

Supporting information

Polyoxometalate-based metal–organic frameworks NENU-5 hybrid materials for photoluminescence tuning by introducing lanthanide ions and their functionalized soft ionogels / thin film

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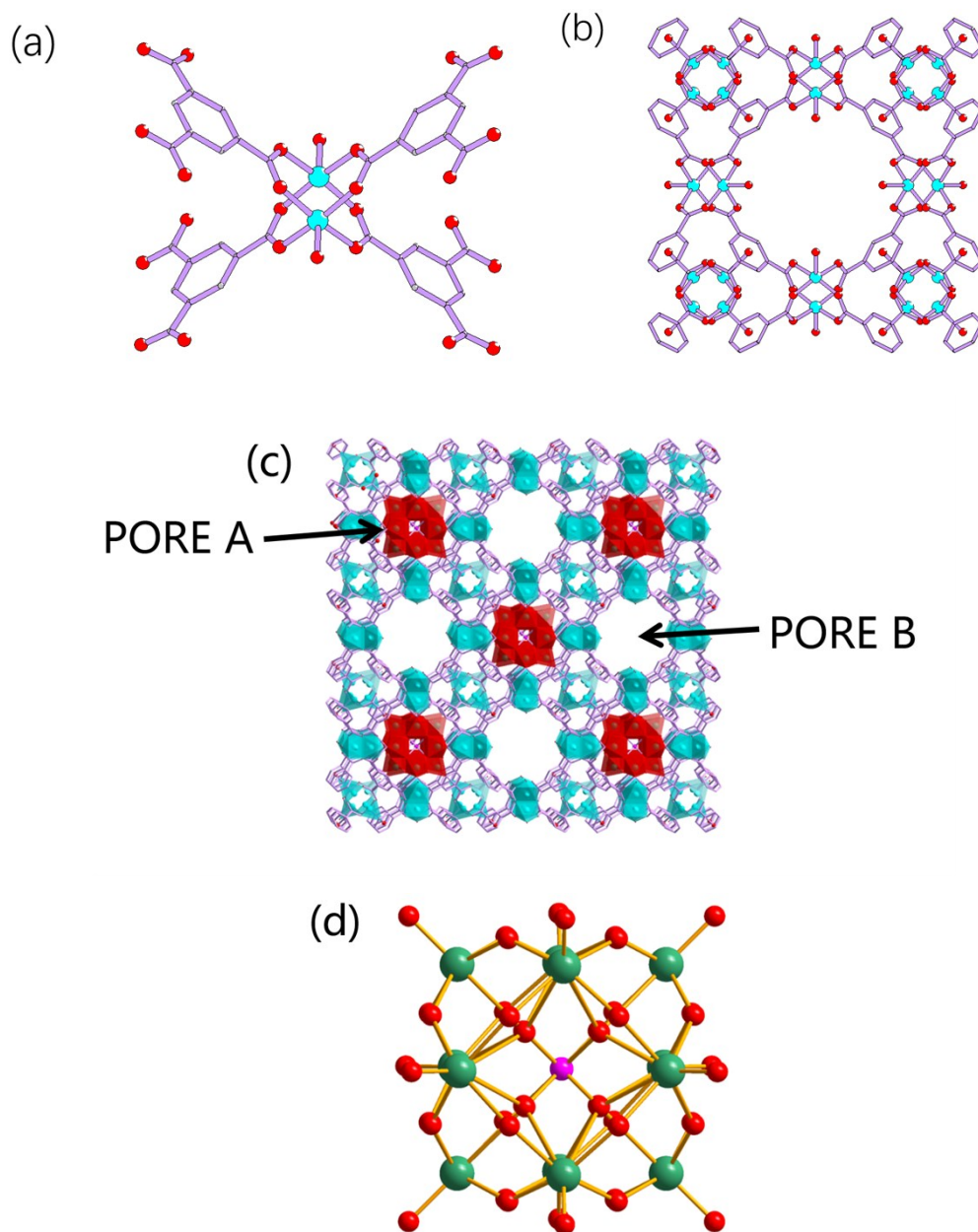


Fig. S1 (a) the paddle-wheel Cu_2 unit; (b) the (3, 4)-connected framework of NENU-5. (c) Components of the crystal structures of NENU-5; (d) the structure of POM $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ in NENU-5. Blue, red, green, purple spheres represent Cu, O, Mo, P atoms, respectively.

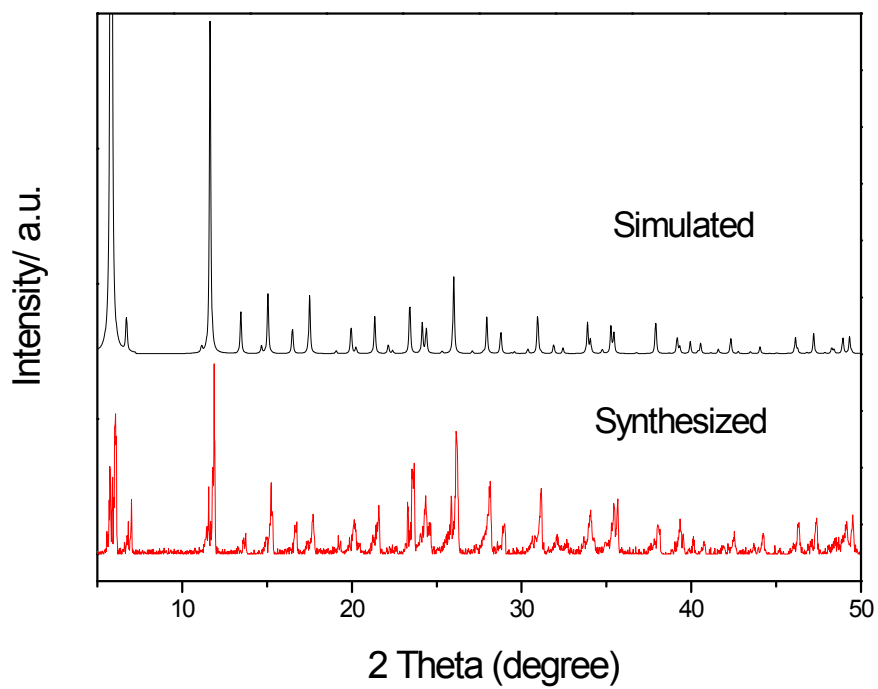


Fig. S2 Powder X-ray diffraction (PXRD) pattern of the synthesized NENU-5 and the simulated.

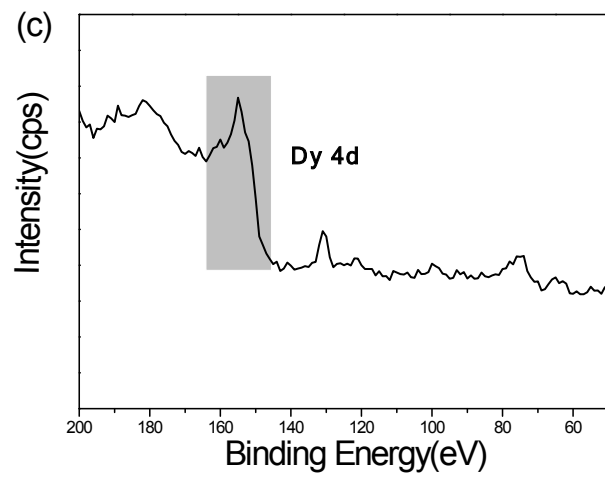
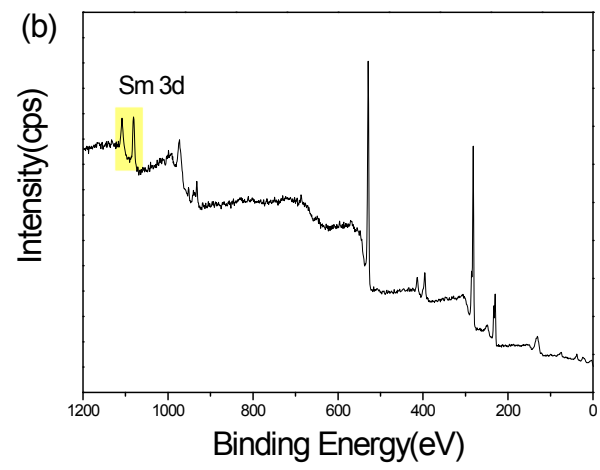
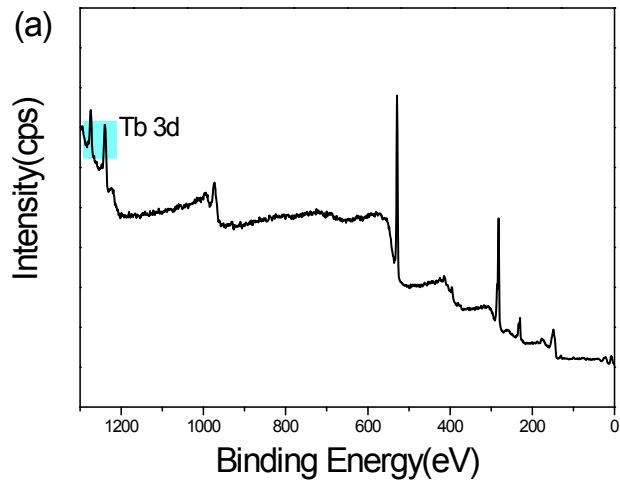


Fig. S3 XPS pattern of Tb^{3+} @NENU-5, Sm^{3+} @NENU-5 and Dy^{3+} @NENU-5

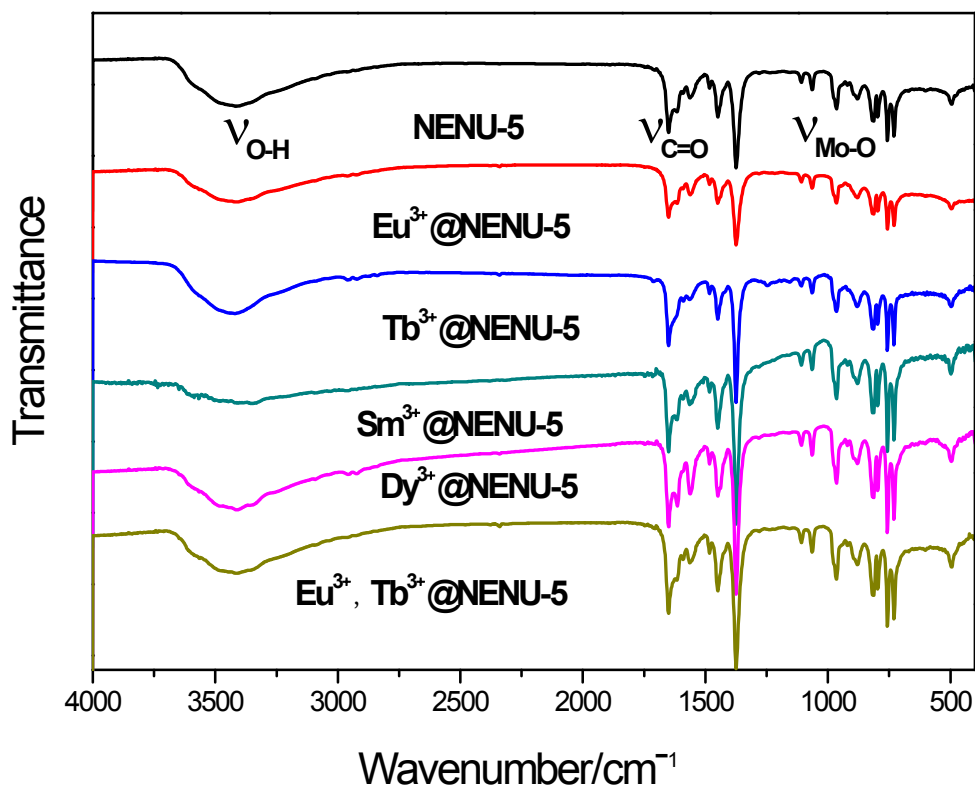


Figure S4 FTIR spectra analysis of NENU-5 and $\text{Ln}^{3+}@NENU-5$ ($\text{Ln} = \text{Eu}, \text{Tb}, \text{Sm}, \text{Dy}, \text{Eu/Tb}$)

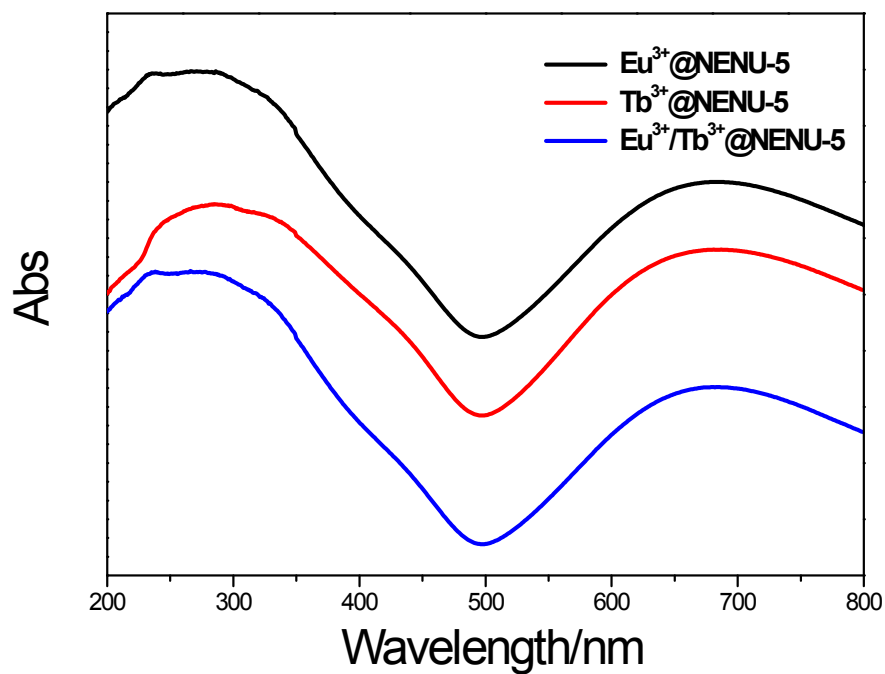


Fig. S5 UV-vis diffuse reflectance spectrum of $\text{Eu}^{3+}@NENU-5$, $\text{Tb}^{3+}@NENU-5$, $\text{Eu}^{3+}/\text{Tb}^{3+}@NENU-5$.

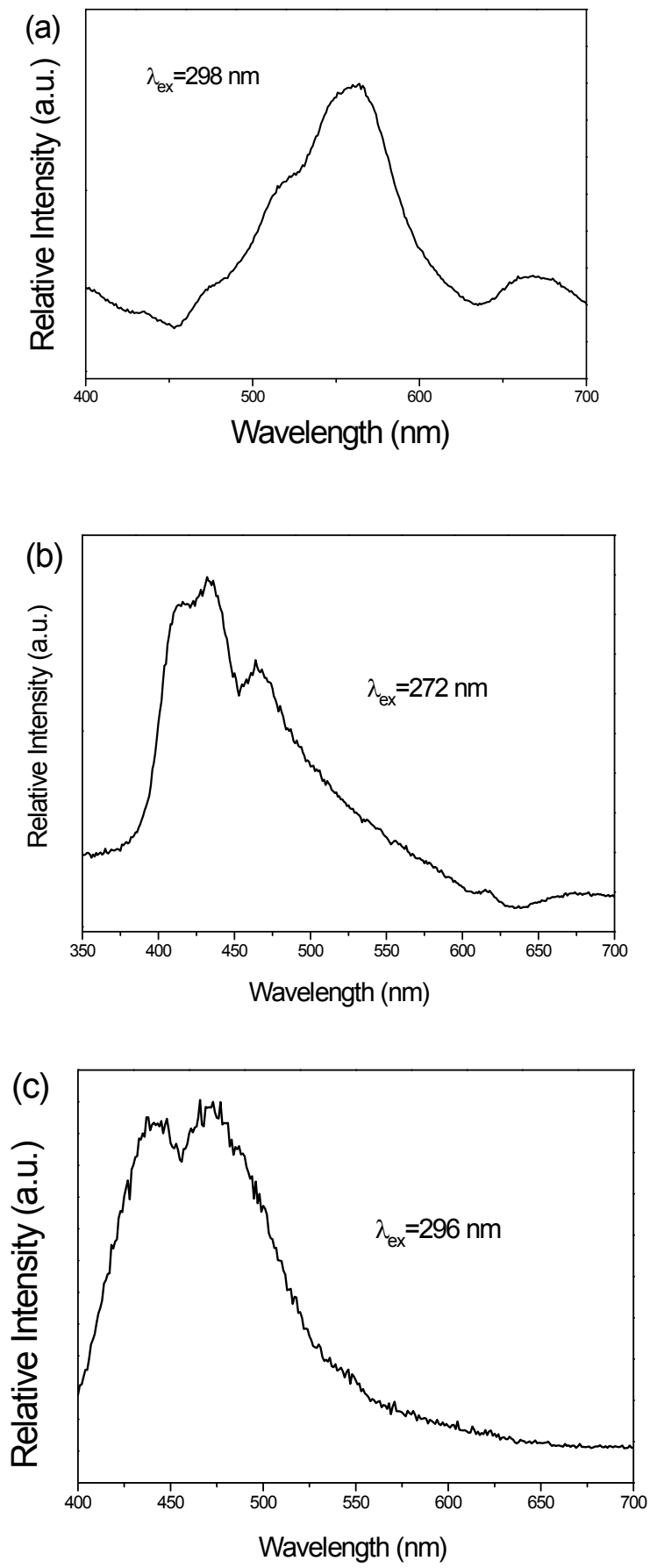


Fig. S6 Emission spectra of H₃BTC (a) , H₃PMo₁₂O₄₀(b) and NENU-5(c)

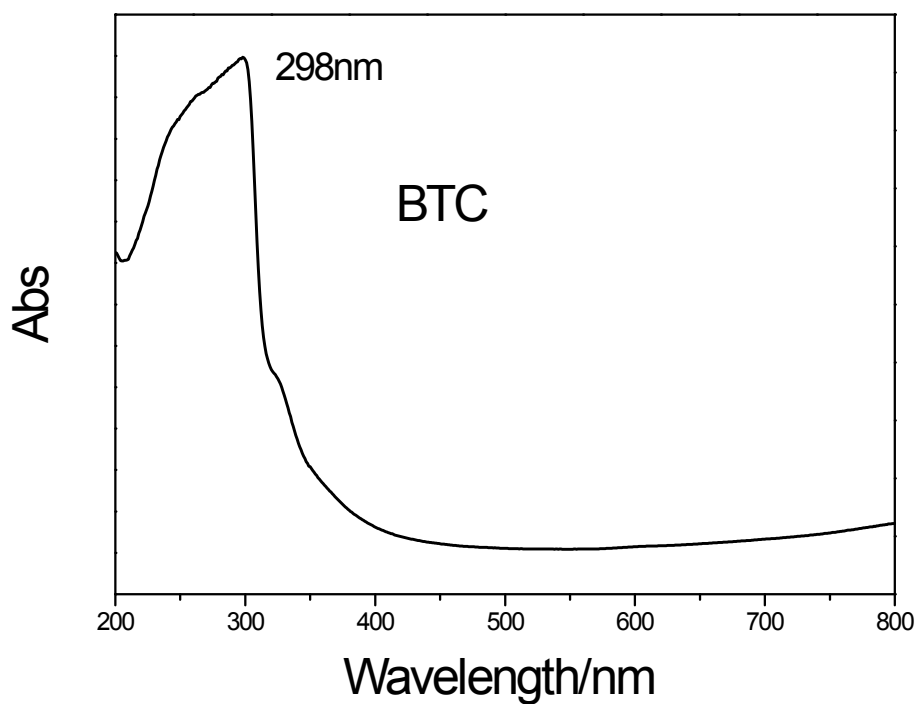


Fig. S7 UV-vis diffuse reflectance spectrum of BTC

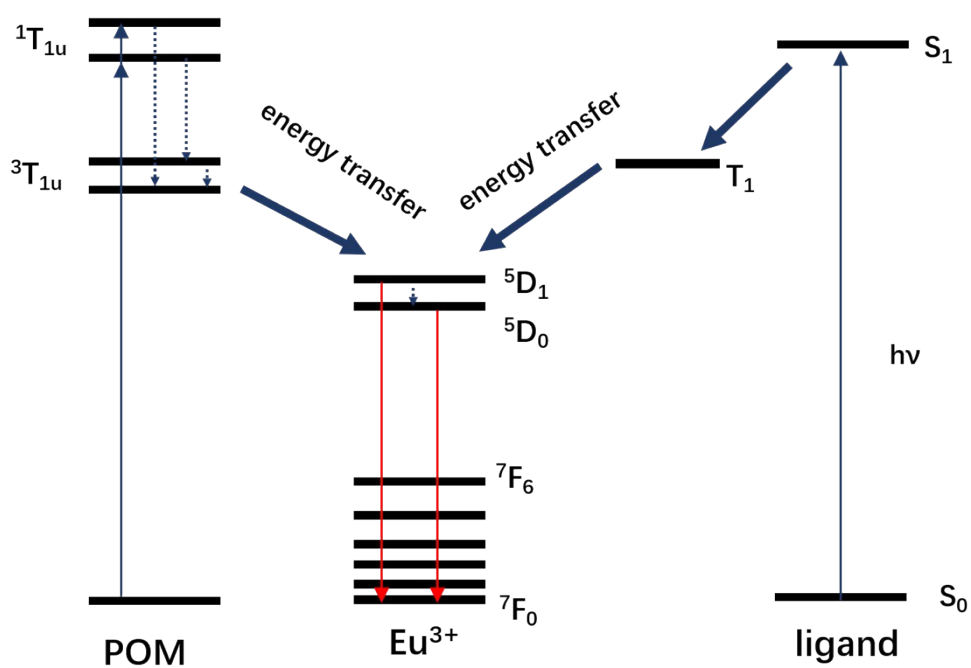


Fig. S8 Simple energy schematic diagram Eu^{3+} emission sensitized by both POM and ligand.

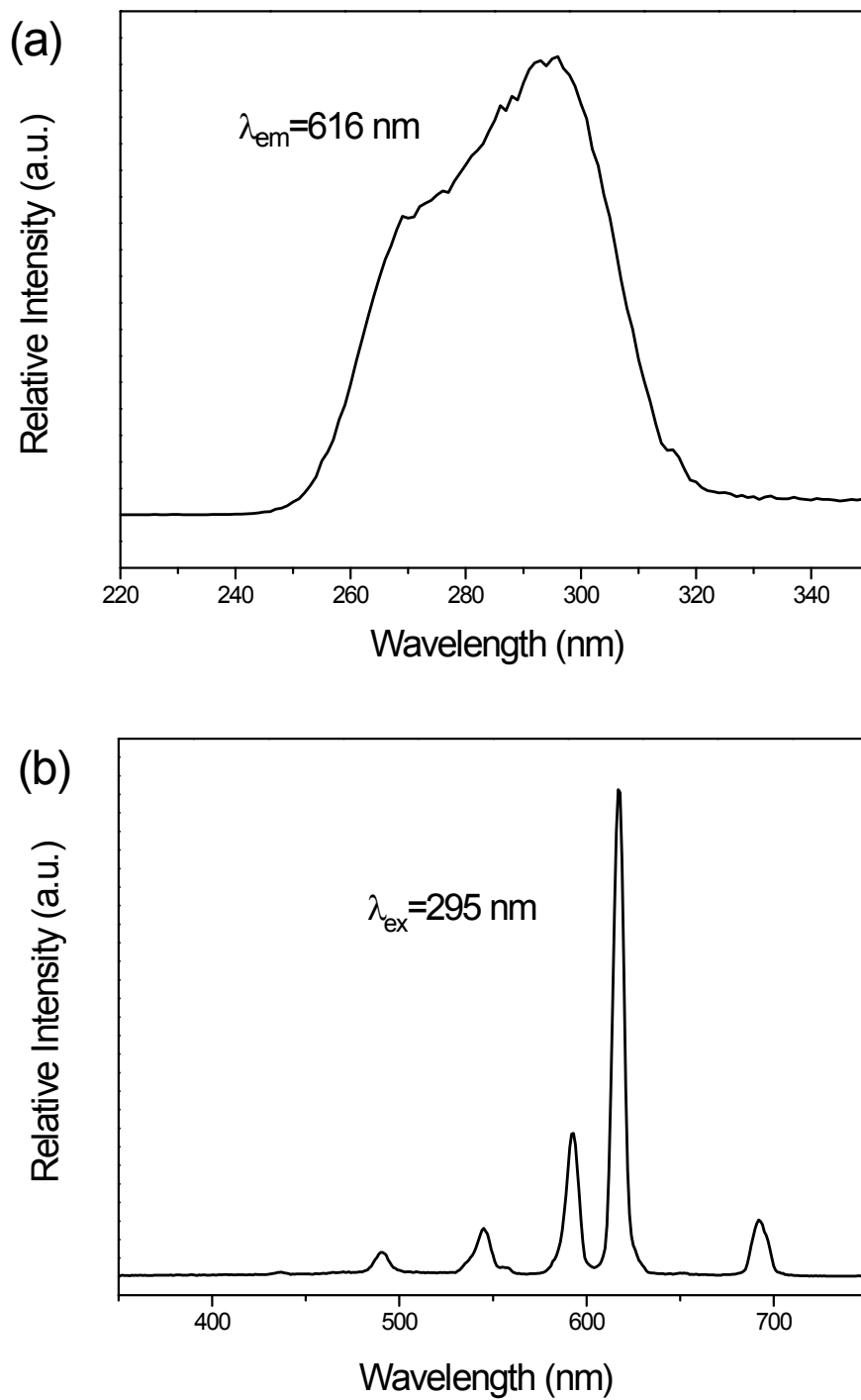


Figure S9 Excitation spectrum(a) and emission spectrum(b) of $\text{Eu}^{3+} / \text{Tb}^{3+}@ \text{NENU-5}$

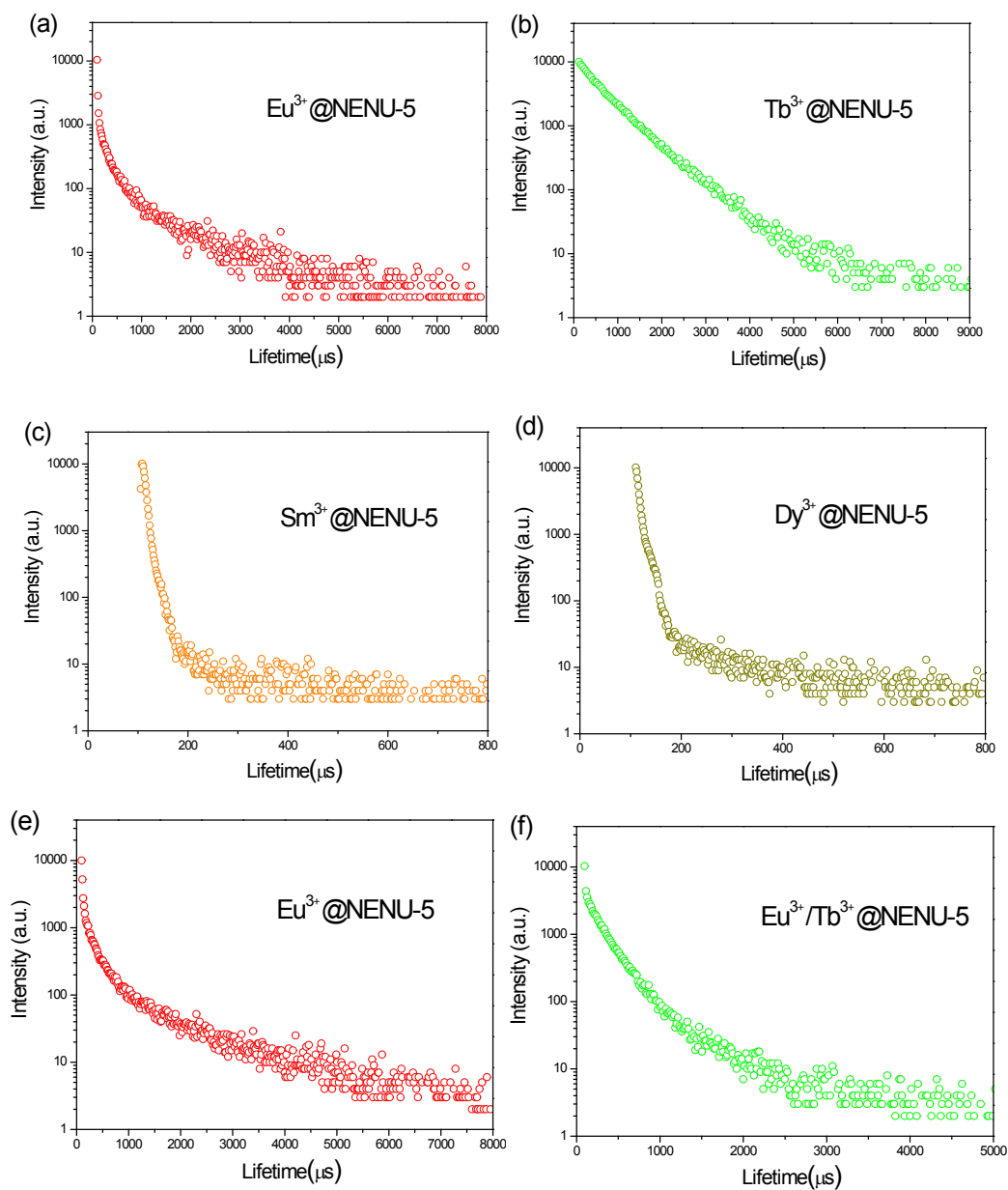


Fig. S10 Decay curves of Eu^{3+} @NENU-5(a) ($\lambda_{\text{em}}=615\text{nm}$), Tb^{3+} @NENU-5(b) ($\lambda_{\text{em}}=543\text{nm}$), Sm^{3+} @NENU-5(c) ($\lambda_{\text{em}}=598\text{nm}$), Dy^{3+} @NENU-5(d) ($\lambda_{\text{em}}=574\text{nm}$), $\text{Eu}^{3+}/\text{Tb}^{3+}$ @NENU-5($\lambda_{\text{em}}=615\text{nm}$)(e), $\text{Eu}^{3+}/\text{Tb}^{3+}$ @NENU-5($\lambda_{\text{em}}=543\text{nm}$)(f).

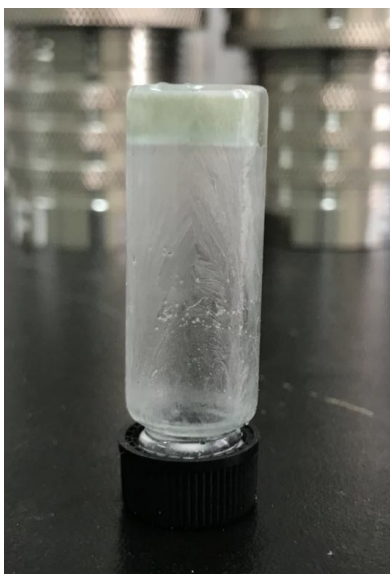


Fig. S11 $\text{Eu}^{3+} / \text{Tb}^{3+}$ @NENU-5 ionic liquid in room temperature

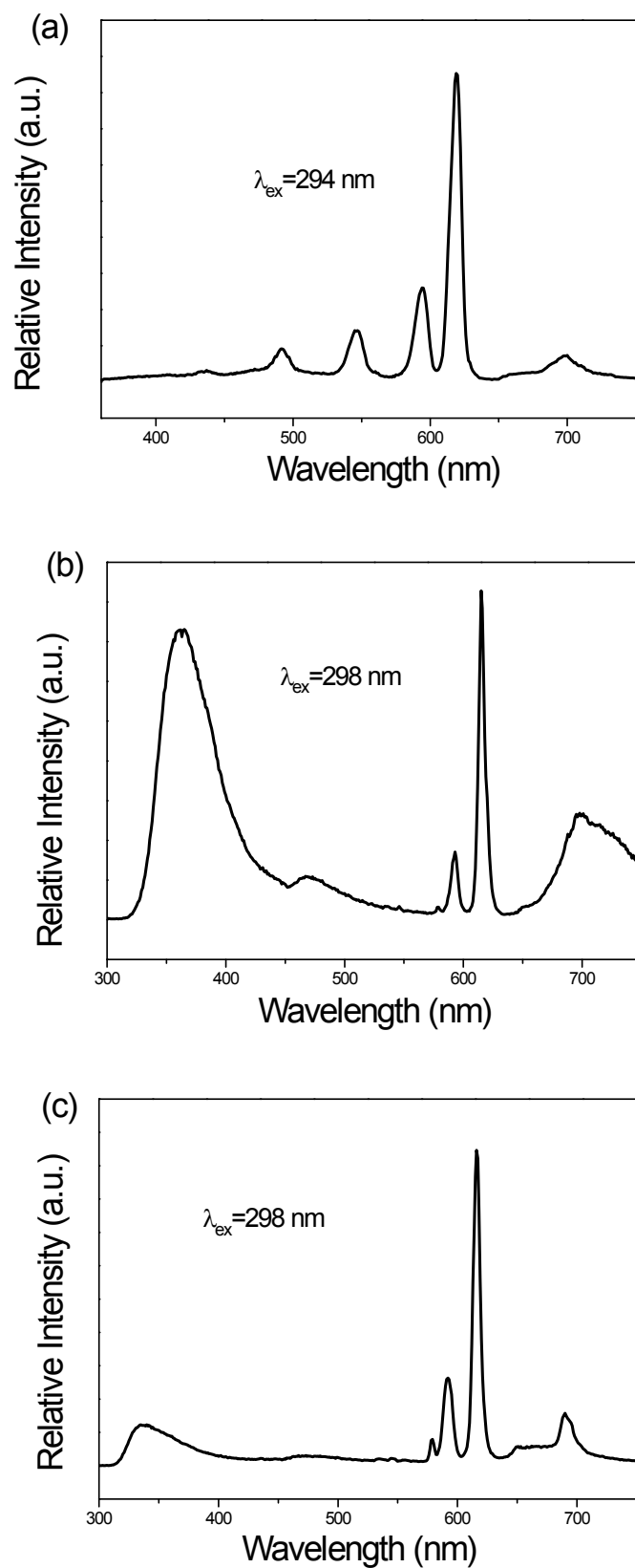


Fig. S12 Emission spectra of the soft ionogel loaded 1g Eu^{3+} / Tb^{3+} @NENU-5(a), the thin film loaded 2.5mg(b) and 7.5mg Eu^{3+} @NENU-5 sample.

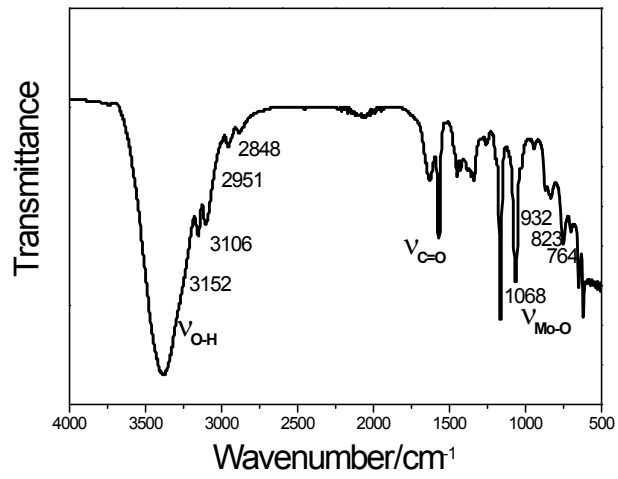


Fig. S13 IR spectrum of Eu³⁺/Tb³⁺@1 soft ionogel

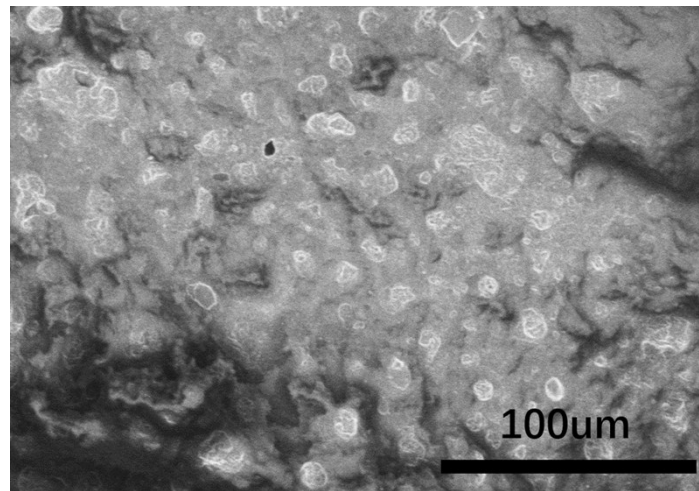


Fig.S14 SEM image of the Eu³⁺@NENU-5 thin film.

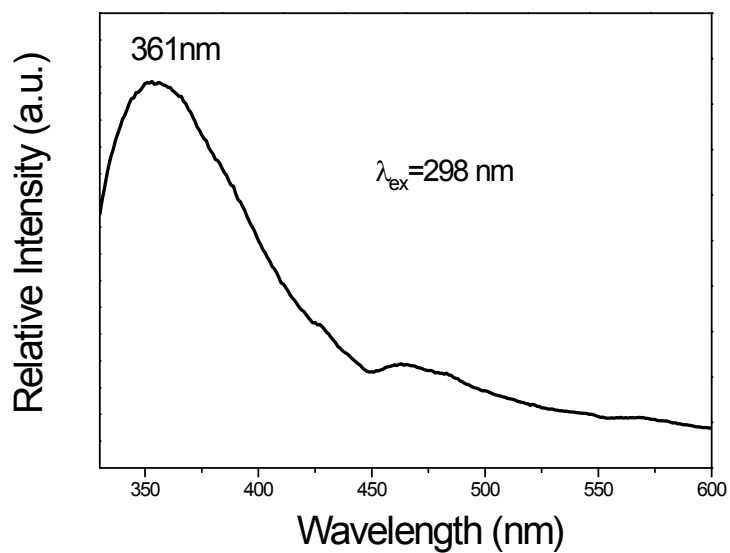


Fig. S15 Emission spectra of the pure thin film.

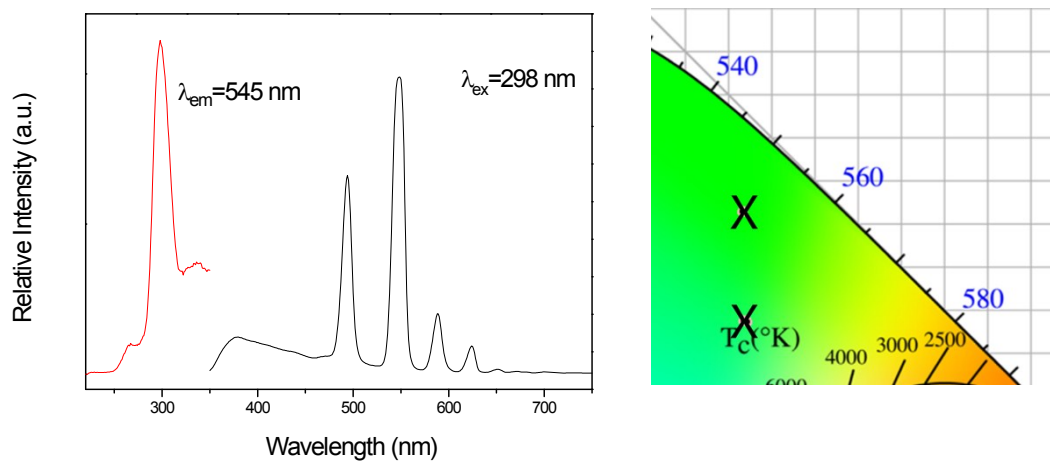


Fig. S16 Photoluminescence spectra of Tb^{3+} @NENU-5 thin film and the comparison of CIE coordinate

Table S1 ICP-MS analysis of Ln³⁺-NENU5(Ln = Eu, Tb, Sm, Dy, Eu/Tb)

Sample	Eu(ppm)	Tb(ppm)	Sm(ppm)	Dy(ppm)	Cu (ppm)	Ln ³⁺ : La ³⁺ (Molar Ratio)
Eu ³⁺ @1	1.84	--	--	--	17.62	1: 22.7
Tb ³⁺ @1	--	3.13	--	--	34.24	1: 23.4
Sm ³⁺ @1	--	--	1.29	--	15.06	1: 26.2
Dy ³⁺ @1	--	--	--	2.18	21.55	1: 25.3
Eu ³⁺ /Tb ³⁺ @1	1.45	0.63	--	--	14.52	1:1: 25.7

Table S2 The peak position and the corresponding transition related to the Ln³⁺ of the Ln³⁺ @NENU-5 materials (Ln = Eu, Tb, Sm, Dy).

Sample	Position (nm)	transition
Eu ³⁺ @NENU-5	584	⁵ D ₀ → ⁷ F ₀
	592	⁵ D ₀ → ⁷ F ₁
	615	⁵ D ₀ → ⁷ F ₂
	649	⁵ D ₀ → ⁷ F ₃
	695	⁵ D ₀ → ⁷ F ₄
Tb ³⁺ @NENU-5	489	⁵ D ₄ → ⁷ F ₆
	545	⁵ D ₄ → ⁷ F ₅
	583	⁵ D ₄ → ⁷ F ₄
	621	⁵ D ₄ → ⁷ F ₃
Sm ³⁺ @NENU-5	562	⁴ G _{5/2} → ⁶ H _{5/2}
	596	⁴ G _{5/2} → ⁶ H _{7/2}
	642	⁴ G _{5/2} → ⁶ H _{9/2}
	704	⁴ G _{5/2} → ⁶ H _{11/2}
Dy ³⁺ @NENU-5	481	⁷ F _{9/2} → ⁶ H _{15/2}
	575	⁷ F _{9/2} → ⁶ H _{13/2}

Table S3 CIE chromaticity coordinates of Sm³⁺@NENU-5 in various excitation from 255 to 300nm.

Excitation wavelength	X	Y
255nm	0.3212	0.3289
260nm	0.3577	0.3366
265nm	0.3691	0.3381
270nm	0.3544	0.3322
275nm	0.3348	0.3214
280nm	0.332	0.3187
285nm	0.3333	0.3162
290nm	0.3365	0.3193
295nm	0.3241	0.315
300nm	0.3367	0.3171

Table S4 Luminescence lifetimes (τ) of Ln³⁺@NENU-5((Ln = Eu, Tb, Sm, Dy, Eu/Tb))

Sample	λ_{ex} (nm)	λ_{em} (nm)	τ (μ s)
Eu ³⁺ @ NENU-5	294	615	351.61
Tb ³⁺ @ NENU-5	295	543	637.51
Sm ³⁺ @ NENU-5	296	598	15.63
Dy ³⁺ @ NENU-5	294	574	33.68
Eu ³⁺ /Tb ³⁺ @ NENU-5	295	614	476.25
Eu ³⁺ /Tb ³⁺ @ NENU-5	295	543	278.21