Title

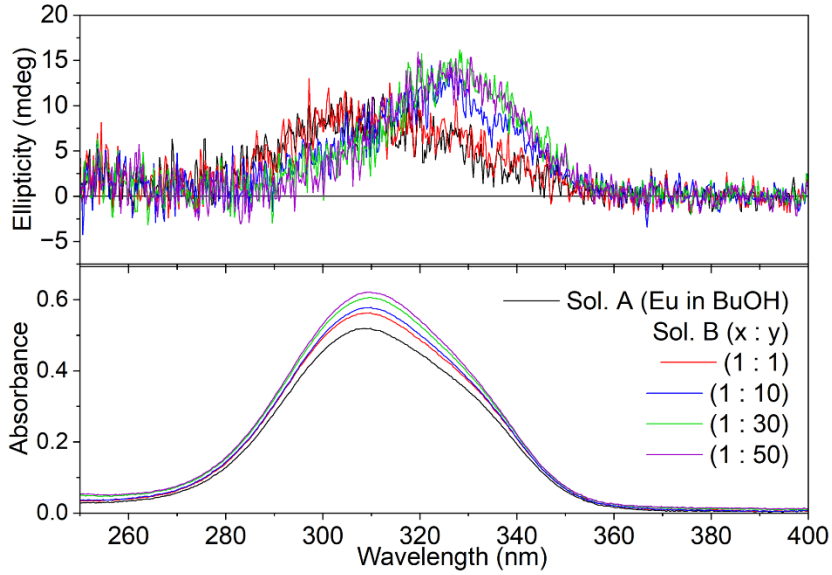
Enhanced Circularly Polarized Luminescence and Thermal Stability of Eu(*D*-facam)$_3$ in Imidazolium-Based Ionic Liquid EMImOAc

Authors

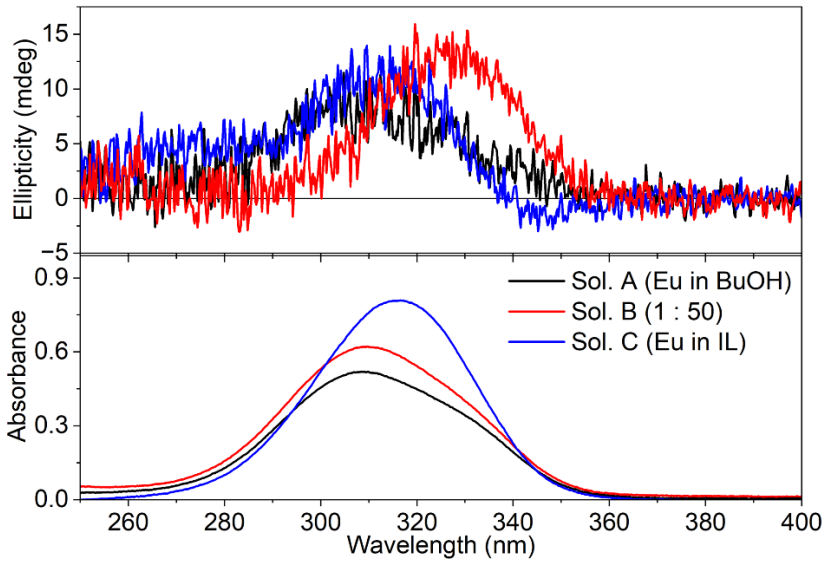
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Affiliation

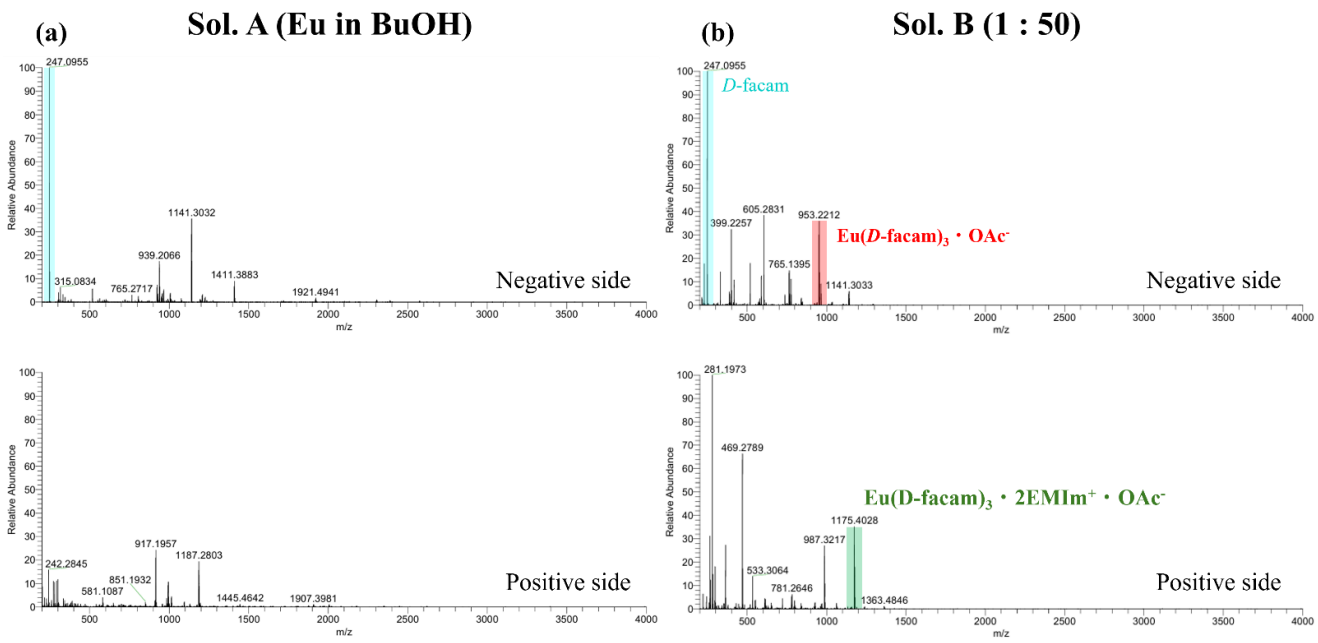
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S1. Absorption and CD spectra of Sol. B with various mixing ratios.



S2. Absorption and CD spectra of Sol. A (Eu in BuOH), Sol. B (1 : 50) and Sol. C (Eu in IL).



S3. Experimental ESI-MS spectra of (a) Sol. A (Eu in BuOH) and (b)Sol. B (1 : 50).

Calculation of the luminescence properties

The transitions $^5D_0 \rightarrow {}^7F_{0,\,2,\,3,\,4}$ are electric dipole transitions whose intensities are increased by reducing the coordination symmetry of the Eu^{3+} complex. The $^5D_0 \rightarrow {}^7F_1$ transition, in contrast, is a magnetic dipole transition that is independent of the coordination structure. The relationship between the shape of the emission spectrum of Eu^{3+} and its radiative rate constant (k_r) is expressed as

$$k_r = A_{MD,0} n^3 \left(\frac{I_{tot}}{I_{MD}}\right) \quad (S1)$$

Here, $A_{MD,0}$, n, and (I_{tot}/I_{MD}) represent the spontaneous luminescence rate of the $^5D_0 \rightarrow {}^7F_1$ transition in vacuo (14.65 s^{-1}), refractive index of the medium, and ratio of the total area of the Eu^{3+} luminescence spectrum to the area of the $^5D_0 \rightarrow {}^7F_1$ transition band, respectively.

According to equation (4) in the main text, the nonradiative rate constant (k_{nr}) from the $^5D_0$ state is expressed as

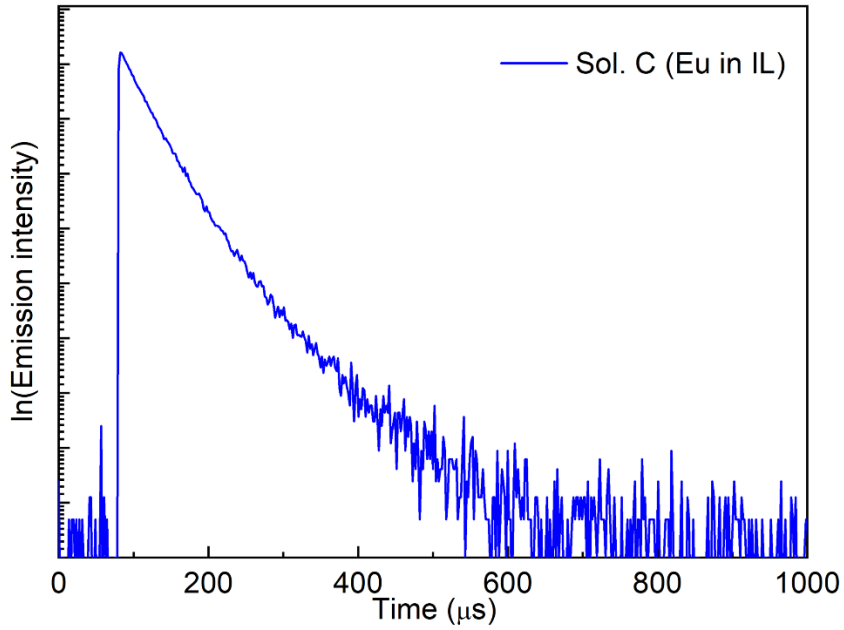
$$k_{nr} = \frac{1}{\tau_{ave}} - k_r \quad (S2)$$

The quantum yield of Eu^{3+} luminescence (ϕ_{Ln}) and overall photosensitization efficiency (η_{sens}) were determined as follows:

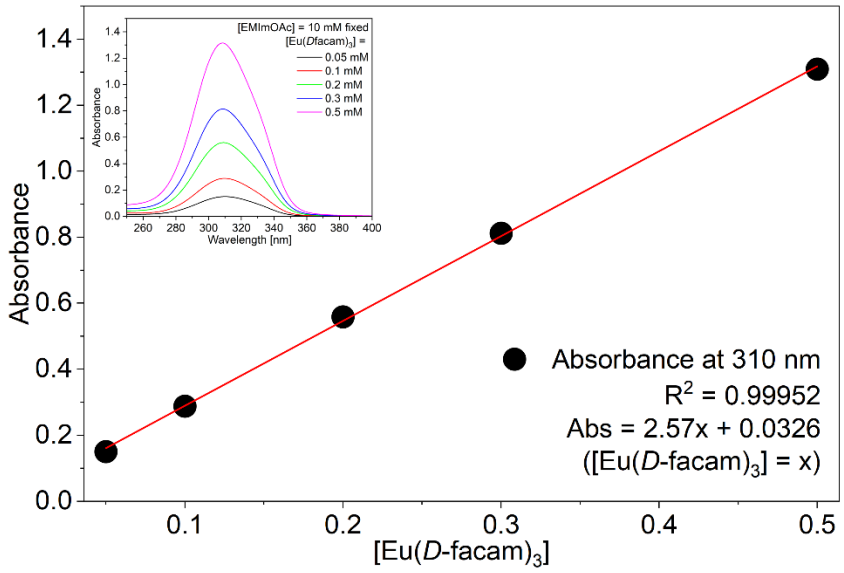
$$\phi_{Ln} = \frac{k_r}{k_r + k_{nr}} \quad (S3)$$

$$\phi_{tot} = \eta_{sens} \times \phi_{Ln} \quad (S4)$$

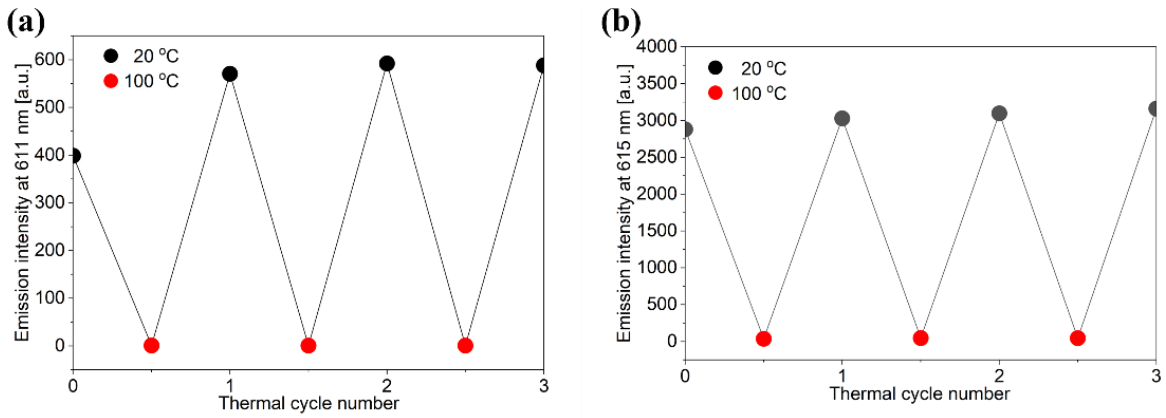
Since it is hard to excite Eu^{3+} directly in the solution state, ϕ_{Ln} was estimated indirectly from the above equation.



S4. Emission decay profile of Sol. C (Eu in IL) (λ_{em} = 612 nm).



S5. The corresponding absorbance at 310 nm plotted as a function of Eu(*D*-facam)$_3$ concentration. (Inset) Absorption spectra of Eu(*D*-facam)$_3$ at different concentrations with a fixed EMImOAc concentration (10 mM).



S6. Emission intensity monitored during repeated heating–cooling cycles between 20 and 100 °C for (a) Sol. B (1:50) and (b) Sol. C (Eu in IL).

Possible influence of residual water in EMImOAc

It should be noted that acetate-based ionic liquids are hygroscopic, and trace amounts of water may be present when the reagents are used as received. While -OH vibrational modes are known to act as efficient quenchers of Eu^{3+} emission, the amount and local environment of residual water in EMImOAc are fundamentally different from those in -OH containing solvents such as 1-butanol. The pronounced extension of the emission lifetime and the enhanced thermal stability of luminescence observed in the EMImOAc-based systems therefore suggest that -OH vibrational quenching by residual water is not a dominant deactivation pathway in the present IL environment, and that such water is unlikely to exist as coordinated species in the coordination environment of the Eu^{3+} ion acting as an effective quencher.