Solvatochromic Luminescence Based on the Excimer Formation of Bipyridine Platinum(II) Complexes with Linear Alkyl Chains

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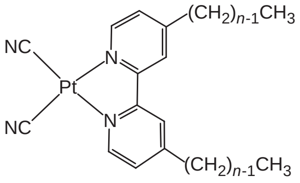
Luminescent mononuclear bipyridine platinum(II) complexes bearing linear alkyl chains, $[Pt(CN)_2(dC_n bpy)]$ ($n = 9$ and 11) have been prepared and characterized. These complexes are soluble in various organic solvents and exhibit remarkable solvent dependence and concentration dependence of the luminescence at room temperature. Such solvatochromic luminescence is attributed to the formation of the excimer of the platinum complexes.

Square-planar platinum(II) complexes often exhibit characteristic luminescence when they are stacked to generate platinum–platinum interactions and/or π–π interactions of the ligands.[1] Such properties of the platinum complexes are mostly studied in the solid state because of the low solubility of the assembled complexes. Introduction of long alkyl chains to various chemical systems is an important strategy to construct self-assembled nanostructures in solution or at interface, and it has been also applied for many supramolecular systems of metal complexes including platinum complexes recently.[2] We report here remarkable solvatochromic luminescence based on the excimer formation for novel dicyano(4,4′-dialkyl-2,2′-bipyridine)-platinum(II), $[Pt(CN)_2(dC_n bpy)]$ ($n = 9$ and 11) (Scheme 1).

The platinum complexes were prepared by refluxing the mixture of the platinum dicyanide and the $dC_n bpy$ ligand in DMF/28% NH_3 (aq.)[3] By recrystallization of the reaction product from acetonitrile and chloroform, white crystals of the complexes were obtained. Those are characterized by means of NMR, IR and melting point measurements and X-ray crystallography.[4,5]

Figure 1 shows the crystal structure of $[Pt(CN)_2(dC_9 bpy)]$ as an acetonitrile-solvated form. The complexes are arranged forming a layer of alkyl chains. Between the alkyl-chain layers, square-planar coordination moieties are arranged in a face-to-face fashion. The interplanar spacing between the coordination planes is estimated to be 3.79(2) Å. The Pt atoms are apart from each other indicating no interactions in the crystal (Pt···Pt = 4.984(1) Å). $[Pt(CN)_2(dC_{11} bpy)]$ was also found to take the isostructure of the $dC_9 bpy$ complex (Figure S1).[6] The layer structures of these dicyano complexes are also similar to those found in the corresponding dichloro complexes.[7]



$[Pt(CN)_2(dC_n bpy)]$ ($n = 9, 11$)

Scheme 1.

The white crystals of the complexes emit blue luminescence even at room temperature. The luminescence spectra having vibronic structures with the maximum of ca. 480 nm are the typical one assignable to the emission from the $^3\pi$–π^*(bpy) state (Table 1).[1b] The additional characteristics are that the complexes are soluble in various organic solvents and exhibit luminescence at room temperature. The luminescence spectra in dilute chloroform are almost the same as that for the crystals (Table 1). Interestingly, with increasing concentration, the intensity of the structured spectrum decreases and instead, a broad spectrum occurs at longer wavelength as shown in Figure 2. The absorption spectra of the complexes, however, do not show any concentration dependence (Figure 2). In addition, in the time-resolved measurements of the emission, a rising followed by an exponential decay was observed for the solution of higher concentration (5.5×10^{-3} mol dm^{-3}) although the decay curve for the dilute solution ($\approx 10^{-5}$ mol dm^{-3}) decreased single-exponentially (Figure S2).[6] These behaviors indicate that the broad luminescence spectrum is assignable to the excimer emission.[9] The triplet excimer emis-

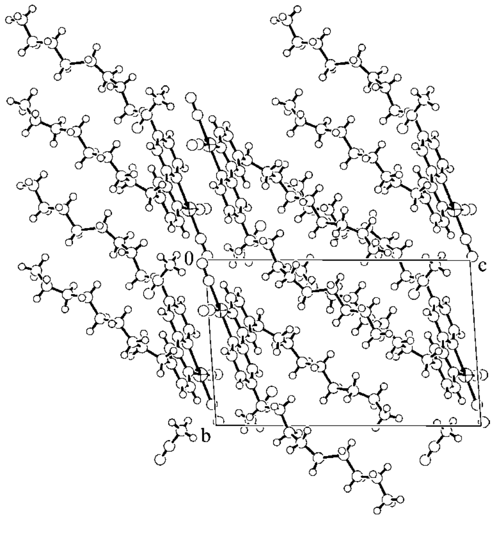


Figure 1. Packing structure of $[Pt(CN)_2(dC_9 bpy)]\cdot CH_3CN$.

Table 1. Emission data for $[Pt(CN)_2(dC_n bpy)]$ at room temperature

	in $CHCl_3$[a]			Neat crystals	
	λ_{max}/nm[b]	τ/µs[c]	ϕ[d]	λ_{max}/nm[e]	τ/µs[c]
$n = 9$	453, 483, 510	0.68	0.020	452, 481, 520	6.2
$n = 11$	453, 484, 514	0.66	0.033	453, 484, 520	2.0

[a] 4×10^{-5} mol dm^{-3}. [b] $\lambda_{ex} = 316$ nm. [c] $\lambda_{ex} = 337$ nm. [d] Calculated using $[Ru(bpy)_3]^{2+}$ as standard ($\phi = 0.090$).[8] [e] $\lambda_{ex} = 350$ nm.

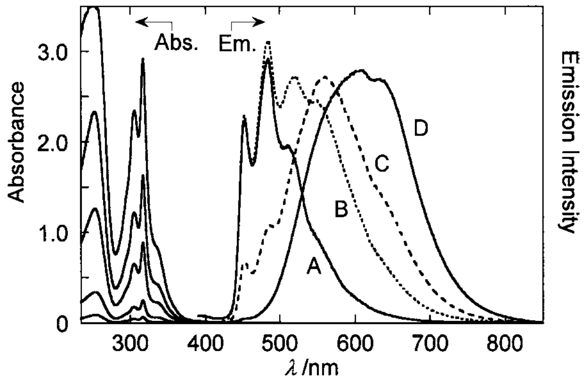


Figure 2. Absorption and emission spectra of [Pt(CN)$_2$(dC$_9$bpy)] in CHCl$_3$ at different concentrations (c): For absorption spectra, $c = 3.6 \times 10^{-5}$–2×10^{-3} mol dm^{-3} (in 1-mm cuvette) from the bottom to the top. For emission spectra, $c = 4.4 \times 10^{-5}$ (A), 2.2×10^{-4} (B), 1.1×10^{-3} (C), and 5.5×10^{-3} (D) mol dm^{-3}. Emission intensities are corrected so as to be equal intensity of excitation ($\lambda_{ex} = 316$, 340, 360, and 395 nm, respectively).

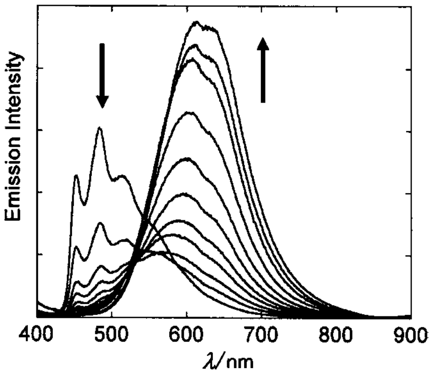


Figure 3. Emission spectral changes of [Pt(CN)$_2$(dC$_9$bpy)] in different ratios of CHCl$_3$/toluene ($c = 5.0 \times 10^{-5}$ mol dm^{-3}, $\lambda_{ex} = 320$ nm): the ratio changes from 100% CHCl$_3$ (100/0) to 100% toluene (0/100) by 10% each.

sion for the platinum(II) complexes containing aromatic ligands, in particular, has attracted much attention recently from the viewpoint of white luminescent materials for electroluminescence devices.[10] It is noteworthy that the excimer formation for [Pt(CN)$_2$(dC$_n$bpy)] strongly depends on the solvent. In methanol and acetonitrile solutions, the blue luminescence originating from the monomer complexes was always observed within the measured concentrations (10^{-6}–10^{-3} mol dm^{-3}). The concentration dependence of the luminescence mentioned above was observed in chloroform and dichloromethane. In the case of toluene solution, however, the broad emission spectrum at around 600 nm was observed even in the dilute solution of 10^{-5} mol dm^{-3}. The preferential formation of excimer in toluene would be related to the low polarity of the solvent. In toluene, the platinum complexes could assemble in an alternate arrangement like that found in the crystal structure so as to compensate the dipole moments. However, the assemblage in toluene should be weak to generate the electronic interactions in the ground state. The excimer formation in toluene at room temperature is also supported by the fact that only blue luminescence due to the monomer complexes appears in frozen state at 77 K (Figure S3).[6] As an interesting result, the remarkable changes in luminescence are attained in the mixed solvent of CHCl$_3$ and toluene by the control of the ratio as shown in Figure 3. The excimer emission has the intensity ($\phi = 0.029$) comparable to that for the monomer emission (Table 1). Thus, the complexes exhibit solvent-sensitive luminescence depending on the formation of the excimer. The study on the properties of such triplet excimer is in progress.

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3 The dC$_9$bpy ligand was purchased from Tokyo Kasei Co., while dC$_{11}$bpy was prepared by similar way to the literature (D. K. Ellison, R. T. Iwamoto, *Tetrahedron Lett.* **1983**, *24*, 31.): ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.87 (t, 2H), 1.25–1.32 (broad, 16H), 1.68 (t, 2H), 2.7 (t, 2H), 7.12 (d, 1H), 8.22 (s, 1H), 8.56 (d, 1H). ESI-MS m/z: 465 (M + 1). Mp 68–70 °C.

4 For [Pt(CN)$_2$(dC$_9$bpy)], ^{1}H NMR (in CDCl$_3$); δ 0.88 (t, 3H), 1.28–1.38 (br, 12H), 1.75 (m, 2H), 2.86 (t, 2H), 7.39 (d, 1H), 7.96 (s, 1H), 9.12 (d, 1H). ^{13}C NMR (in CDCl$_3$); δ 14.1, 22.6, 29.2, 29.3, 29.4, 29.6, 29.8, 31.8, 36.0, 106.8, 123.5, 127.6, 151.1, 155.6, 158.2. IR (KBr, cm^{-1}); 2135, 2146 (ν_{CN}). Mp 181 °C. For [Pt(CN)$_2$(dC$_{11}$bpy)], ^{1}H NMR (in CDCl$_3$); δ 0.88 (t, 3H), 1.27–1.38 (br, 16H), 1.75 (t, 2H), 2.86 (t, 2H), 7.38 (d, 1H), 7.96 (s, 1H), 9.08 (d, 1H). ^{13}C NMR (in CDCl$_3$); δ 14.1, 22.6, 29.2, 29.3, 29.3, 29.4, 29.5, 29.5, 29.8, 31.8, 36.0, 106.9, 123.5, 127.6, 151.3, 155.6, 158.1. IR (KBr, cm^{-1}); 2135, 2146 (ν_{CN}). Mp 185 °C.

5 Crystal data for [Pt(CN)$_2$(dC$_9$bpy)]•CH$_3$CN, Formula: C$_{32}$H$_{47}$N$_5$Pt$_1$, $M_r = 696.85$, triclinic, $a = 9.829(3)$, $b = 10.325(4)$, $c = 16.264(6)$ Å, $\alpha = 84.824(9)°$, $\beta = 83.338(9)°$, $\gamma = 78.820(9)°$, $U = 1604.6(10)$ Å^3, $T = 173$ K, space group $= P\bar{1}$, $Z = 2$, $D_{calcd} = 1.442$ g cm^{-3}. For [Pt(CN)$_2$(dC$_{11}$bpy)]•CH$_3$CN, Formula: C$_{36}$H$_{55}$N$_5$Pt$_1$, $M_r = 752.95$, triclinic, $a = 9.7952(2)$, $b = 10.3271(5)$, $c = 18.3967(5)$ Å, $\alpha = 80.567(7)°$, $\beta = 82.046(7)°$, $\gamma = 79.745(7)°$, $U = 1795.0(1)$ Å^3, $T = 173$ K, space group $= P\bar{1}$, $Z = 2$, $D_{calcd} = 1.393$ g cm^{-3}. Full crystallographic details have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-658486 and 658485, respectively.

6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journal/chem-lett/index.html.

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