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Luminescent Dinuclear Platinum(II) Terpyridine Complexes with a Flexible Bridge and "Sticky Ends"**

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Luminescent square-planar d^8 platinum(II) complexes have attracted much attention because of their intriguing photophysical and spectroscopic properties.[1–8] In particular, platinum(II) derivatives with terpyridyl ligands and their analogues have been widely studied for their luminescence behavior.[3–7] Owing to their planar coordination geometry, which permits easy access to important frontier orbitals of the metal center, d^8–d^8 metal–metal interactions as well as π–π interactions between chromophores of the polypyridyl plat-

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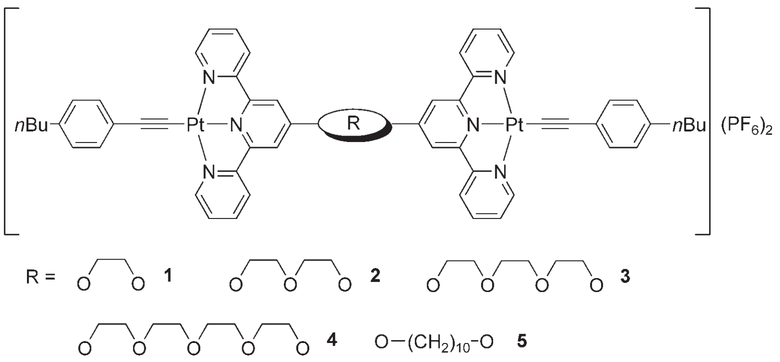
inum(II) complexes lead to extensive polymorphism of these complexes in the solid state.[5a,c,7,8]

Recently, we showed that mononuclear alkynyl platinum(II) terpyridyl complexes could show interesting intermolecular aggregation and oligomerization phenomena in the solution state with drastic color changes and luminescence enhancement caused by polymer-induced or solvent-induced self-assembly of the metal complexes.[5] Tunable solution-state intermolecular Pt···Pt interactions and π–π stacking were suggested to be responsible for these remarkable spectroscopic changes upon variations in the solvent composition, counteranion, and pH value of the polyelectrolyte. However, the related intramolecular association or self-assembly of this class of complexes in solution were not extensively explored.[3b–d]

In this context, we prepared a series of dinuclear alkynyl platinum(II) terpyridyl complexes in which the two platinum(II) units are linked through a flexible bridge (Scheme 1) and studied their solution-state intramolecular aggregation properties. The two platinum(II) terpyridyl moieties of the molecule showed a high tendency towards intramolecular association. The effect of temperature on the aggregation and deaggregation properties of these dinuclear platinum(II) complexes was investigated by ^{1}H NMR, electronic absorption, and emission spectroscopy. The present work demonstrates the versatility of the platinum(II) terpyridyl chromophore as reporters of intramolecular association and the ability of metal–metal and π–π interactions in providing the driving force for intramolecular aggregation or "molecular sticking" that can be controlled by temperature modulation.

The dinuclear chloroplatinum(II) precursor complexes were synthesized according to a modified literature synthesis for $[Pt(tpy)Cl]^+$ (tpy = 2,2′:6′,2″-terpyridyl)[7a,9] by the reaction of the corresponding bridged terpyridyl ligands with $K_2[PtCl_4]$ in a 1:2 molar ratio. Reaction of the newly synthesized dinuclear chloroplatinum(II) precursors and 4-*n*-butylphenylacetylene in the presence of a base and a catalytic amount of copper(I) iodide, followed by a metathesis reaction in saturated methanolic ammonium hexafluorophosphate solution gave the dinuclear platinum(II) complexes $[(4\text{-}n\text{Bu-}C_6H_4C{\equiv}C)Pt(tpy{-}R{-}tpy)Pt(C{\equiv}C\text{-}C_6H_4\text{-}n\text{Bu-4})](PF_6)_2$ (R = OCH_2CH_2O **1**; $O(CH_2CH_2O)_2$ **2**; $O(CH_2CH_2O)_3$ **3**; $O(CH_2CH_2O)_4$ **4**; $O(CH_2)_{10}O$ **5**) in moderate yield. All the complexes gave satisfactory elemental analyses and were characterized by ^{1}H NMR spectroscopy, IR spectroscopy, and FAB mass spectrometry.



Scheme 1. Structure of the dinuclear alkynyl platinum(II) terpyridyl complexes **1**–**5**.

The ^{1}H NMR spectra of **1** and **2** in [D$_6$]DMSO at 25 °C showed sharp signals with chemical shifts and splitting patterns consistent with their chemical formulation. In contrast, broad signals that were relatively upfield-shifted and poorly resolved were observed for **3**–**5** under the same conditions. Attempts to record the ^{1}H NMR spectra of dilute solutions of **3**–**5** by reducing the concentration from 10^{-3} to 10^{-5} M to minimize intermolecular interactions did not yield any improvement in the bandwidth and the resolution of the NMR signals. However, increasing the solution temperature dramatically improved the resolution of the ^{1}H NMR signals of **3**–**5**, and the signals became sharpened. At 90 °C, the signals were well resolved with a downfield shift of the signals corresponding to the terpyridyl protons. The ^{1}H NMR spectra of **4** in [D$_6$]DMSO at different temperatures are shown in Figure 1. The upfield shift and broadening of the proton resonances of **3**–**5** at lower temperature are independent of concentration and suggest the presence of molecular interactions or self-assembly processes, probably intramolecular in nature.

Similar line broadening and upfield shifts were also observed in planar aromatic metal complexes[10] and were ascribed to self-assembly. It is likely that complexes **1** and **2**, which have short bridging ligands, do not undergo self-association or aggregation at room temperature, as revealed by their NMR spectra. In contrast, complexes **3**–**5** with longer flexible bridges could readily self-associate and aggregate in solution, with complexes **4** and **5** occurring more readily than the shorter chain **3**, as reflected in their variable-temperature NMR spectra. As a result, intramolecular aggregation is predominant in solution at room temperature for **3**–**5**, whereas deaggregation takes place when the samples are heated (Figure 2). Self-assembly of two platinum(II) terpyridyl units in a molecule

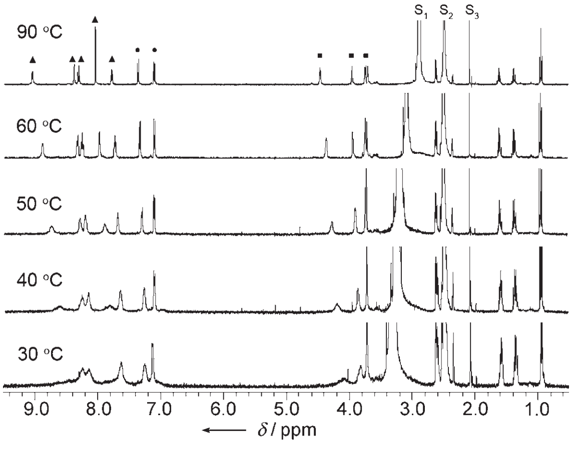


Figure 1. Variable-temperature ^{1}H NMR spectra of **4** in [D$_6$]DMSO. Proton signals correspond to the terpyridyl moiety (▲), the phenyl ring (●), and the oligo(oxyethylene) group (■). S$_1$, S$_2$, and S$_3$ represent the H_2O, DMSO, and acetonitrile signals, respectively.

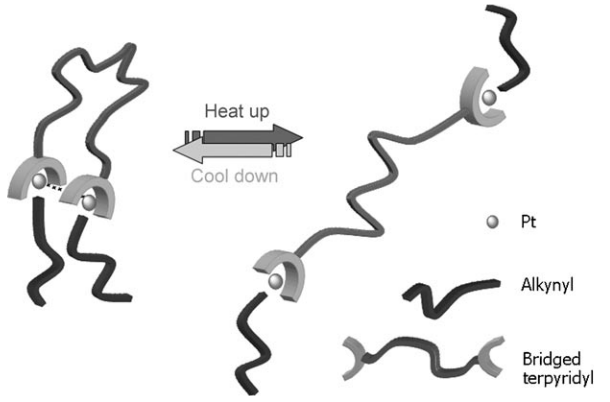


Figure 2. Aggregation and deaggregation of the platinum(II) complexes by temperature modulation.

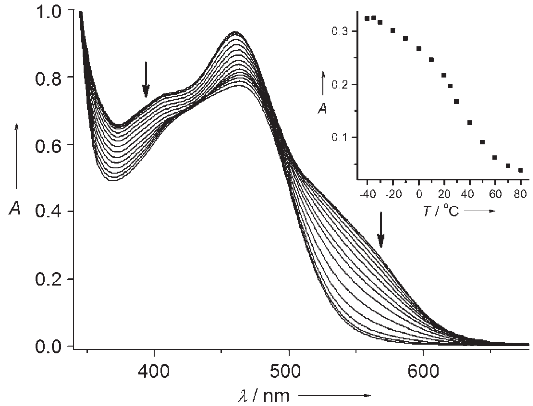


Figure 3. UV/Vis spectra of **4** with increasing temperature from −40 to 80 °C. Inset: Absorbance at 555 nm against temperature.

gave rise to intramolecular Pt···Pt and π–π stacking interactions that accounted for the NMR signal broadening and upfield shift. The length of the bridge was shown to play an important role in governing the occurrence and the extent of intramolecular aggregation.

Dissolution of **1**–**5** in acetonitrile gave yellow-to-orange solutions with similar UV/Vis absorption patterns at 25 °C that consisted of intense absorption bands at 280–350 nm and a low-energy absorption at 400–480 nm. With reference to previous spectroscopic work on alkynyl platinum(II) terpyridyl complexes,[4a,c,d,5] the higher-energy absorption bands are assigned as intraligand (IL) [π→π*] transitions of the terpyridyl and alkynyl ligands, whereas the low-energy absorption is assigned as a metal-to-ligand charge-transfer (MLCT) [dπ(Pt)→π*(tpy)] transition mixed with an alkynyl-to-terpyridine ligand-to-ligand charge-transfer (LLCT) [π(C≡C)→π*(tpy)] transition.

Electronic absorption spectra of the complexes in acetonitrile were measured in the temperature range between −40 and 80 °C. In general, temperature effects on the spectral changes of **1** and **2** were negligible when compared with those of **3**–**5**. At low temperature (−40 °C), a prominent absorption shoulder at about 550 nm appears in **3**–**5**, which is in a region typical of metal-metal-to-ligand charge-transfer (MMLCT) transitions.[5] The absorbance of this shoulder decreased with increasing temperature of the sample solutions and approached zero upon heating to 80 °C. Solutions of **4** and **5** change color from orange to yellow upon heating. The absorption spectra of **4** are shown in Figure 3 with an inset showing the absorbance changes at 555 nm as a function of temperature. It is believed that the newly formed absorption shoulder originates from the MMLCT transition as a result of intramolecular association within the complexes brought about by the Pt···Pt and π–π interactions between the platinum(II) terpyridyl moieties. The sigmoid curve in the inset of Figure 3 reflects the degree of aggregation and indicates complete aggregation at low temperature and almost complete deaggregation at elevated temperature. The electronic spectra agree well with the proton NMR studies, which suggest that **3**–**5** form aggregates at room temperature and at lower temperature, whereas **1** and **2** do not, even when they are cooled down to the freezing point of the solvent.

With reference to the analogous DNA hairpin studies,[11] the equilibrium absorbance spectra were analyzed in terms of a two-state van't Hoff model.[12] The melting temperatures T_m for **4** and **5** are 299 and 287 K, respectively. The enthalpy changes $\Delta H°$ for the deaggregation process (Figure 2) of **4** and **5** were determined to be $+37\,\mathrm{kJ\,mol^{-1}}$ ($+8.8\,\mathrm{kcal\,mol^{-1}}$) and $+35\,\mathrm{kJ\,mol^{-1}}$ ($+8.5\,\mathrm{kcal\,mol^{-1}}$), respectively, and the entropy changes $\Delta S°$ were found to be $+124\,\mathrm{J\,mol^{-1}\,K^{-1}}$ ($+29.6\,\mathrm{cal\,mol^{-1}\,K^{-1}}$) and $+123\,\mathrm{J\,mol^{-1}\,K^{-1}}$ ($+29.5\,\mathrm{cal\,mol^{-1}\,K^{-1}}$), respectively.

In acetonitrile at 25 °C, all complexes except **2** are emissive upon excitation at $\lambda > 400$ nm. Complex **1** exhibits an emission band at 658 nm, which was assigned to an excited state of predominantly ^{3}MLCT character, whereas the emission maxima of **3**–**5** are significantly red-shifted to about 830 nm. This substantial red shift, together with the self-association revealed from ^{1}H NMR and UV/Vis absorption studies, suggested that the emission is of ^{3}MMLCT origin, similar to that found for other alkynyl platinum(II) terpyridyl systems.[5] The change in the emission origin from the short-chain complex **1** to the longer-chain complexes **3**–**5** clearly demonstrates the difference in their solution-state intramolecular self-association behavior. In line with the NMR and absorption studies, no obvious intramolecular self-association of **1** at room temperature is evident, whereas effective intramolecular Pt···Pt and π–π interactions do exist in **3**–**5** under the same conditions.

Solutions of **3**–**5** in acetonitrile were then subjected to variable-temperature emission experiments in the temperature range from 5 to 75 °C. The complexes were excited at the isosbestic points of the UV/Vis spectra. As the temperature was increased, a gradual decrease in intensity of the ^{3}MMLCT emission band at 830 nm was observed with a mild and concomitant growth of an emission band at about 600–650 nm. The variable-temperature emission spectra of **5** are shown in Figure 4. Although nonradiative decay of the excited molecules would become more efficient at high temperature, the major reason for the diminishment of the ^{3}MMLCT emission band is the deaggregation of the "sticky"

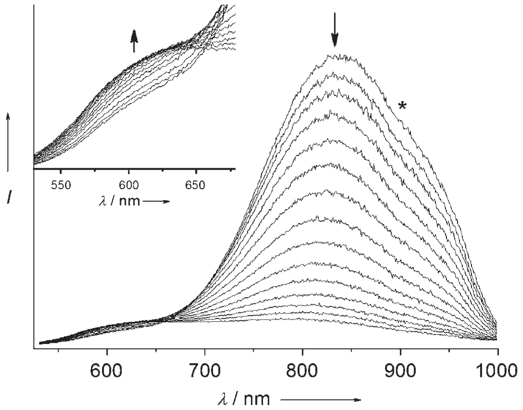


Figure 4. Corrected emission spectral changes of **5** upon an increase in temperature from 5 to 75 °C. Inset: Expansion of emission spectra in the 530–680 nm region. (λ_{ex} = 405 nm, * denotes an instrumental artifact.)

Pt(tpy) units, as the slight increase in the intensity of the ^{3}MLCT band eliminates the possible influence of the contribution from the nonradiative decay in this case.

In conclusion, we have demonstrated the first examples of dinuclear platinum(II) complexes that show a high tendency towards spontaneous solution-state intramolecular self-association by using ^{1}H NMR, UV/Vis absorption, and emission spectroscopy. The self-assembly of these systems was found to be dependent on bridge length and temperature. One may visualize such controllable aggregation and deaggregation properties in this class of molecules as synthetic organometallic analogues of DNA hairpin mimics with sticky ends. The present work demonstrates the versatility of Pt···Pt and π–π interactions in providing the driving force for molecular self-association and assembly.

Experimental Section

Dinuclear chloroplatinum(II) precursor complexes **P1**–**P5** with triflate ($CF_3SO_3^-$) as the counteranion were synthesized by a modified literature method for the synthesis of $[Pt(tpy)Cl]^+$.[7a,9] Complexes **1**–**5** were synthesized by a modification of the Cu^I-catalyzed reaction for alkynyl platinum(II) complexes.[13] The corresponding dinuclear chloroplatinum(II) precursor was dissolved in degassed *N*,*N*-dimethylformamide containing triethylamine, and 4-*n*-butylphenylacetylene and a catalytic amount of copper(I) iodide were added. The reaction mixture was stirred overnight at room temperature, after which diethyl ether was added and stirred for 10 min. The precipitate that formed was isolated by filtration and washed with diethyl ether. A saturated methanolic solution of ammonium hexafluorophosphate was added to a solution of this precipitate in methanol. The PF_6^- salt of the product complex was isolated by filtration, washed with methanol, and dried. Subsequent recrystallization of the complexes was accomplished by diffusion of diethyl ether vapor into solutions of the complexes in acetonitrile.

The characterization data for a representative complex (detailed characterization data for **P1**–**P5**, **1**–**3**, and **5** are given in the Supporting Information): **4**: Yield: 144 mg (82 %). ^{1}H NMR (500 MHz, [D$_6$]DMSO, 363 K): δ = 9.05 (d, J = 5.6 Hz, 4H, terpyridyl H), 8.39 (d, J = 8.0 Hz, 4H, terpyridyl H), 8.31 (t, J = 8.0 Hz, 4H, terpyridyl H), 8.04 (s, 4H, terpyridyl H), 7.79 (d, J = 5.6 Hz, 4H, terpyridyl H), 7.36 (d, J = 8.0 Hz, 4H, -C_6H_4-), 7.11 (t, J = 8.0 Hz, 4H, -C_6H_4-), 4.47 (t, J = 4.6 Hz, 4H, OCH_2CH_2O), 3.96 (t, J = 4.6 Hz, 4H, OCH_2CH_2O), 3.76–3.69 (m, 8H, OCH_2CH_2O), 2.63 (t, J = 7.4 Hz, 4H, -*n*Bu), 1.61 (q, J = 7.4 Hz, 4H, -*n*Bu), 1.39 (s, J = 7.4 Hz, 4H, -*n*Bu), 0.95 ppm (t, J = 7.4 Hz, 6H, -*n*Bu); IR (nujol): $\tilde{\nu}$ = 2118(w) ν(C≡C), 842(s) cm^{-1} ν(P-F); positive-ion FAB-MS: m/z 1506 $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{62}H_{62}F_{12}N_6O_5P_2Pt_2$: C 45.10, H 3.78, N 5.09; found: C 45.34, H 3.54, N 4.99.

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[12] For analysis of the equilibrium absorbance measurements, a two-state transition $A(T) = \theta(T)[A_U(T) - A_L(T)] + A_L(T)$ was used in which A_U and A_L represent upper and lower baselines, and $\theta(T)$ is a van't Hoff function [Eq. (1)] with straight lines for the asymptotes.

$$\theta(T) = 1/\{1 + \exp[-\Delta H/R(1/T - 1/T_m)]\} \qquad (1)$$

Here ΔH is the enthalpy change for the deaggregation process and is assumed to be temperature independent, T_m is the melting temperature of the molecule, and the upper and lower baselines were parameterized as straight lines with independently varying slopes.

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