Lanthanide-based Coordination Polymers: A Fluorometric frontier in Explosive sensing

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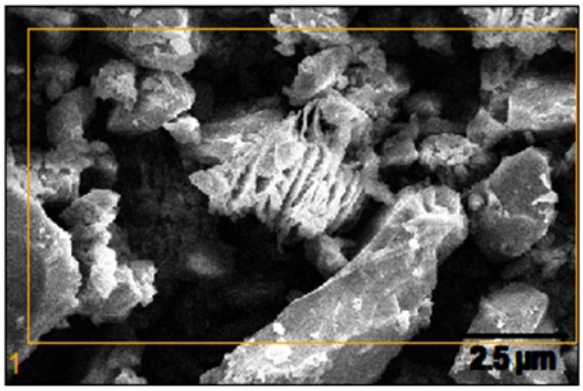
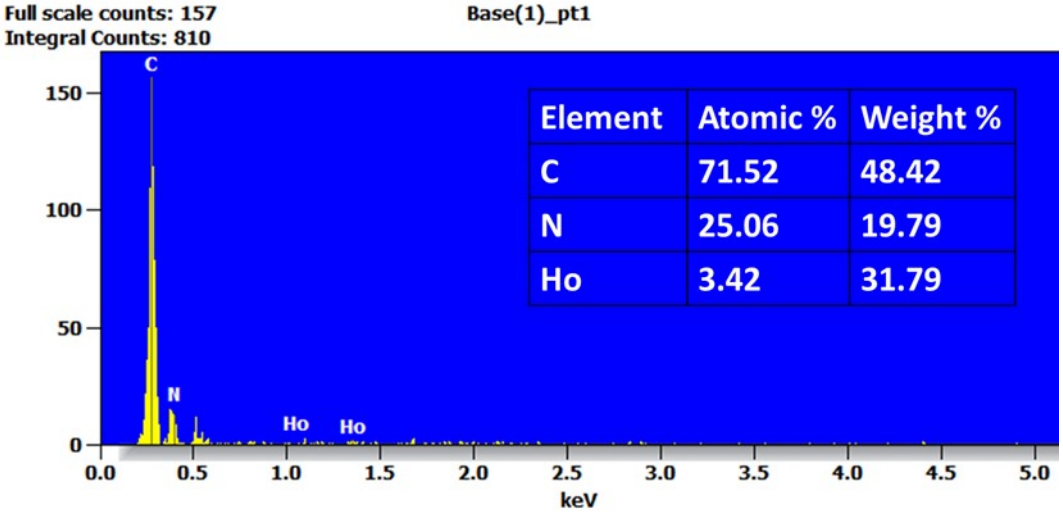
Supporting Information





Element	Atomic %	Weight %
C	71.52	48.42
N	25.06	19.79
Ho	3.42	31.79

Figure S1. EDS spectrum of Ho(DAB).

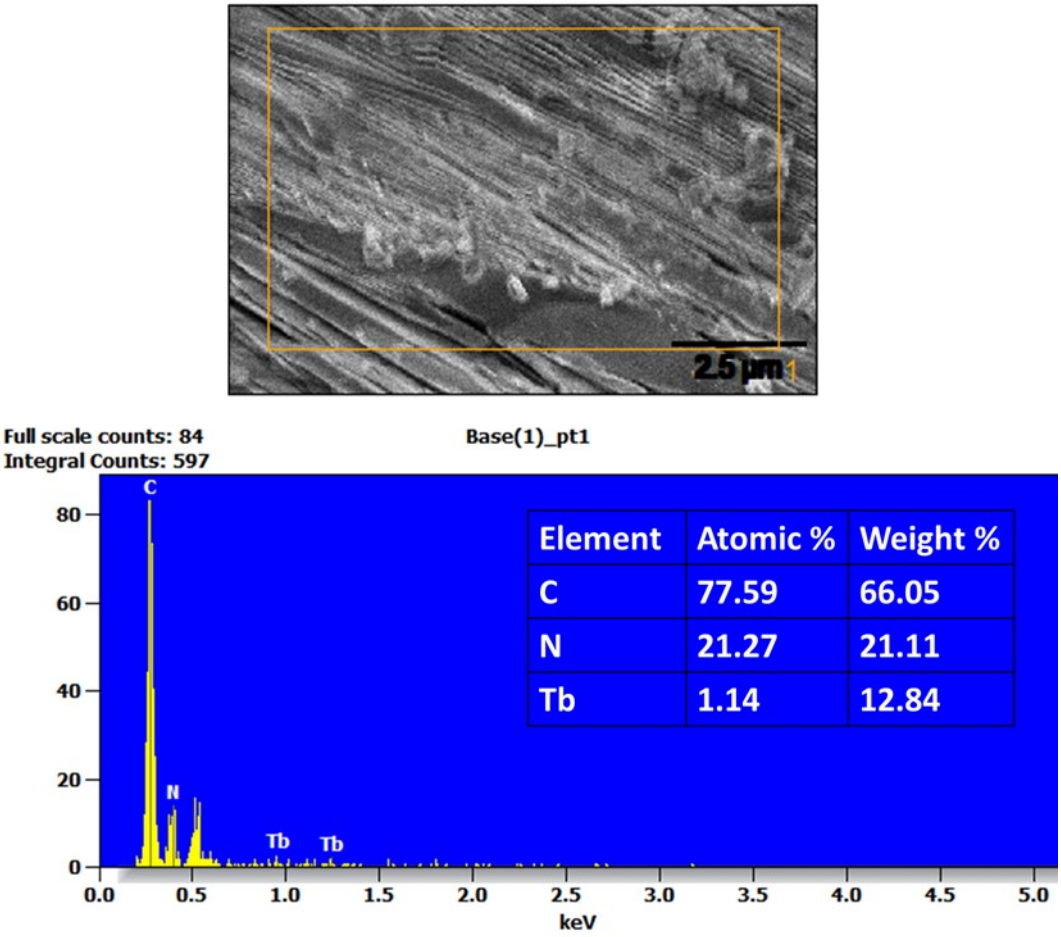


Figure S2. EDS spectrum of Tb(DAB).

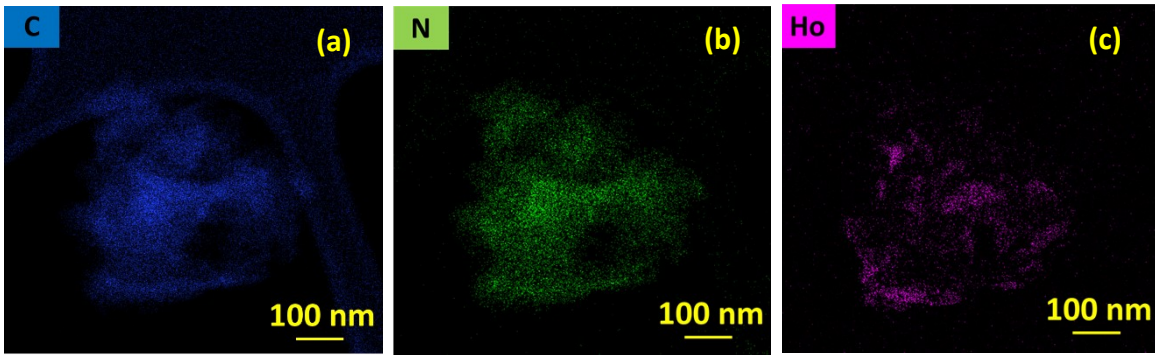


Figure S3. HAADF-STEM elemental mapping of (a) C, (b) N, and (c) Ho, in Ho(DAB).

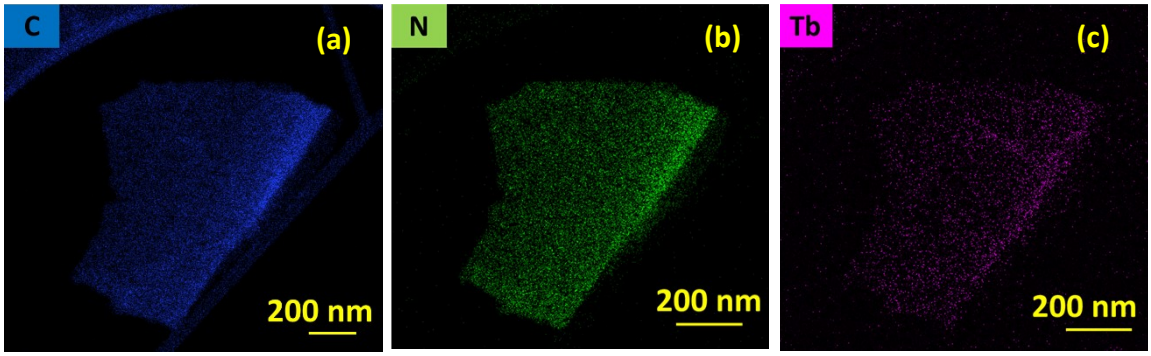


Figure S4. HAADF-STEM elemental mapping of (a) C, (b) N, and (c) Tb, in Tb(DAB).

Quantum yield:

Quantum yield is a measure of the efficiency with which absorbed photons are converted into emitted photons in a photophysical process, such as fluorescence. It is defined as the ratio of the number of emitted photons to the number of absorbed photons. To calculate quantum yield using the calibration curve method, a sample's fluorescence intensity is compared with that of a reference standard with a known quantum yield (quinine sulphate, here). The method involves recording the fluorescence emission spectra of both the sample and reference under identical experimental conditions. A calibration curve is constructed by plotting the integrated fluorescence intensity of both the sample and the reference standard against their respective absorbance values. Using this curve, the quantum yield of the sample can be determined based on Equation S1.

$$\phi_x = \phi_{ref}\left(\frac{grad_x}{grad_{ref}}\right)\left(\frac{{\eta_x}^2}{{\eta_{ref}}^2}\right) \qquad (S1)$$

$\phi_x = Quantum\ yield\ of\ COP$

$\phi_{ref} = Quantum\ yield\ of\ ref\ (for\ quinine\ sulphate = 0.55)$

$grad_x$ $= Gradient\ of\ linear\ plot\ of\ integrated\ emission\ intensity\ vs\ al$

$grad_{ref}$ $= Gradient\ of\ linear\ plot\ of\ integrated\ emission\ intensity\ vs\ al$

$\eta_x = Refractive\ index\ of\ solvent\ used\ for\ COP\ (for\ DMF = 1.42)$

$\eta_x = Refractive\ index\ of\ solvent\ used\ for\ ref\ (for\ 0.1\ M\ H_2SO_4 = 1.33)$

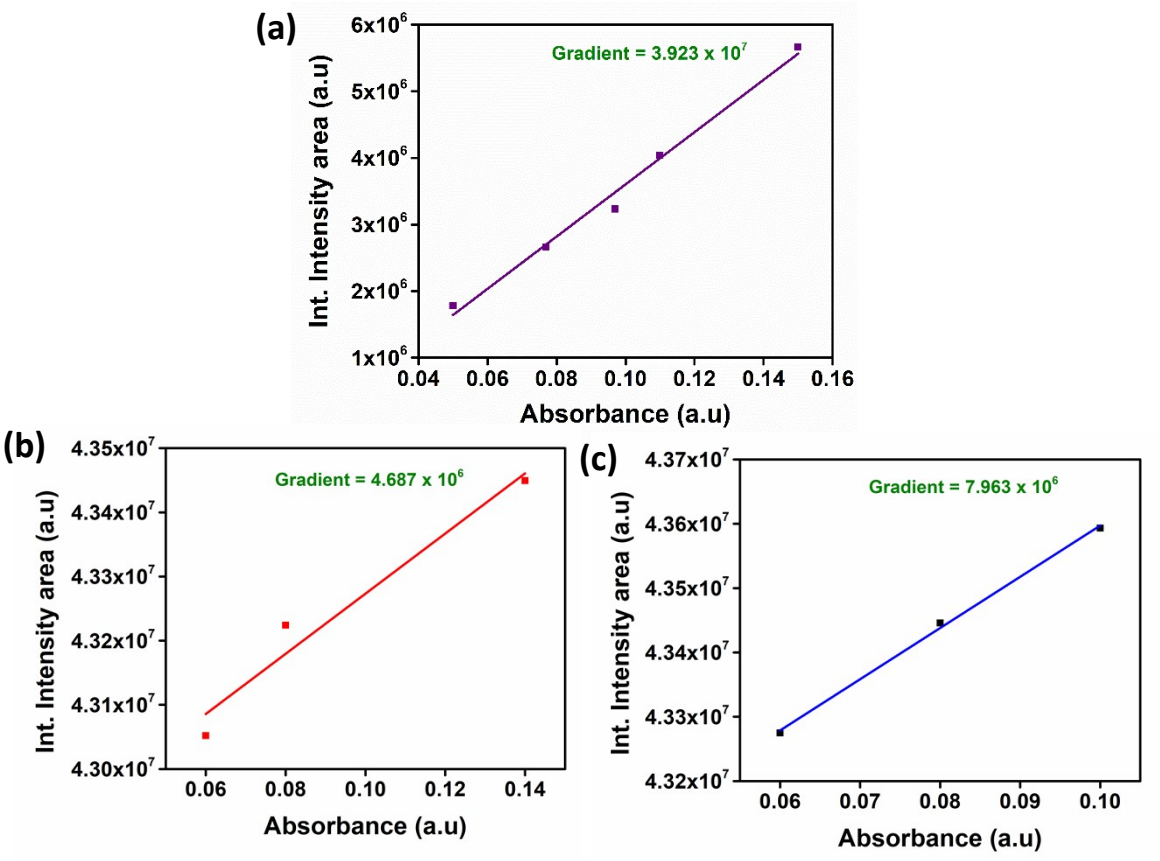


Figure S5. Linear plot of integrated emission intensity vs absorbance of (a) Quinine sulfate (b) Ho(DAB) (c) Tb(DAB)

Table S1. Quantum yield obtained for Ln-COPs

	Quantum yield (%)
Ho(DAB)	7.49
Tb(DAB)	12.73

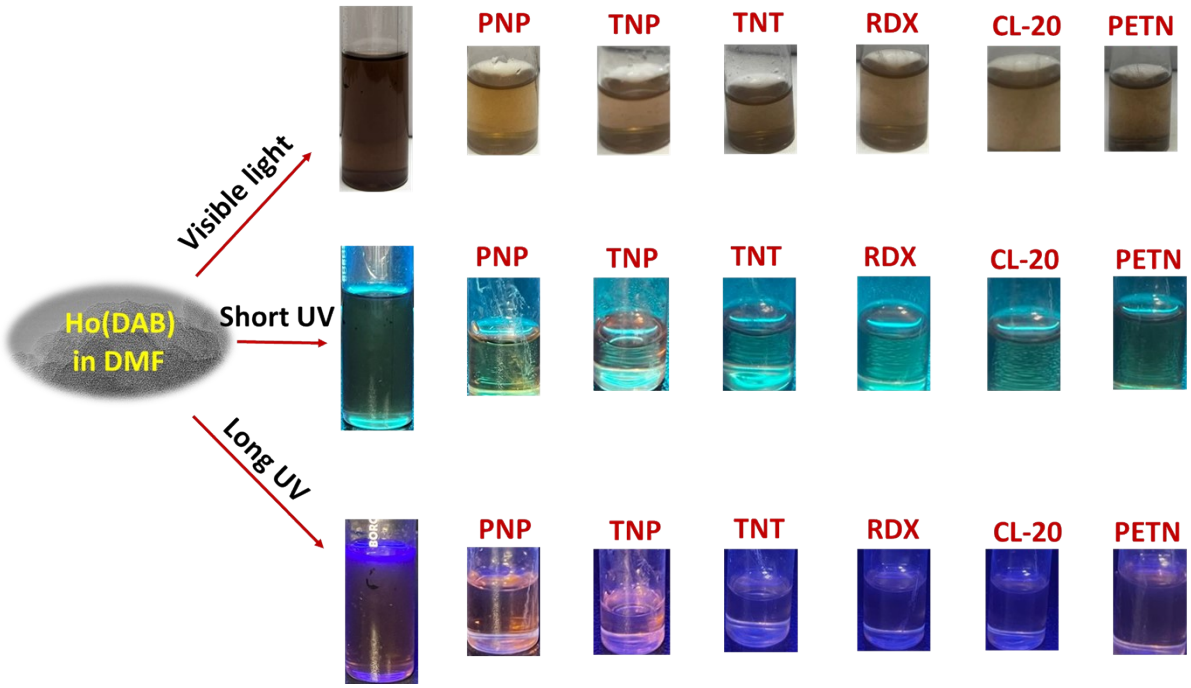


Figure S6. Real time images of fluorescence quenching observed in Ho(DAB) on adding HEMs.

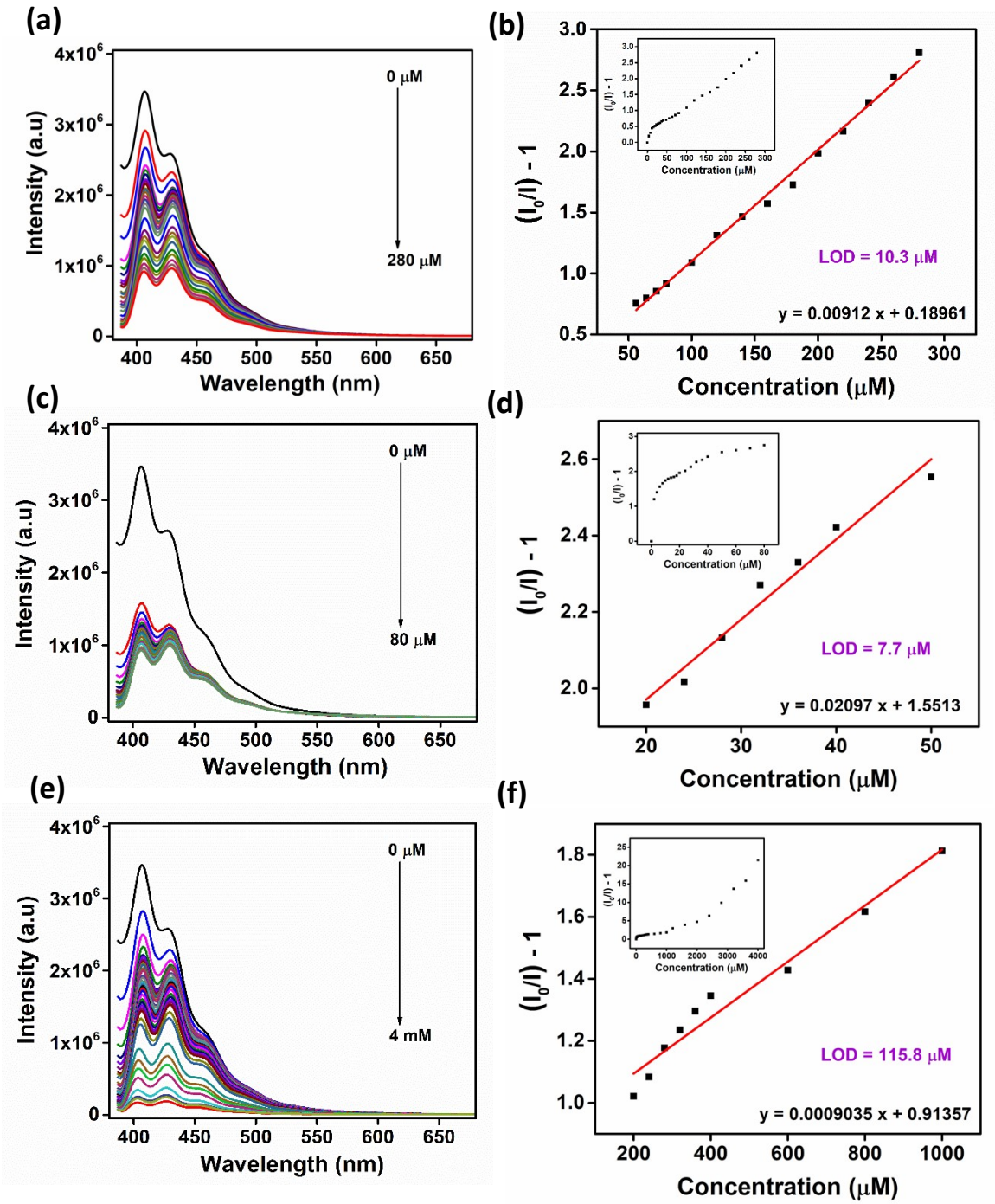


Figure S7. Fluorescence spectra of Tb(DAB) suspended in DMF were recorded following the stepwise addition of micromolar concentrations of (a-b) PNP, (c-d) TNP and (e-f) TNT, dissolved in acetone, along with their corresponding Stern-Volmer plots.

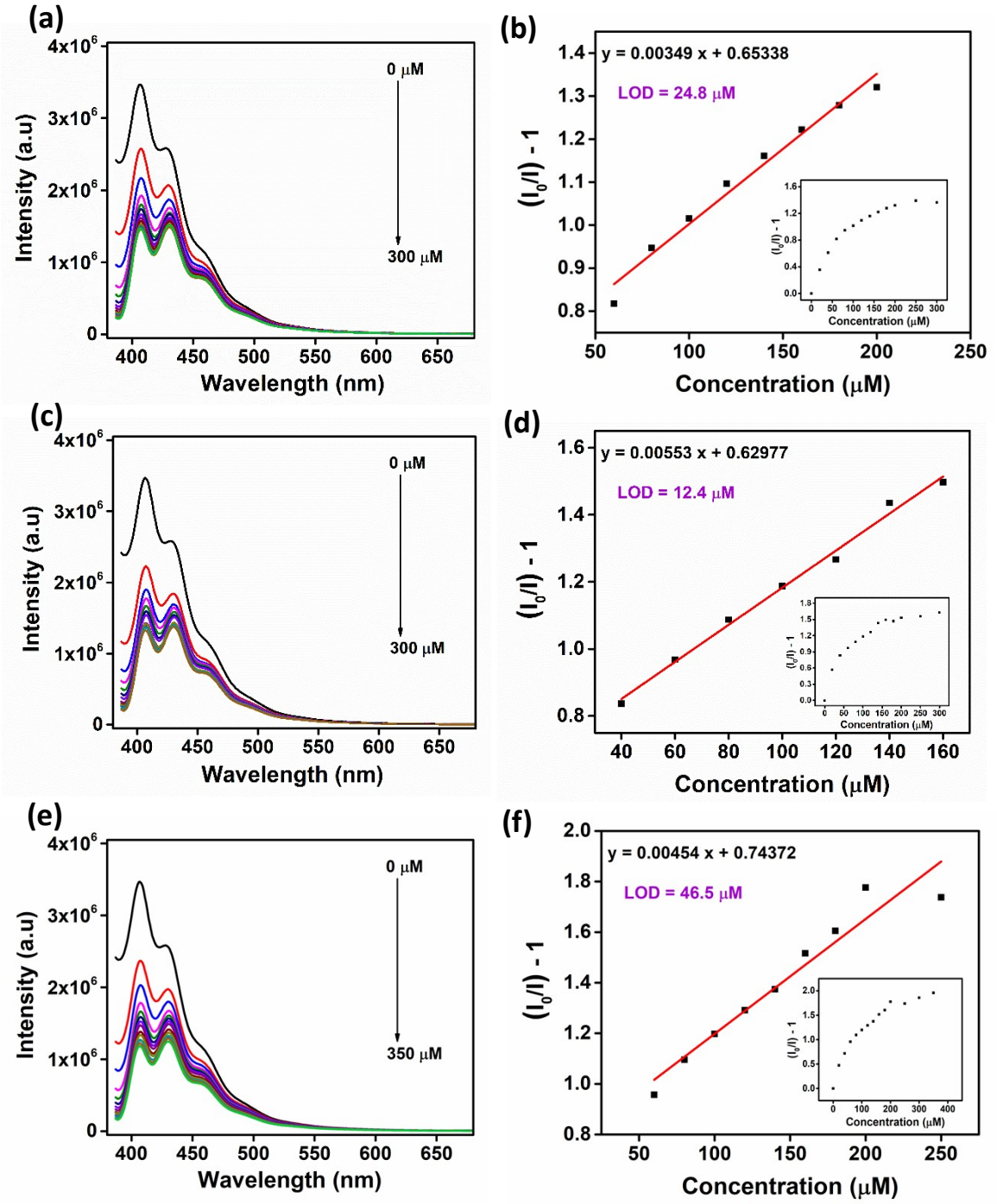


Figure S8. Fluorescence spectra of Tb(DAB) suspended in DMF were recorded following the stepwise addition of micromolar concentrations of (a-b) RDX (c-d) PETN and (e-f) CL-20, dissolved in acetone, along with their corresponding Stern-Volmer plots.

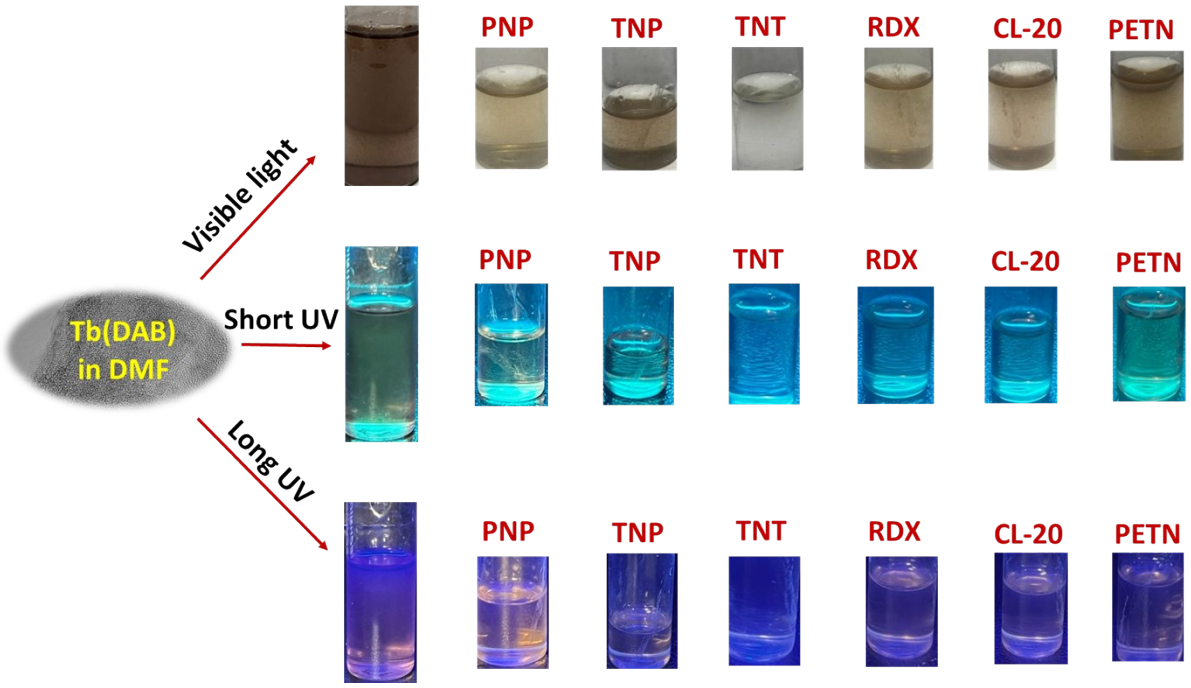


Figure S9. Real time images of fluorescence quenching observed in Tb(DAB) on adding HEMs.

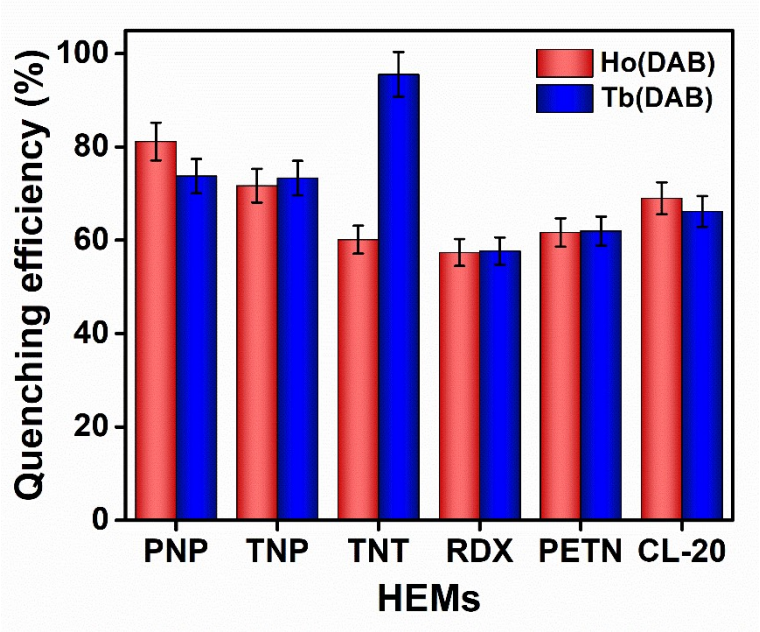


Figure S10. Graphical representation of quenching efficiency obtained for HEMs using Ho(DAB) and Tb(DAB).

Table S2. Summary of literature reports based on Ho and Tb based COPs for fluorometric detection of HEMs

Sl. No.	COP	HEMs	LOD	Reference

1.	$[Tb_2L_{1.5}(NMP)_2]_n$ (H_4L = [1,1′:4′,1″-terphenyl]-2′,4,4″,5′-tetracarboxylic acid; NMP = N-methyl-2-pyrrolidone)	TNP	0.11 µM	[1]
2.	$[Tb(BDPO)(H_2O)_4]$ (BDPO = N,N′-bis(3,5-dicarboxyphenyl)-oxalamide ligand)	TNP	0.21 µM	[2]
3.	Tb @ 1 (1 = $[Zn(L)_2]\cdot(CH_3OH)_{0.5}.H_2O$)	TNP 2,4-NA PNP	6.268×10^{-5} M 4.18×10^{-5} M, 1.1×10^{-4} M	[3]
4.	[Tb(bpbd) $(H_2O)_2(NO_3)]\cdot xH_2O$ (K_2bpbd = 2,2′-(butane-1,4-diylbis((pyridin-2-ylmethyl)azanediyl))diacetate)	TNP	0.35 ppm	[4]
5.	$\{[Tb_2(L^{30})_3(H_2O)_2]\cdot 21\ H_2O\}_n$	TNP	67 ppb	[5]
6.	**Ho(DAB)**	**TNP**	**16.4 µM**	**This work**
7.	**Tb(DAB)**	**TNP**	**7.7 µM**	**This work**

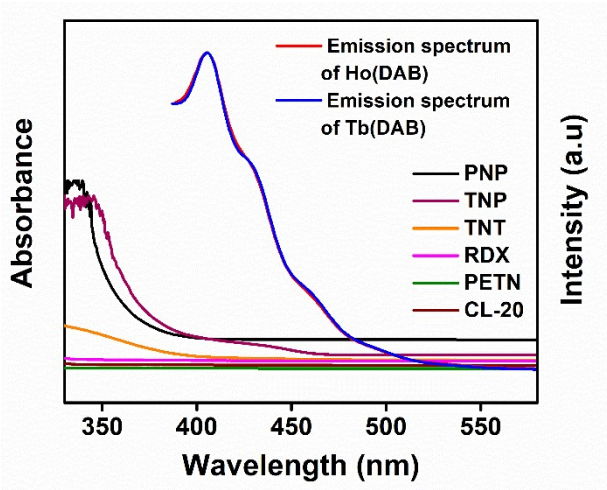


Figure S11. Overlaid Absorption spectra of HEMs and emission spectra of Ln-COPs

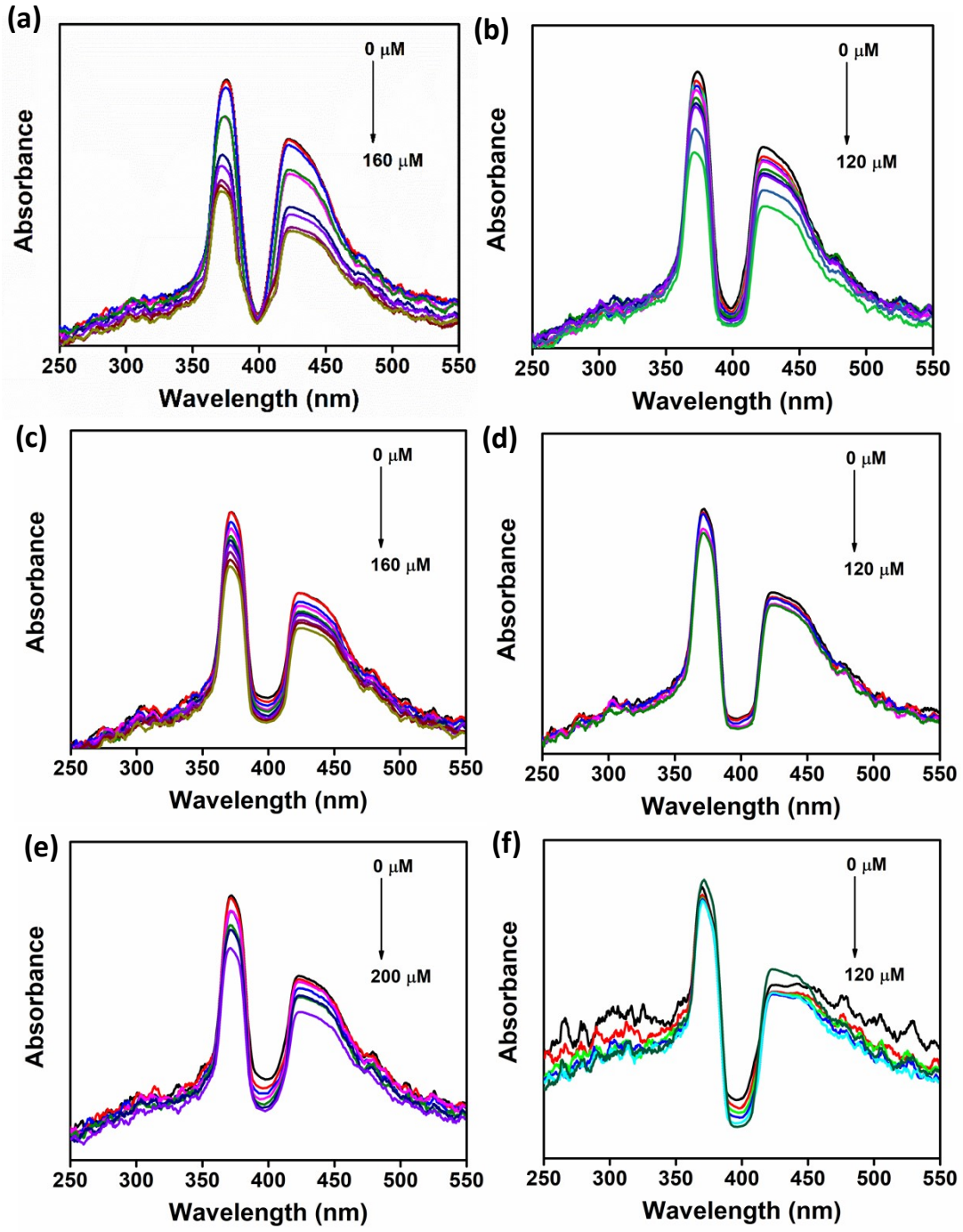


Figure S12. UV-Vis spectra of Ho(DAB) suspended in DMF were recorded following the stepwise addition of micromolar concentrations of (a) PNP (b) TNP (c) TNT (d) RDX (e) PETN (f) CL-20, dissolved in acetone.

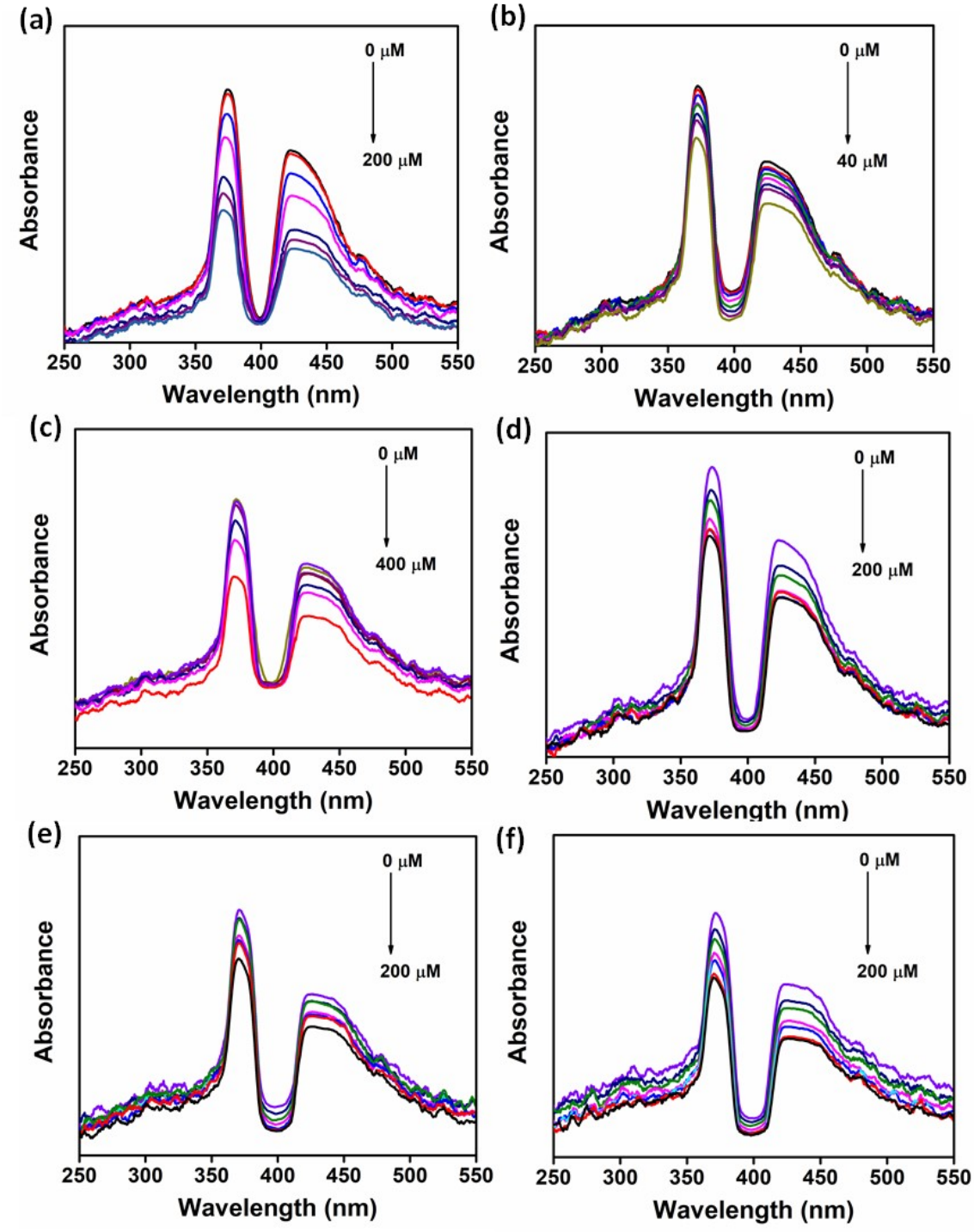


Figure S13. UV-Vis spectra of Tb(DAB) suspended in DMF were recorded following the stepwise addition of micromolar concentrations of (a) PNP (b) TNP (c) TNT (d) RDX (e) PETN (f) CL-20, dissolved in acetone.

Fluorescence lifetime decay:

Fluorescence lifetime decay refers to the process by which the fluorescence emission from a molecule diminishes over time after the molecule absorbs light. This phenomenon occurs as a

result of the molecule's transition from an excited state back to its ground state, with the emission of photons. The fluorescence lifetime (τ) is defined as the average time the molecule spends in its excited state before returning to the ground state. The fluorescence decay of a sample can be better described using a biexponential decay model (Equation S2). In this biexponential model, the two components represent the contributions from different relaxation processes or environments within the sample, such as different excited state populations or energy transfer between different species. Average fluorescence lifetime is calculated using Equation S3.

$$A + B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2} \quad (S2)$$

$$Average\ lifetime = \frac{B_1 {\tau_1}^2 + B_2 {\tau_2}^2}{B_1 \tau_1 + B_2 \tau_2} \quad (S3)$$

Table S3. Average lifetime calculated for Ln-COPs with and without addition of quencher

	Average Lifetime (ns)
Ho(DAB)	1.108
Ho(DAB) + TNP	1.047
Tb(DAB)	0.868
Tb(DAB) + TNP	0.998

References:

1 L. Li, J. Cheng, Z. Liu, L. Song, Y. You, X. Zhou and W. Huang, Ratiometric Luminescent Sensor of Picric Acid Based on the Dual-Emission Mixed-Lanthanide Coordination Polymer, *ACS Appl. Mater. Interfaces*, 2018, **10**, 44109–44115.

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