change or degradation of the platinum(II) complexes occurred and their identity remained intact during the process of adding acid and base.

It is interesting to note that when the metal complex loading per polymer chain was lowered, that is, when more poly(acrylic acid) was added, no induction of complex aggregation was observed. For example, the UV/Vis absorption spectra for a mixture containing complex **1** (0.15 mM), poly(acrylic acid) (22.5 mM carboxylic acid unit), and TBAH (0.45 mM) [complex/carboxylic acid unit/base = 1/150/3 in MeOH/CH$_3$CN (2:1, v/v)] was very similar to that of a solution of complex **1** (0.15 mM) in the same solvent. As the concentration of the poly(acrylic acid) was gradually reduced, the MMLCT band began to appear and became more intense (Figure 3, left). Since the concentration of the base remained constant throughout the experiments, the use of a higher poly(acrylic acid) concentration would give rise to a lower average number of deprotonated carboxylic acid groups on each polymer chain, thus rendering them widely spaced and isolated, which, in turn, would lead to the platinum complexes bound to the anionic carboxylate groups also becoming more isolated from each other and thus preventing aggregate formation.

When the concentration of the polymer and base was kept constant and the concentration of the complex was increased, the MMLCT band intensity at peak maximum (543 nm) increased gradually (Figure 3, right), which suggests that a higher degree of ordering occurs at higher concentrations of the complex. With the concentration of complex **1** fixed and equimolar amounts of the carboxylic acid unit and base added, the absorbance of the MMLCT band of the complex at 543 nm reached a maximum at a complex/carboxylic acid unit/base molar ratio of 1/3/3; further increase of the poly(acrylic acid) and base concentration caused a decrease in the absorbance. In addition, concomitant with the color and absorbance changes, a new emission band, attributed to a ^{3}MMLCT emission, appeared at about 800 nm (Figure 4), and again reached maximum intensity at the complex/carboxylic acid unit/base molar ratio of 1/3/3. This new emission band disappeared completely when HCl was added to the solution and could be regenerated by adding TBAH. Similar results were observed with complex **2**, with an emission maximum at about 840 nm. These results indicate that the availability of too many polymer binding sites reduces the tendency of the complex to aggregate. More importantly, the same trend in the changes of the UV/Vis absorbance and emission intensity suggests that they have a similar origin—the self-assembly of the complex molecules into the aggregated state. Further support for such a ^{3}MMLCT transition came from solid-state emission studies,[5,6c] as well as the observation of an excitation band at about 543 nm in the excitation spectrum of complex **1** monitored at the ^{3}MMLCT emission band.

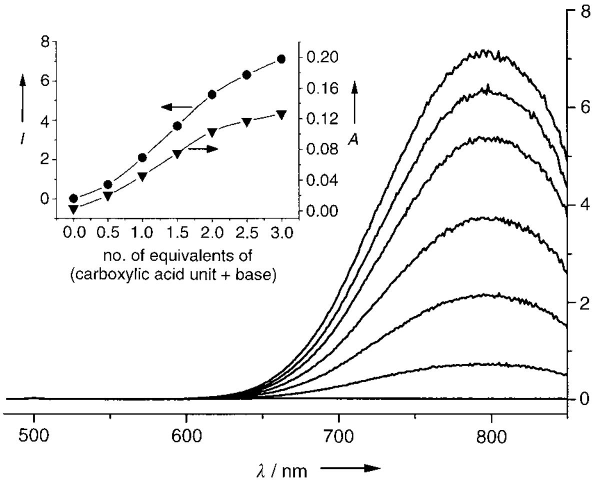

Figure 4. Emission enhancement of **1** (0.075 mM) upon addition of equimolar amounts of carboxylic acid unit and base. Inset: Plot of the emission intensity at 800 nm or absorbance at 543 nm versus the ratio of the polymer and base added. The emission intensities are expressed in arbitrary units.

In conclusion, we have demonstrated for the first time that a polyelectrolyte, namely poly(acrylic acid), upon deprotonation can indeed induce self-assembly of terpyridylplatinum(II) complexes, and, in turn, induce remarkable UV/Vis and emission intensity changes. It is possible that the UV/Vis and emission properties could be finely tuned by selection of other suitable metal complexes, optimization of assay conditions, and varying the structure of the polyelectrolyte. We envisage that such changes in the electronic absorption and luminescence properties may be exploited for probing conformational and microenvironmental changes in polymers and biomolecules.

Experimental Section

The monomer 1-(ethoxy)ethyl acrylate was prepared from the addition reaction of ethyl vinyl ether with acrylic acid.[12e] CuCl complexed with *N,N',N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) was used as the catalyst, with methyl 2-bromopropionate as the initiator and toluene as the solvent. The molecular weight of the resulting polymer before deprotection was determined by GPC (calibration standard: poly(methyl methacrylate) (PMMA); eluent: *N*-methylpyrrolidone (NMP); $M_n = 8612$, $M_w = 10971$, PDI = 1.27), which gave an average of about 59 carboxylic acid functional groups on each polymer chain.

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[1] a) *Extended Linear Chain Compounds, Vol. 1* (Ed.: J. S. Miller), Plenum, New York, **1982**; b) J. S. Miller, A. J. Epstein, *Prog. Inorg. Chem.* **1976**, *21*, 1; c) M. Atoji, J. W. Richardson, R. E. Rundle, *J. Am. Chem. Soc.* **1957**, *79*, 3017; d) P. M. Kiernan, A. Ludi, *J. Chem. Soc. Dalton Trans.* **1978**, 1127; e) R. S. Osborn, D. Rogers, *J. Chem. Soc. Dalton Trans.* **1974**, 1002.

[2] a) V. M. Miskowski, V. H. Houlding, *Inorg. Chem.* **1989**, *28*, 1529; b) V. M. Miskowski, V. H. Houlding, *Inorg. Chem.* **1991**, *30*, 4446; c) V. H. Houlding, V. M. Miskowski, *Coord. Chem. Rev.* **1991**, *111*, 145.

[3] a) H. K. Yip, C.-M. Che, Z. Y. Zhou, T. C. W. Mak, *J. Chem. Soc. Chem. Commun.* **1992**, 1369; b) J. A. Bailey, V. M. Miskowski, H. B. Gray, *Inorg. Chem.* **1993**, *32*, 369; c) M. G. Hill, J. A. Bailey, V. M. Miskowski, H. B. Gray, *Inorg. Chem.* **1996**, *35*, 4585.

[4] a) J. A. Bailey, M. G. Hill, R. E. Marsh, V. M. Miskowski, W. P. Schaefer, H. B. Gray, *Inorg. Chem.* **1995**, *34*, 4591; b) R. Büchner, C. T. Cunningham, J. S. Field, R. J. Haines, D. R. McMillin, G. C. Summerton, *J. Chem. Soc. Dalton Trans.* **1999**, 711.

[5] V. W.-W. Yam, K. M.-C. Wong, N. Zhu, *J. Am. Chem. Soc.* **2002**, *124*, 6506.

[6] a) G. Arena, G. Calogero, S. Campagna, L. M. Scolaro, V. Ricevuto, R. Romeo, *Inorg. Chem.* **1998**, *37*, 2763; b) S. W. Lai, M. C. W. Chan, K.-K. Cheung, C.-M. Che *Inorg. Chem.* **1999**, *38*, 4262; c) V. W.-W. Yam, R. P.-L. Tang, K. M.-C. Wong, K.-K. Cheung, *Organometallics* **2001**, *20*, 4476; d) D. R. McMillin, J. J. Moore, *Coord. Chem. Rev.* **2002**, *229*, 113; e) V. W.-W. Yam, K. M.-C. Wong, N. Zhu, *Angew. Chem.* **2003**, *115*, 1438; *Angew. Chem. Int. Ed.* **2003**, *42*, 1400.

[7] a) J. A. Zuleta, C. A. Chesta, R. Eisenberg, *J. Am. Chem. Soc.* **1989**, *111*, 8916; b) J. A. Zuleta, M. S. Burbery, R. Eisenberg, *Coord. Chem. Rev.* **1990**, *97*, 47; c) W. Paw, R. J. Lachicotte, R. Eisenberg, *Inorg. Chem.* **1998**, *37*, 4139.

[8] a) M. Hissler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte, R. Eisenberg, *Inorg. Chem.* **2000**, *39*, 447; b) C. E. Whittle, J. A. Weinstein, M. W. Geore, K. S. Schanze, *Inorg. Chem.* **2001**, *40*, 4053; c) S. C. Chan, M. C. W. Chan, Y. Wang, C. M. Che, K. K. Cheung, N. Zhu, *Chem. Eur. J.* **2001**, *7*, 4180; d) W. Lu, M. C. W. Chan, N. Zhu, C. M. Che, Z. He, K. Y. Wong, *Chem. Eur. J.* **2003**, *9*, 6155.

[9] a) C. E. Buss, C. E. Anderson, M. K. Pomije, C. M. Lutz, D. Britton, K. R. Mann, *J. Am. Chem. Soc.* **1998**, *120*, 7783; b) C. E. Buss, K. R. Mann, *J. Am. Chem. Soc.* **2002**, *124*, 1031.

[10] a) A. J. Goshe, I. M. Steele, B. Bosnich, *J. Am. Chem. Soc.* **2003**, *125*, 444; b) V. Adamovich, J. Brooks, A. Tamayo, A. M. Alexander, P. I. Djurovich, B. W. D. Andrade, C. Adachi, S. R. Forrest, M. E. Thompson, *New J. Chem.* **2002**, *26*, 1171.

[11] a) *Handbook of Polyelectrolytes and Their Applications* (Eds.: S. K. Tripathy, J. Kumar, H. S. Nalwa), American Scientific, Stevenson Ranch, **2002**; b) F. M. Gray, *Polymer Electrolytes*, The Royal Society of Chemistry, Cambridge, **1997**; c) H. Dautzenberg, W. Jaeger, J. Kötz, B. Philipp, Ch. Seidel, D. Stscherbina, *Polyelectrolytes: Formation, Characterization and Application*, Hanser, Munich, **1994**.

[12] a) K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921; b) D. A. Shipp, J.-L. Wang, K. Matyjaszewski, *Macromolecules* **1998**, *31*, 8005; c) K. A. Davis, K. Matyjaszewski, *Macromolecules* **2000**, *33*, 4039; d) S. Lu, Q.-L. Fan, S.-Y. Liu, S.-J. Chua, W. Huang, *Macromolecules* **2002**, *35*, 9875; e) H. Zhang, E. Ruckenstein, *Macromolecules* **1998**, *31*, 7575.