

Intramolecular Energy Transfer in a One-Dimensional Europium Tetracyanoplatinate

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The one-dimensional, polymeric compound $(C_{15}H_{11}N_3)Eu(H_2O)_2(NO_3)(Pt(CN)_4) \cdot CH_3CN$ (**1**) has been shown to display an efficient donor–acceptor intramolecular energy-transfer (IET) process where ligand donors transfer energy to the Eu^{III} acceptor. Single-crystal X-ray diffraction has been used to investigate the structural features of this compound in order to help understand the observed IET process. Crystallographic data: **1**, monoclinic, space group $P2_1/c$, $a = 12.835(1)$ Å, $b = 15.239(1)$ Å, $c = 13.751(2)$ Å, $\beta = 105.594(9)^\circ$, $V = 2590.8(5)$ Å³, and $Z = 4$ ($T = 290$ K).

Chromophoric ligands that photosensitize lanthanide-ion luminescence are of intense current interest. Such complexes are used in technological applications such as fluoro-immunoassays,^{1,2} cellular imaging,³ chemosensors,⁴ optical communications,^{5,6} and optoelectronic devices.⁷ The usual impediment in lanthanide-ion systems is that direct absorption of the $f-f$ excited states is very inefficient. Hence, a light-harvesting ligand is essential to enhance the emission from the metal cation site. Ligands used for such applications usually have strong absorbance in the UV or visible regions and transfer their excited energy to the acceptor species.^{8–10}

The structures of compounds containing $Pt(CN)_4^{2-}$ are often characterized by simulated one-dimensional chains of planar anions.¹¹ The in-chain metal–metal interactions provide spectral properties that are very tunable, being highly dependent on the Pt–Pt separations. Prior studies have established the correlations between the in-chain metal–metal interactions and the spectroscopic properties.^{12–14} The $Pt(CN)_4^{2-}$ anion has a charge-transfer transition with rather high intensities of $\epsilon = 1200$ cm⁻¹ M⁻¹. A broad-band emission characterizes this excitation. The tetracyanoplatinate donor system has been shown to undergo energy transfer to selected lanthanide cations.^{15–17} In addition to $Pt(CN)_4^{2-}$, other Pt-based systems have been reported to also contain Pt^{II} ions with a square-planar environment that act as energy donors or acceptors.^{8,18}

Another donor system that absorbs in the UV and has been shown to undergo energy-transfer processes with select lanthanide cations is the terpyridine system. A number of compounds have been reported that contain terpyridine, or derivatives thereof, that act as light-harvesting antennae and can subsequently transfer absorbed energy to coordinated Ln³⁺ cations.^{8,19} One of our research aims is to prepare compounds that contain both of these donor groups in an effort to broaden the energy range over which light harvesting can occur in these systems.

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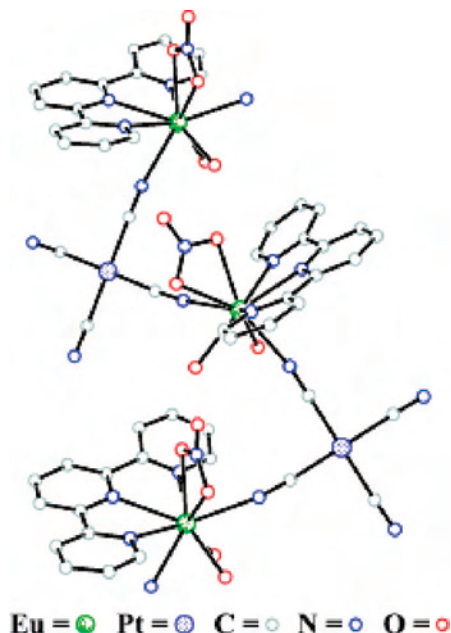


Figure 1. Representation of the one-dimensional chains in **1**. Each Eu^{3+} is coordinated by two water molecules, one tridentate terpyridine ligand, one bidentate nitrate, and two tetracyanoplatinates.

$(\text{C}_{15}\text{H}_{11}\text{N}_3)\text{Eu}(\text{H}_2\text{O})_2(\text{NO}_3)(\text{Pt}(\text{CN})_4) \cdot \text{CH}_3\text{CN}$ (**1**) was prepared by the reaction of 2,2':6',2''-terpyridine, $\text{K}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$, and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ²⁰ and was isolated in the form of colorless, plate-shaped single crystals. The structure of this compound was subsequently determined using single-crystal X-ray diffraction.²¹ Compound **1** incorporates both terpyridine and tetracyanoplatinate anions that are both directly coordinated to the Eu^{3+} cation.

The structure of **1** consists of neutral, one-dimensional $[[(\text{C}_{15}\text{H}_{11}\text{N}_3)\text{Eu}(\text{H}_2\text{O})_2(\text{NO}_3)(\text{Pt}(\text{CN})_4)]$ chains. The chains are formed by the linkage of the Eu cations by cis-bridging tetracyanoplatinate anions as shown in Figure 1. The coordination spheres of the Eu atoms also contain one tridentate terpyridine ligand, a bidentate nitrate anion, and two water molecules. The overall coordination environment of the Eu site is nine and has a geometry that is best described as a tricapped trigonal prism. The Eu–N and Eu–O bond distances range from 2.498(6) to 2.579(5) Å and from 2.389(6) to 2.577(5) Å, respectively. The Pt–C distances vary from 1.974(6) to 1.999(7) Å. All of these bond distances are within normal ranges.^{22,23}

The packing of the one-dimensional chains in the structure does not result in quasi-one-dimensional chains of tetracyanoplatinate anions as found in the structures of other lanthanide tetracyanoplatinates.¹³ In the structure of **1**, however, dimers of tetracyanoplatinate anions are observed that contain a Pt–Pt separation of 3.556 Å. These dimers are formed by interchain interactions between two tetracyanoplatinate anions. The packing diagram of **1** found in the Supporting Information illustrates these interactions. One acetonitrile solvate molecule is also found between the chains in the structure.

The emission spectra of **1** are shown in Figure 2. The 396 nm light was used for direct f–f (${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ level) excitation in the Eu^{3+} ion. After cascading to the lowest excited state, emission originates from the ${}^5\text{D}_0$ level. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition shows a well-defined single peak at 580 nm, while the ${}^5\text{D}_0 \rightarrow$

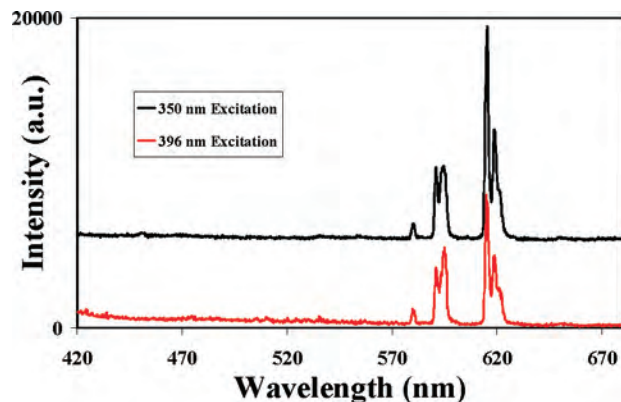


Figure 2. Emission spectra of **1** upon direct excitation at the Eu^{3+} ion f–f level at 396 nm (bottom) or ligand-based excitation at 350 nm (top).

${}^7\text{F}_1$ region has weakly resolved broader bands at 591, 593, and 595 nm. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ region displays the most intense band at 615 nm. Weak bands (not shown) are also observed at ~ 700 nm corresponding to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transitions. The relative intensities of the 0–0, 0–1, and 0–2 emission bands at 580, 594, and 615 nm remain the same at both 295 and 77 K with a normalized peak-to-height ratio of 0.1:0.3:1.0, respectively.

When the emission spectra of **1** are compared with the emission reported by Yersin for $\text{Eu}_2[\text{Pt}(\text{CN})_4]_3 \cdot 18\text{H}_2\text{O}$ (EuCP),¹⁵ there are distinct differences. (1) At room temperature EuCP does not display line emission originating from Eu^{III} , but rather only broad-band emission assignable to the tetracyanoplatinate moieties is observed. (2) At 77 K, Eu^{III} emission is seen in EuCP, but the broad-band emission is also still observed, indicating that the energy-transfer process in EuCP is not efficient. In **1**, however, broad-band emission from $\text{Pt}(\text{CN})_4^{2-}$ is not observed at 295 or 77 K, indicating an efficient IET process; only Eu^{III} line emission is observed.

The excitation spectrum of **1** shown in Figure 3 was collected by monitoring the Eu^{3+} emission band at 615 nm. The spectrum consists of several sharp bands overlaying on a dominant broad band that covers the high-energy side of the spectrum. The bands at 395, 416, 465, 526, 535, and 580 nm are sharp f–f transitions characteristic of the Eu^{3+} ion. These bands correspond to transitions from the ground ${}^7\text{F}_0$ level to the ${}^5\text{L}_6$, ${}^5\text{D}_3$, ${}^5\text{D}_2$, ${}^5\text{D}_1$, and ${}^5\text{D}_0$ states, respectively. The dominant broad band, which is centered at 350 nm with

(20) Compound **1** was prepared by first mixing 1 mL of 0.12 M $\text{Eu}(\text{NO}_3)_3$ (Strem Chemicals, 99.9%) and ~ 1 mL of 0.15 M $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ (Alfa Aesar, 99.9%). Next, a 1 mL solution of 0.10 M 2,2':6',2''-terpyridine (Aldrich 98%) was layered onto the mixture. The $\text{Eu}(\text{NO}_3)_3$ and terpyridine solutions were prepared in CH_3CN , while the $\text{K}_2[\text{Pt}(\text{CN})_4]$ solution was made by dissolving $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ in 1 mL of acetonitrile and then adding H_2O dropwise until all of the salt dissolved. Evaporation of the solvent over a period of 2 weeks resulted in the crystallization of **1** as single crystals (57.6% yield).

(21) Crystal data for **1**: dimensions 0.48 \times 0.27 \times 0.08 mm, monoclinic, $P2_1/c$, $Z = 4$, $a = 12.835(1)$ Å, $b = 15.239(1)$ Å, $c = 13.751(2)$ Å, $\beta = 105.594(9)^\circ$, and $V = 2590.8(5)$ Å³ ($T = 290$ K); Enraf-Nonius CAD-4 diffractometer: $\theta_{\text{max}} = 50.74^\circ$, Mo $\text{K}\alpha$, $\lambda = 0.71073$ Å. The structure was solved by direct methods, anisotropic refinement of F^2 by full-matrix least squares with 351 parameters.²⁶ $R1 = 0.0296$ ($I > 2\sigma(I)$), $wR2 = 0.0780$. Additional crystallographic details are contained in the Supporting Information.

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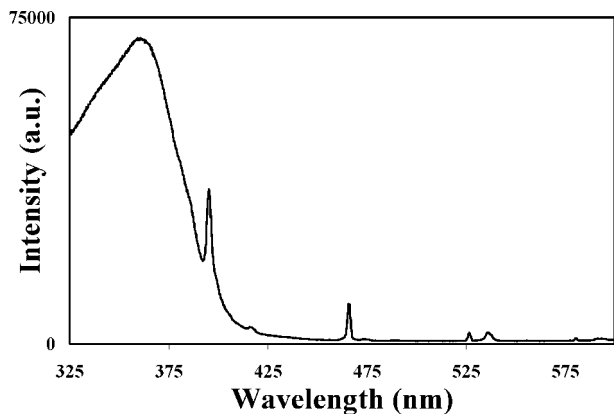


Figure 3. Excitation spectrum of **1** monitored at the Eu^{3+} emission line of 615 nm. Observation of the broad band is direct evidence for the existence of intramolecular energy transfer in **1**.

a shoulder at ~ 330 nm, is uncharacteristic of f–f transitions. Observation of characteristic Eu^{3+} emission lines upon excitation into this broad band (Figure 2) unambiguously demonstrates that the sensitized emission is achieved through Pt-based antenna triplet states and/or a terpyridine-based π – π^* intraligand transition.²⁴

Sensitization of lanthanide luminescence is traditionally achieved by π -conjugated organic aromatic chromophores that are directly coordinated to the metal centers.⁸ An alternative approach for lanthanide sensitization is with transition-metal-containing antenna chromophores.^{8–10,13,18} One advantage afforded by the latter is a better energy match between the d-block donors and the Ln^{3+} acceptor electronic levels.¹³ The energy match between donor/acceptor levels results in less waste in excited energy. Some other added advantages include the relatively high triplet quantum yield obtained from the rapid intersystem crossing (due to the heavy-atom effect), and the facile detection of both quenching of the d-block chromophores and the sensitized emission from the lanthanide centers.²⁵

The absorption profile of the “free” terpyridine ligand has a maximum at ~ 320 nm, with the tail of the band extending to 400 nm. Comparison of the ligand’s absorption spectrum and the excitation profile of **1** indicates that the excitation maximum appears at the tail of the ligand absorption band. Additionally, the excitation spectra have maxima in the ~ 330 – 340 nm region in other Eu/terpyridine systems where energy-transfer processes have been reported.¹⁹ The excitation spectra of the tetracyanoplatinate moieties in several systems provide a very broad featureless band in the 300–400 nm region. Hence, the absorptions of the terpyridine and tetracyanoplatinate moieties appear to overlap in the 300–400 nm region. For example, the lanthanum tetracyanoplatinate²⁶ compound (**2**) studied by us shows a broad emission band maximizing at ~ 530 nm and has a featureless excitation spectrum in the 300–400 nm region. Because the La^{3+} ion is nonluminescent, the broad emission

in the visible region of **2** is assignable to a charge-transfer state within the tetracyanoplatinate ion. The broad excitation band covering the near-UV region in **1** appears to indicate that sensitization proceeds by both the terpyridine ligand and the $\text{Pt}(\text{CN})_4^{2-}$ anion, which are both directly coordinated to Eu^{3+} . This is a rare example of a system where the normally weak lanthanide emissions are enhanced through a cooperative effect of multiple donor systems.

The large Pt–Pt distance exhibited in **1** suggests minimal influence of a metal–metal-to-ligand charge-transfer (MMLCT) transition that arises when relatively short Pt–Pt interactions (~ 3 – 3.5 Å) exist. The short metal–metal interaction is known to provide low-energy emission.¹³ In contrast, the metal-to-ligand charge-transfer (MLCT) transition of $\text{Pt}(\text{CN})_4^{2-}$ consists of higher energy absorption and emission bands¹³ when compared with the MMLCT systems. The total lack of emissions assignable to the donor systems in **1** implies that the emission from the $\text{Pt}(\text{CN})_4^{2-}$ ions is entirely quenched because of energy transfer to the acceptor Eu^{3+} cation. Although no emission from the tetracyanoplatinate groups has been observed in **1**, even at liquid-nitrogen temperature, the Pt/terpyridine/tetracyanoplatinate²⁶ system (**3**) studied by us does show emission assignable to the platinum tetracyanide moiety at ~ 420 nm upon excitation at 380 nm. This is a significant blue shift when compared to many other systems that show a MMLCT transition,¹³ which is consistent with the relatively long and, hence, weak Pt–Pt interaction²⁷ in this compound. Comparison of the emission spectra of **1** with those of **3** supports the argument presented earlier that energy transfer from the platinum tetracyanide to the Eu^{3+} ion in **1** efficiently quenches the emission assignable to the donor species.

The emission from the Eu^{3+} ion in **1** dominates the spectral profile, with the intensities increasing significantly as the temperature is reduced to 77 K. The excitation spectrum dominated by the broad band at 350 nm is indicative of the presence of a donor/acceptor-type interaction in the system. The peak–height comparison indicates that the sensitized emission from Eu^{3+} has increased by more than 2-fold when compared with the emission intensity for the direct f–f excitation. Hence, an efficient IET is inferred in this system. On the basis of the excitation profile, it is suggested that both the terpyridine ligand and the metal-centered triplet state operate as sensitizers of the lanthanide emission. Time-dependent spectroscopic studies are also currently in progress to discern the contributions of each coordinating species to the overall energy-transfer process.

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Supporting Information Available: X-ray data for **1** in CIF format, additional figures, and experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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