



# Emission Enhancement through Dual Donor Sensitization: Modulation of Structural and Spectroscopic Properties of Lanthanide Tetracyanoplatinates.

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## Abstract

Lanthanides containing dual donor systems were analyzed. Terpyridine and tetra cyano platinate (II) were the dual donors used while assessing the emission enhancement of europium and samarium. Although they do not have strong luminescent properties by themselves, lanthanides such as europium and samarium are known for their optical properties; thus the need for luminescent enhancing. The terpyridine acts as the organic ligand, while the tetra cyano platinate (II) acts as the metal donor. These dual donor systems affect the intramolecular energy transfer mechanism which causes the enhanced photosensitization of the lanthanide acceptor. The emission and excitation studies of europium and samarium were assessed at room temperature by photoluminescence.

## Introduction

Trivalent lanthanides are used in luminescence studies because of their optical properties. One such lanthanide, europium, is known to be used in color television screens due to its red phosphors. Samarium is used as a sensitizer for phosphors excited in the infrared region of the electromagnetic spectrum. These characteristic optical properties of lanthanides enable them to act as sensors for the detection of air pollutants, volatile organic compounds, oxygen, and etc.

## Methods

$K_2[Pt(CN)_4] \cdot 3H_2O$  (99.99%), terpyridine (97%), and  $Ln(NO_3)_3 \cdot 3H_2O$  (99.9%) were purchased from Alfa Aesar. All chemicals were used without further purification. Distilled and millipore-filtered water with a resistance of 17.0 M $\Omega$ -cm was used in aqueous reactions. Reactions were also carried out in methanol, ethanol, acetonitrile, and mixed solvents. The syntheses are carried out between soluble salts of the lanthanide cations and tetracyanoplatinate anions in single and/or multiple solvents. Solutions of the reactants were layered and left for slow evaporation providing single crystals suitable for x-ray diffraction and spectroscopic studies.<sup>0</sup>

## Results and Discussion

Figure 1. Structure of  $[Sm(C_{15}H_{11}N_3)(H_2O)_3]_2 [Pt(CN)_4]_3 \cdot H_2O$

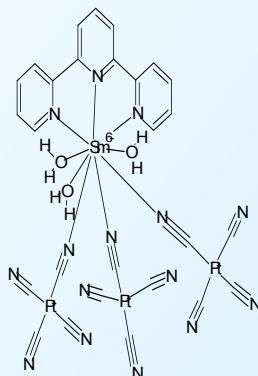
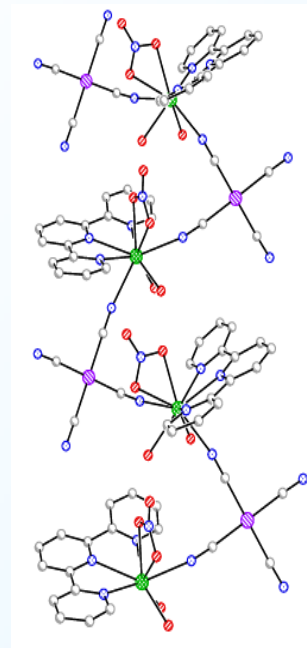
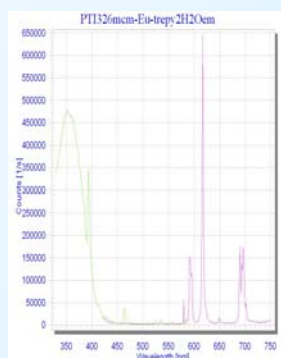


Figure 2. Structure of  $\{Eu(terpy)(H_2O)_2(NO_3)(Pt(CN)_4)\} \cdot CH_3CN$



Shown in Figure 1 and Figure 2 are the structures of  $[Sm(C_{15}H_{11}N_3)(H_2O)_3]_2 [Pt(CN)_4]_3 \cdot H_2O$  and  $\{Eu(terpy)(H_2O)_2(NO_3)(Pt(CN)_4)\} \cdot CH_3CN$ . Their direct coordination of the terpyridine ligand and tetra cyano platinate (II) ligands are shown.

Figure 3. Overlap of the excitation (green) and emission (pink) spectra of europium terpy tetracyano platinate (II)



The emission spectrum (pink) and the excitation spectrum (green) of  $\{[Pt(CN)_4]_3 [Eu(H_2O)_2(NO_3)(Pt(CN)_4)]_2 \cdot 2H_2O\}$  is shown in the above figure 3. When excited at 392 nm the most intense emission band is observed at 617 nm corresponding to the  $^5D_0 \rightarrow ^7F_2$  transition. Other emissions characteristic to the  $Eu^{3+}$  f-f transitions are also evident. The main feature of the excitation spectrum, which was monitored at the 617 nm, is the observance of a broad band that maximizes at 350 nm. The broad band is uncharacteristic f-f transitions and suggests the presence of an efficient energy transfer from the donor anion  $Pt(CN)_4^{2-}$  to the acceptor cation  $Eu^{3+}$ .

Figure 4. Emission and excitation spectrum of samarium terpy tetracyano platinate (II)

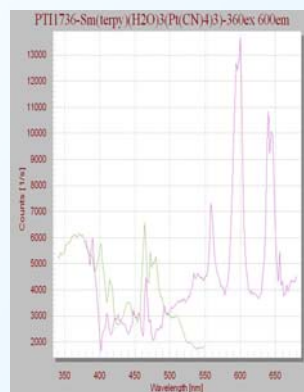


Figure 4 shows the emission spectrum (pink) and excitation spectrum (green) of  $[Sm(C_{15}H_{11}N_3)(H_2O)_3]_2 [Pt(CN)_4]_3 \cdot H_2O$ . The emission spectrum was collected after excitation at 360 nm wavelength. In contrast the excitation spectrum was monitored at the 600 nm emission wavelength. The emission spectrum shows three prominent peaks located at 510 nm, 600 nm, and 640 nm.

Figure 5. Excitation and Emission spectrum of Samarium terpy tetracyano platinate (II)

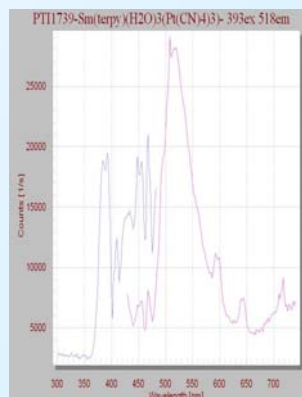


Figure 5 shows the emission and excitation spectrum of  $[Sm(C_{15}H_{11}N_3)(H_2O)_3]_2 [Pt(CN)_4]_3 \cdot H_2O$ . The emission spectra (pink) was collected upon excitation at 393 nm wavelength. A broad band which maximizes at 518 nm is dominant. This broad band is uncharacteristic of f-f transition and corresponds to the  $Pt(CN)_4^{2-}$  moiety indicating a less efficient energy transfer to the samarium ion. The excitation spectrum (blue) was collected by monitoring at the 518 nm emission. Several peaks are evident at 393, 410, 450, 454, and 470 nm. When the excitation spectrum is monitored at 600 nm a subtle difference exist as shown in Figure 6.

Fig 6. Excitation and emission spectrum of samarium terpy tetracyano platinate (II)

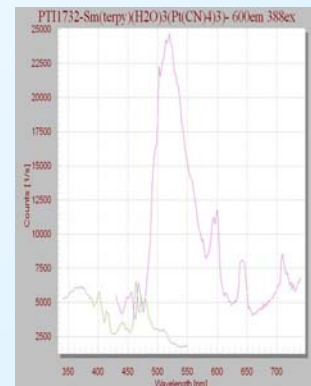


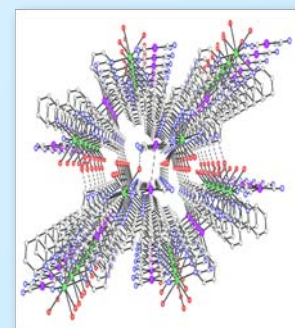
Figure 6 shows the emission spectrum (pink) and excitation spectrum (green) of  $[Sm(C_{15}H_{11}N_3)(H_2O)_3]_2 [Pt(CN)_4]_3 \cdot H_2O$ . The emission spectrum was excited at 388 nm wavelength, while the excitation spectrum was monitored at the 600 nm emission band. The emission spectrum shows a broad peak at 518 nm, and peaks at 600, and 640 nm. The excitation spectrum shows a broad peak maximized at 370 nm, and subsequent peaks at 400 nm and 464 nm.

## Discussion

The metal complex donor, tetracyano platinate, and organic ligand, terpyridine, were successful in transferring energy simultaneously to the europium acceptor cations. In contrast the energy transfer to the samarium ion is minimal although the structural feature of the two cation complexes are similar. The result suggests that apart from the structural features energy match up between donor and acceptor levels is a rigid requirement to observe efficient transfer of excited energy in these types of lanthanide complexes.

These experiments show that the complexes have great promise for detecting volatile organic compounds. The packing diagram shows that there are open channels that can accommodate various volatile organics within the structures of the complexes.

Figure 6. Packing diagram of the complexes showing open channels that may accommodate VOC.s



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