

## A Luminescent Nonlinear-chain Tetracyanoplatinate(II) Forming a Charge-transfer Complex with Methyl Viologen

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We display that a tetracyanoplatinate(II) forming a charge-transfer complex with methyl viologen dication in the crystal exhibits intense luminescence despite no direct Pt··Pt interaction.

Recently, luminescent platinum complexes have attracted much attention because of their application to electroluminescent emitting-materials for organic light-emitting diodes (OLEDs).<sup>1</sup> Crystalline linear-chain tetracyanoplatinum(II) salts,  $M_x[\text{Pt}(\text{CN})_4] \cdot n\text{H}_2\text{O}$  ( $M$  = alkali metals, alkaline-earth metals, and rare-earth metals) are well-known luminescent platinum complexes. Luminescence of the tetracyanoplatinum(II) salts in the crystalline phase<sup>2</sup> and of  $\text{Pt}(\text{CN})_4^{2-}$  oligomers formed in solution of high solute concentration<sup>3</sup> has been studied in detail for a very long time. The luminescence occurs from excitation due to the transition from  $a_{1g}$  ( $\text{Pt-}5d_{z^2}$ ) to  $a_{2u}$  ( $\text{Pt-}6p_z$ ,  $\text{CN-}\pi^*$ ) in the electronic structure based on the metal–metal interaction. No luminescence has been established for isolated monomers of  $\text{Pt}(\text{CN})_4^{2-}$ .<sup>3b,3c</sup> Metal–metal ( $d$ – $p$ ) interaction with a columnar structure has been regarded as indispensable for luminescence of  $\text{Pt}(\text{CN})_4^{2-}$  compounds. However, a luminescent noncolumnar, crystalline tetracyanoplatinate(II),  $\text{Ti}_2\text{Pt}(\text{CN})_4$  has been reported.<sup>4</sup>  $\text{Ti}_2\text{Pt}(\text{CN})_4$  with a short Pt–Ti distance of 3.14 Å is considered a pseudo-trimer system because the  $6s$  and  $6p_z$  orbitals of the  $\text{Ti}^{\text{I}}$  can act similarly to the  $5d_{z^2}$  and  $6p_z$  orbitals of the  $\text{Pt}^{\text{II}}$ . These indicate that such metal–metal interaction as  $d$ – $p$  or  $d(s)$ – $p$  interaction is important for the appearance of luminescence of  $\text{Pt}(\text{CN})_4^{2-}$ .

The  $d$ – $p$  interaction of linear-chain  $\text{Pt}(\text{CN})_4^{2-}$  can be regarded as a self-species donor–acceptor interaction, in which the full  $5d_{z^2}$  band and the empty  $6p_z$  band act as donor band and acceptor band, respectively. In this consideration, another electron acceptor can be used as substitute for an origin of the acceptor band, leaving the self-species system of donor and acceptor. Such a combination of the  $\text{Pt}(\text{CN})_4^{2-}$  donor with a suitable cationic acceptor can be expected to be luminescent

even if it has no metal–metal interaction. In this study, methyl viologen dication ( $N,N'$ -dimethyl-4,4'-bipyridinium dication,  $\text{MV}^{2+}$ ), which is one of the most familiar electron acceptors,<sup>5</sup> has been chosen as the acceptor. Here, we report that  $\text{MV}[\text{Pt}(\text{CN})_4]$  (**1**) is a charge-transfer (CT) complex and luminescent. So far **1** has been only reported in an article of the crystal structure of  $\text{MV}[\text{Ni}(\text{CN})_4]$ ,<sup>6</sup> as being isostructural with the nickelate.

The complex salt **1** was prepared by adding an aqueous solution (30 mL) of methyl viologen iodide,  $\text{MVI}_2$  (1.2 g), prepared according to a literature method,<sup>6</sup> to an aqueous solution (20 mL) of  $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$  (1.2 g). The mixture solution gave immediately white powder precipitate (yield 1.1 g, 84%).<sup>7</sup> Pale-yellow single crystals suitable for X-ray diffraction and optical measurements were obtained by recrystallization of the white powder from  $\text{H}_2\text{O}$ /dimethylformamide 1:1 mixture. The well-grown single crystals looked luminescent even under room light though the powder, which was luminescent under UV-light, looked not so under room light.

The result of X-ray analysis<sup>8</sup> confirms that the structure is isostructural with  $\text{MV}[\text{Ni}(\text{CN})_4]$ .<sup>6</sup> The  $\text{Pt}(\text{CN})_4^{2-}$  anion has a typically square-planar form. The average distances of Pt–C and C–N in the anion are 1.998 and 1.142 Å, respectively. These values are in good agreement with those of other tetracyanoplatinate(II),  $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot n\text{H}_2\text{O}$  ( $n = 0, 1, \text{ and } 3$ ).<sup>9</sup> The bond distances and angles of  $\text{MV}^{2+}$  are in good agreement with those of other bipyridinium dication.<sup>5</sup>  $\text{MV}^{2+}$  lies on an inversion center. Thus, the two pyridinium rings of the cation are coplanar. As shown in Figure 1, the crystal structure of **1** is built up from columns composed of planar  $\text{Pt}(\text{CN})_4^{2-}$  moieties and planar  $\text{MV}^{2+}$  moieties stacked alternately along the  $b$  axis. The plains of  $\text{Pt}(\text{CN})_4^{2-}$  and  $\text{MV}^{2+}$  separated by the distance of 3.475(2) Å are parallel to each other while the normal of the

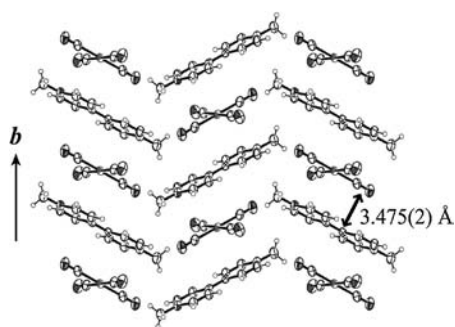


Figure 1. Crystal structure of **1**.

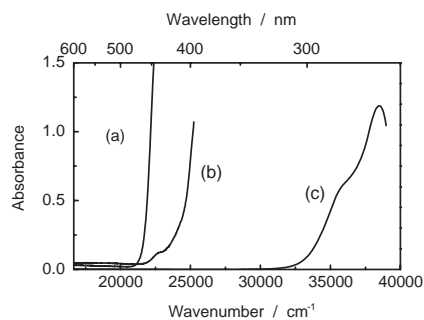
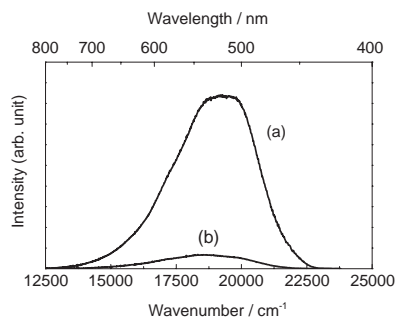


Figure 2. Polarized single-crystal absorption spectra ((a)  $E \parallel$  the  $b$  axis, (b)  $E \perp$  the  $b$  axis, crystal thickness = 0.4 mm), and (c) an absorption spectrum of  $\text{H}_2\text{O}/\text{DMF}$  mixed solution ( $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ).



**Figure 3.** Optical micrograph of single crystal **1** under 366-nm light.



**Figure 4.** Polarized single-crystal emission spectra of **1** under 366-nm unpolarized light ((a)  $E_{\text{emit}} \parallel$  the  $b$  axis, (b)  $E_{\text{emit}} \perp$  the  $b$  axis).  $E_{\text{emit}}$  notes the electric field vector of the emission. Beam direction  $\perp$  (101).

plains cants to the stacking  $b$  axis. Intracolumnar Pt...Pt distance [7.7481(9) Å] and intercolumnar ones [8.0664(9), 8.3265(6), and 9.2071(7) Å] indicate no direct Pt...Pt interaction in the crystal.

Figure 2 shows the solution and single-crystal absorption spectra of **1** in the UV-vis region. Although the solution spectrum seems to be a superposition of the spectra of both  $\text{Pt}(\text{CN})_4^{2-}$  anion<sup>10</sup> and  $\text{MV}^{2+}$  cation,<sup>11</sup> new absorption bands appear in the single-crystal absorption spectra with the band edges at 440 and 400 nm in the polarization parallel and perpendicular to the  $b$  axis, respectively. The new bands are assigned to a charge-transfer (CT) transition between  $\text{Pt}(\text{CN})_4^{2-}$  and  $\text{MV}^{2+}$  because of the similarity with additional bands, which are not observed for constituent molecules, assigned to CT transitions between inorganic donors and  $\text{MV}^{2+}$ .<sup>5</sup> The onset of the CT band in the spectrum parallel to the  $b$  axis is lower than that in the spectrum perpendicular to the  $b$  axis. The result exhibits that the CT interaction of the intracolumn is stronger than that of the intercolumn.

The single crystal of **1** luminesces brightly under excitation with ultra-violet or visible light as given in Figure 3. As shown in Figure 4, the emission band, of which intensity is independent of the polarization of the excitation light, polarized strongly parallel to the  $b$  axis is observed at 545 nm.<sup>12</sup> On the other hand, a tetra- $n$ -butylammonium salt of  $\text{Pt}(\text{CN})_4^{2-}$ , which has no Pt-chain structure,<sup>13</sup> was not luminescent in the same experimental condition as **1** was measured. Since isolated  $\text{MV}^{2+}$  exhibits no luminescence<sup>14</sup> as well as isolated  $\text{Pt}(\text{CN})_4^{2-}$ , the results indicate that the luminescence on this non-Pt-chain system is associated with the excited state based on the CT interaction between the cations and the anions stacked along the  $b$  axis. These structural and spectroscopic results reveal that the luminescence without direct metal-metal interaction occurs successfully on **1** according to our plan of replacing the empty  $6p_z$  band of  $\text{Pt}(\text{CN})_4^{2-}$  with the acceptor band of  $\text{MV}^{2+}$ . In this concept,

the modification of the CT interaction by the substitution of cationic acceptor can tune easily the luminescent properties. More detailed studies on the emission spectroscopy of **1**, such as the combination of polarization of emission and excitation light, and excitation-wavelength dependence, are in progress.

## References and Notes

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- 7 Found: C, 38.54; H, 2.95; N, 17.12%. Calcd for  $\text{C}_{16}\text{H}_{14}\text{N}_6\text{Pt}$ : C, 39.59; H, 2.91; N, 17.31%. Elemental analysis was carried out by Laboratory of Organic Elemental Analysis, Department of Chemistry, Graduate School of Science, The University of Tokyo.
- 8 Crystal data for **1**:  $\text{C}_{16}\text{H}_{14}\text{N}_6\text{Pt}$ ,  $M_r = 485.41$ , monoclinic,  $P2_1/n$ ,  $a = 8.0664(13)$ ,  $b = 7.7481(9)$ ,  $c = 13.5315(13)$  Å,  $\beta = 98.132(5)^\circ$ ,  $V = 837.21(18)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calcd}} = 1.926$  g cm<sup>-3</sup>,  $T = 296$  K,  $2\theta_{\text{max}} = 54.95^\circ$ , 7624 measured reflections, 1917 independent reflections [ $R_{\text{int}} = 0.029$ ], 1424 observed reflections [ $F_o^2 \geq 2\sigma(F_o^2)$ ], 108 parameters,  $R[F_o^2 \geq 2\sigma(F_o^2)] = 0.0191$ ,  $wR = 0.0437$ , GOF = 1.068. CCDC-675669.
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- 12 Spectroscopic data for the single crystals were measured with a microspectroscopic system composed of an OLYMPUS BX60 microscope and an Ocean Optics USB2000 multichannel CCD spectrometer combined with an optical fiber, using a tungsten lamp for the probe light source of absorption spectra, an ultrahigh-pressure mercury lamp for the excited light source of luminescence spectra, and polarizers for the light polarization. Emission data was corrected for the dichroic-filter transmission, the grating transmission, the CCD-detector efficiency, and the wavelength-wavenumber conversion.
- 13 Crystal data for  $(n\text{-Bu}_4\text{N})_2[\text{Pt}(\text{CN})_4]$ :  $\text{C}_{36}\text{H}_{72}\text{N}_6\text{Pt}$ ,  $M_r = 784.08$ , orthorhombic,  $Cmca$ ,  $a = 23.2816(13)$ ,  $b = 21.3978(13)$ ,  $c = 17.2980(11)$  Å,  $V = 8617.4(9)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_{\text{calcd}} = 1.209$  g cm<sup>-3</sup>,  $T = 296$  K,  $2\theta_{\text{max}} = 64.94^\circ$ , 95564 measured reflections, 8005 independent reflections [ $R_{\text{int}} = 0.043$ ], 4906 observed reflections [ $F_o^2 \geq 2\sigma(F_o^2)$ ], 211 parameters, 20 restraints,  $R[F_o^2 \geq 2\sigma(F_o^2)] = 0.0419$ ,  $wR = 0.1216$ , GOF = 1.029. CCDC-675670.
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