Supplementary information

Understanding the Excited state Dynamics and Redox Behavior of Highly Luminescent and Electrochemically Active Eu (III) - DES complex

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2.2. Instrumentation

Photoluminescence measurement was carried out on Edinburgh F1000 instrument equipped with steady state xenon flash lamp 450 watt and lifetime measurement was carried out using hydrogen filled nanosecond lamp. The lifetime measurement was carried out in an FLS 1000 Edinburgh instrument equipped with microsecond flash lamp of 150 watt with variable frequency of 0.1-100 Hz. The measurement techniques involves multi channel scaling (MCS).

EXAFS data analysis was performed using programs included Demeter software.[1] Phase-shift and backscattering amplitude functions for structural fitting of the EXAFS spectra were generated using FEFF8 program using crystal structures of europium acetate and europium bromide ($EuBr_3$) for Eu-O and Eu-Br scattering paths respectively.[2] Possibility of Eu-C backscattering shell in the fit was checked using the path created from the Eu-acetate crystal structure. Structural (shell-by-shell) fitting of the background-subtracted, normalized and k3-weighted EXAFS data was performed over k-range 2.479 - 8.858 Å^{-1}and the corresponding range in R-space was 1.2 - 4 Å. A Morlet wavelet transform analysis (HAMA software) was used to identify various shells prior to fitting the EXAFS spectra of the Eu-DES complex.[3, 4] This qualitative analysis presents the filtered wavelet-transformed EXAFS amplitude as a function of k and R (uncorrected for phase shift). Resolution of amplitude in two dimensions facilitates the identification of individual contributions in k-space to each peak in the Fourier transform modulus and is therefore better suited to distinguish between heavier and lighter backscattering

atoms, even if they are at the same distance from the central atom. As the aim in the present study was only to identify the type of backscatter atom, overview WT of the whole spectral range was generate using Morlet wavelet parameters $\eta = 15$ and $\sigma = 1$. In this asymptotic case the wavelet ordinate R and the Fourier abscissa R become equal.

Cyclic voltammetric studies of the solutions were conducted using a Metrohm-Autolab electrochemical workstation at room temperature unless mentioned. A glassy carbon disk electrode with an area of 0.07 cm^2 was employed as the working electrode. To clean the electrode, it was polished with alumina powder of decreasing particle size from 1.0 to 0.05 μm. After each polishing step, the electrode was sonicated in water to remove any alumina particles that may have adhered to it. Platinum wires served as both the counter and reference electrodes. All redox potentials were referenced against Fc/Fc$^+$. Each measurement was repeated three times, and the average numerical value of each parameter is presented for discussion, with a relative error of less than $\pm$ 0.1%. The electrochemical cell utilized a single leak-tight compartment, with all electrodes placed within it. The electrochemical cell was kept under an argon atmosphere throughout the study. The glassy carbon electrode was subjected to scans at various scan rates (0.01−0.1 V/s) in a solution of Eu(III) in DES.

2.3. Computational Methodology

All the computations have been carried out in Turbomole-7.2 software.[5] The structures of DES formed by $C_7H_{15}PPh_3Br$ and $C_9H_{19}COOH$ with 1:2 ratio and $[Eu^{III}(DES)(NO_3)_2]^+$ have been optimized using Becke three-parameter exchange and Lee–Yang–Parr correlation (B3LYP) hybrid functional[6, 7] with Grimme's method (DFT-D3) for treating dispersion correction as implemented in Turbomole-7.2 software[5] with def-SV(P) basis set.[8] In the Turbomole basis set library, the def-SV(P) basis set for Eu atom is quite large and consists of (14s13p10d8f1g) functions contracted to [10s8p5d4f1g] with the effective core potential (ECP) of 28 core electrons. Furthermore, the frequency calculation has been performed for all the systems using the same method to obtain minimum energy structure. All the calculated real frequency values confirm the stability of the DES structure and its complex with Eu^{3+} ion.
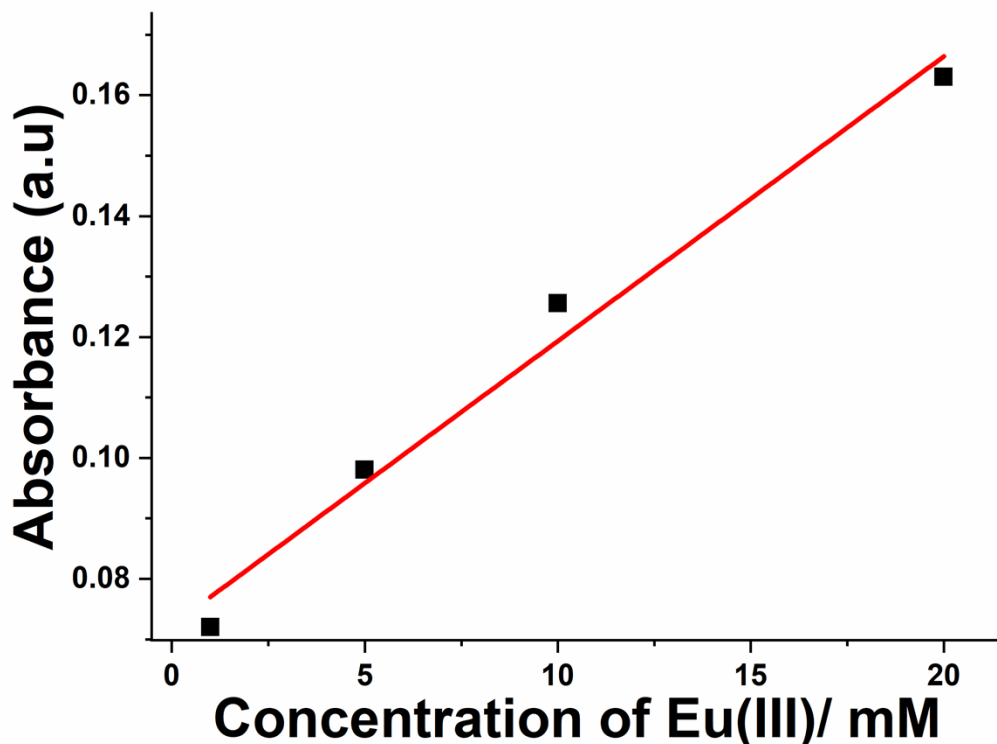
Figure S1. Plot of variation of absorbance with increase in Eu(III) concentration in DES

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