

Supporting Information

Highly thermostable lanthanide metal-organic frameworks exhibiting unique selectivity for nitro explosives

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1. Crystal data for LnL

Table S1. Crystal data and structure refinements of compound **1**

Compound	1
formula	Gd ₂ C ₆₇ H ₇₀ N ₂ O ₁₄
fw	1441.75
<i>T</i> /K	293(2)
λ (Mo K α), Å	0.71073
cryst syst	monoclinic
space group	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	23.321(5)
<i>b</i> (Å)	15.408(4)
<i>c</i> (Å)	18.286(4)
α (deg)	90
β (deg)	98.309(4)
γ (deg)	90
<i>V</i> /Å ³	6502(3)
<i>Z</i>	4
<i>D</i> _{calc} (g·cm ⁻³)	1.473
<i>F</i> (000)	2904
2 θ _{max} (°)	50.44
GOF	1.006
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0343
<i>wR</i> ₂ ^b (all data)	0.0873

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum (|F_o|^2 - |F_c|^2) / \sum |F_o|^2]^{1/2}$.

Table S2. The cell parameters of LnL compounds (Ln = Gd, Eu, Tb, Monoclinic, $C2/c$, $\alpha = \gamma = 90^\circ$)

Ln	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/^\circ$	$V/\text{\AA}^3$
Gd	23.321(5)	15.408(4)	18.286(4)	98.309(4)	6502(3)
Eu	23.291(2)	15.3928(13)	18.2798(16)	98.298(2)	6484(81)
Tb	23.3356(15)	15.3735(9)	18.2341(11)	98.5230(10)	6469(24)

2. Additional figures for structural information of 1

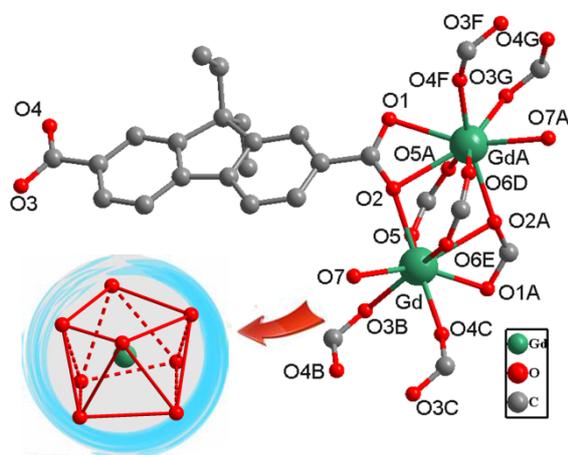


Fig. S1 Local coordination environment of the Gd^{3+} ions in **1**. Hydrogen atoms attached to carbon atoms are omitted for clarity. Symmetry codes: A, $1-x, y, 1.5-z$; B, $0.5-x, 1.5-y, 1-z$; C, $0.5+x, -0.5+y, z$; D, $1-x, -1+y, 1.5-z$; E, $x, -1+y, z$; F, $0.5-x, -0.5+y, 1.5-z$; G, $0.5+x, 1.5-y, 0.5+z$.

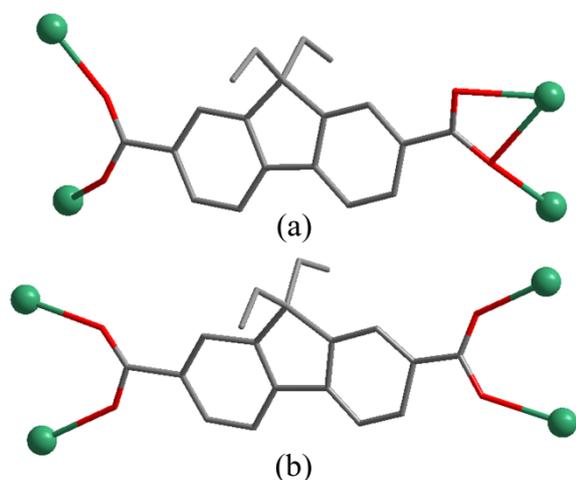


Fig. S2 Coordination modes of carboxylate groups in L^{2-} ligand.

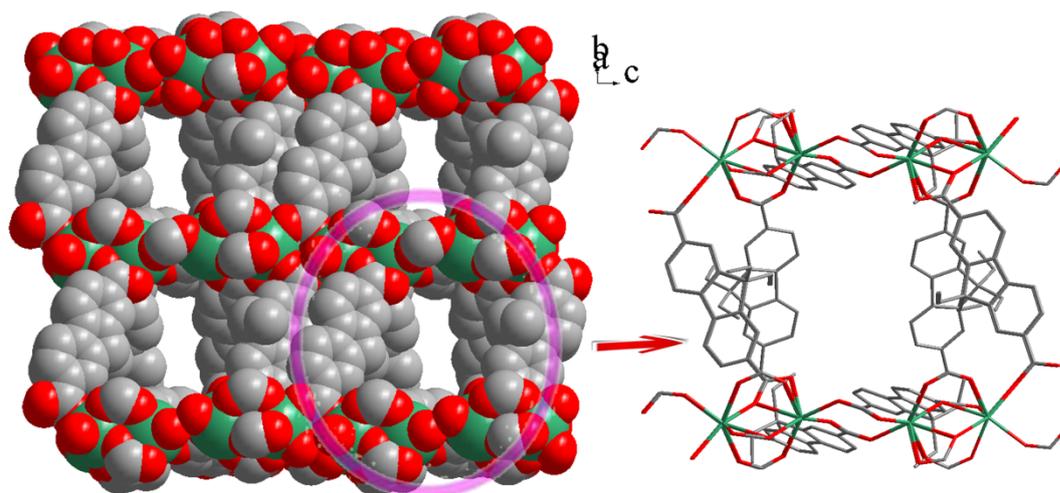


Fig. S3 The 1D channel of 2a.

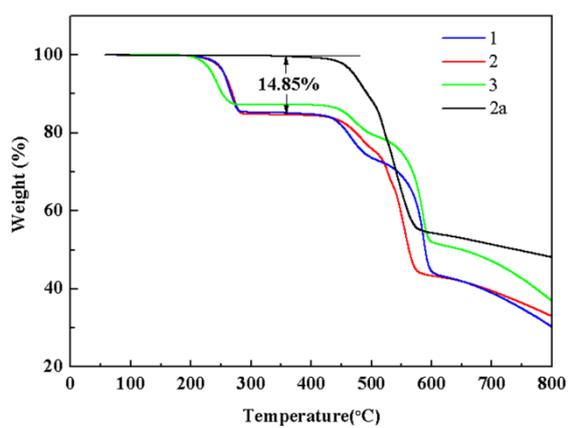


Fig. S4 TGA curves of compounds 1, 2, 3 and 2a

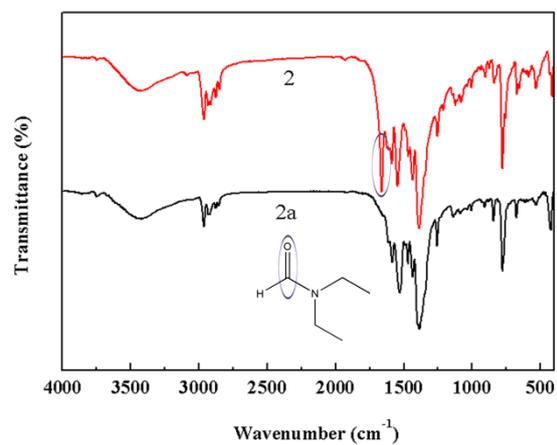


Fig. S5 The FT-IR spectrum of compound 2 and 2a

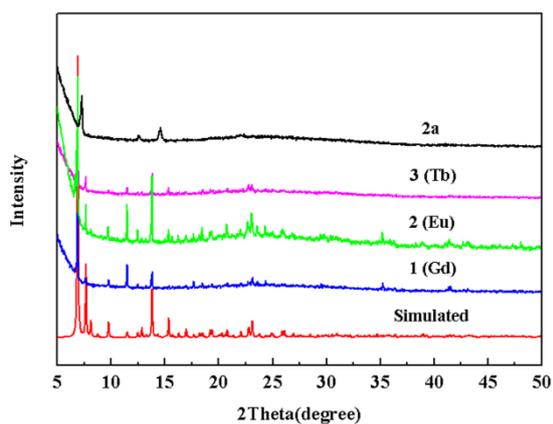


Fig. S6 Power X-ray diffraction (PXRD) pattern of simulated and experimental as-synthesized compounds **1** (Gd), **2** (Eu), **3** (Tb) and **2a**

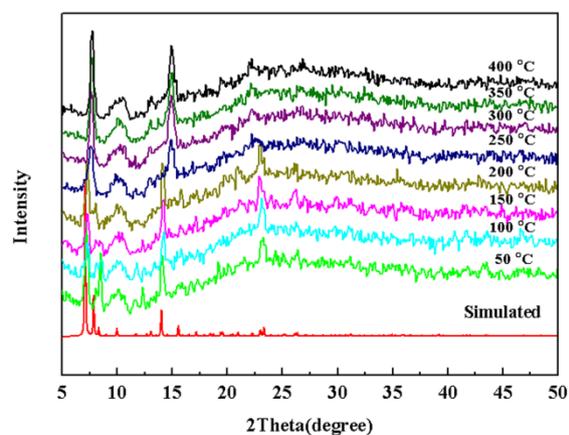


Fig. S7 Power X-ray diffraction pattern of simulated and experimental as-synthesized compounds **2** from 50 °C to 400 °C

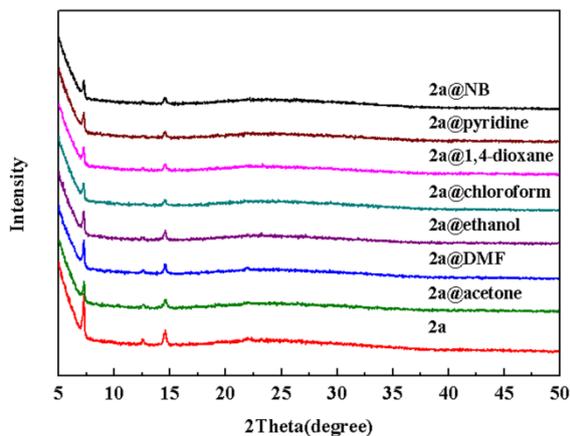


Fig. S8 Powder X-ray diffraction pattern of the solvent treated samples of **2a** with respect to each other and comparison with simulated ones

3. Luminescent Measurements

Photoluminescent sensing experiments

Solvent molecules sensing experiments

The activated and fine grinding sample of **2a** (3 mg) was immersed in different pure organic solvents (5 mL). Then the sample was treated by ultrasonication for 3 h and then aged for 2 days to form a stable emulsion before the fluorescence study. The organic solvents are DMF, ethanol, 2-propanol, ethylacetate, 1-propanol, methanol, acetonitrile, 1,4-dioxane, cyclohexane, chloroform, tetrahydrofuran, dichloromethane, acetone.

Aromatic compounds sensing experiments

The activated and fine grinding sample of **2a** (3 mg) was immersed in DMF (5 mL), treated by ultrasonication for 1 h. Then equal volume (25 μ L) of aromatic molecules was added into the above samples. Finally, stable emulsion was formed by ultrasonication for additional 3 h and then aged for 2 days before the fluorescence study. The aromatic compounds are benzene (Bz), toluene (Tol), nitrobenzene (NB), chlorobenzene (ClBz), bromobenzene (BrBz), aniline, methylphenyl ether (MeO-Bz), and *p*-xylene.

Nitroaromatic explosives sensing experiments

The activated and fine grinding sample of **2a** (3 mg) was immersed in the freshly prepared analyte solutions (1 mmol/L in DMF, 5 mL). Then the sample was treated by ultrasonication for 3 h and then aged for 2 days to form a stable emulsion before the fluorescence study. The nitroaromatic explosives are 2,4,6-trinitrophenol (TNP), 4-nitrophenol (4-NP), 3-nitrophenol (3-NP), *o*-nitrotoluene (*o*-NT), *m*-nitrotoluene (*m*-NT), nitrobenzene (NB) and nitromethane (NM).

2,4,6-trinitrophenol (TNP) sensing experiments (vapor)

The quartz slide was rinsed by de-ionized water and ethanol, and then was dried. A layer of approximately 0.3 mg of solid sample (prior ground into fine power) was deposited on the quartz slide. About 1 g TNP solid sample was placed into a small open vial and the vial was

placed into a bigger capped bottle for several days before the fluorescence sensing experiments to ensure that the equilibrated vapor pressure was reached. The original fluorescence spectra of the layer was collected before placing the slide into the bottle containing the analyte. At the specified exposure time, the slide was taken out and without any delay mounted to the sample holder of the fluorescence spectrophotometer and the fluorescence spectrum was recorded.

Caution! 2,4,6-trinitrophenol (TNP) is potentially explosive and should be handled with the necessary precautions.

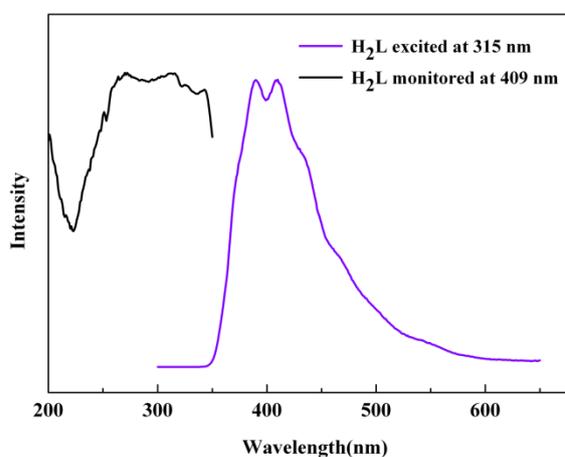


Fig. S9 Room-temperature excitation and emission spectra of compound H₂L in the solid state

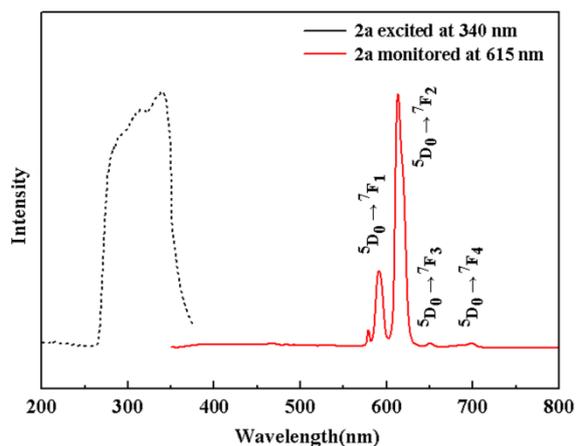


Fig. S10 Room-temperature excitation and emission spectra of compound 2a in the solid state

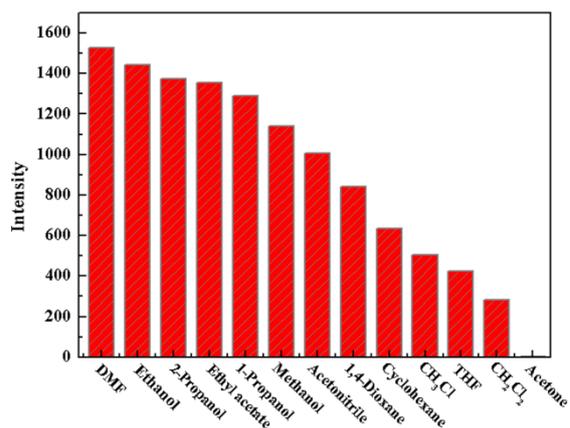


Fig. S11 Photoluminescence spectra of in different solvents. Excitation: 310 nm.

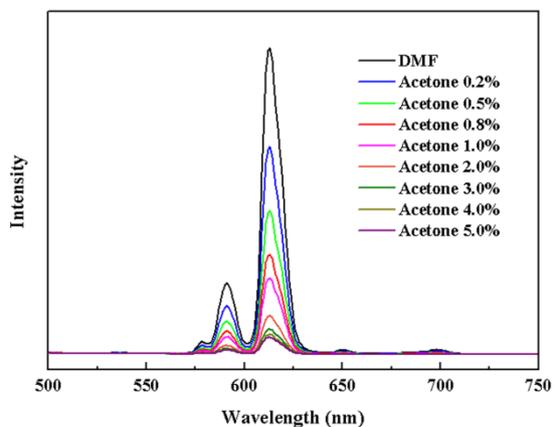


Fig. S12 The photoluminescence spectra of 2a DMF emulsion in the presence of various contents of acetone solvent.

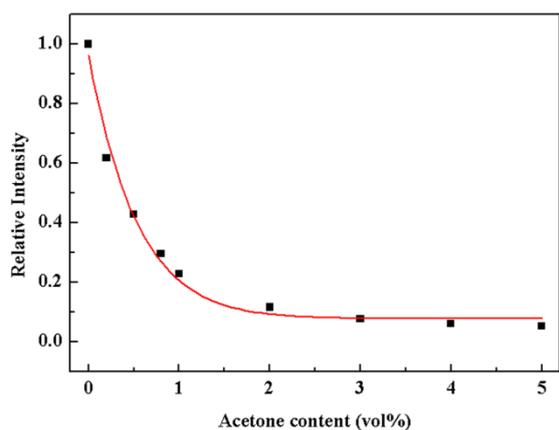


Fig. S13 The photoluminescence relative intensity (the photoluminescence intensity of acetone-incorporated **2a**/acetone-free **2a** at 615 nm) of the **2a** DMF emulsion as a function of acetone content

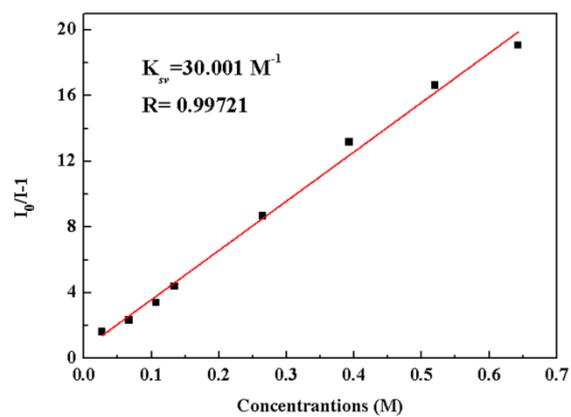


Fig. S14 Stern-Volmer plot for the quenching of **2a** by acetone.

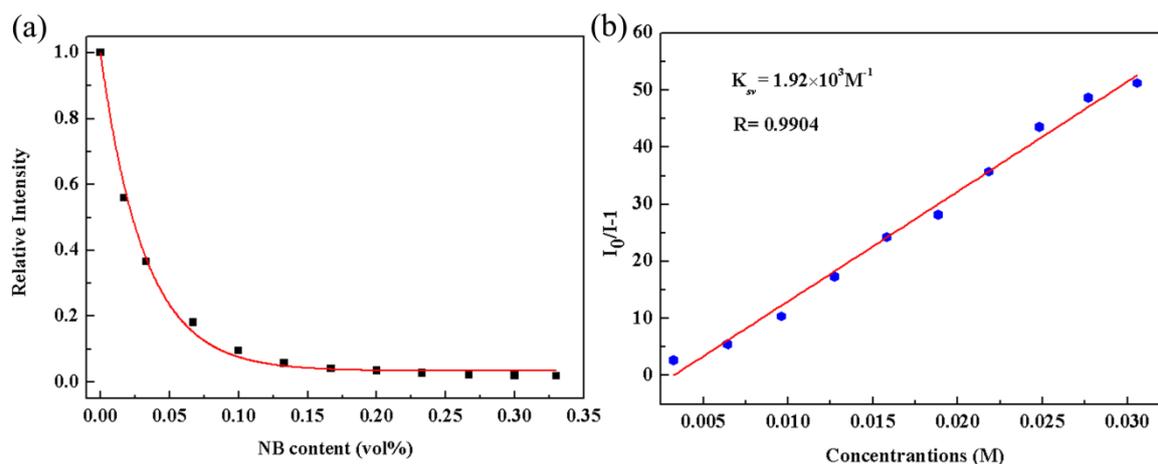


Fig. S15 (a) The photoluminescence relative intensity (the photoluminescence intensity of NB-incorporated 2a/NB-free 2a at 615 nm) of the 2a DMF emulsion as a function of NB content (b) Stern-Volmer plot for the quenching of 2a by NB.

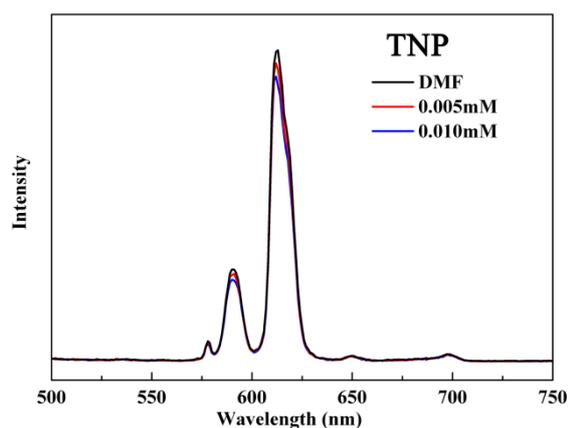


Fig. S16 Reduction in emission intensity of 2a upon addition of TNP solution in DMF.

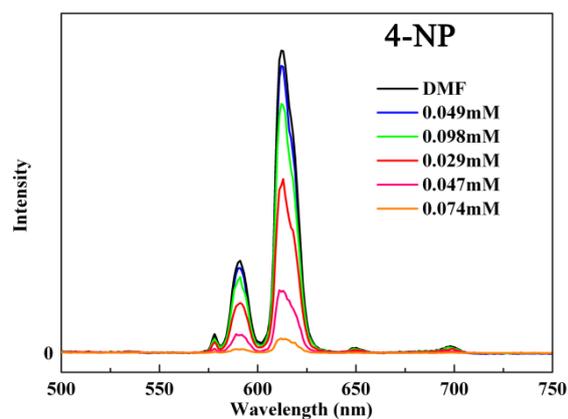


Fig. S17 Emission spectra of 2a dispersed in DMF upon incremental addition of 4-NP solution in DMF.

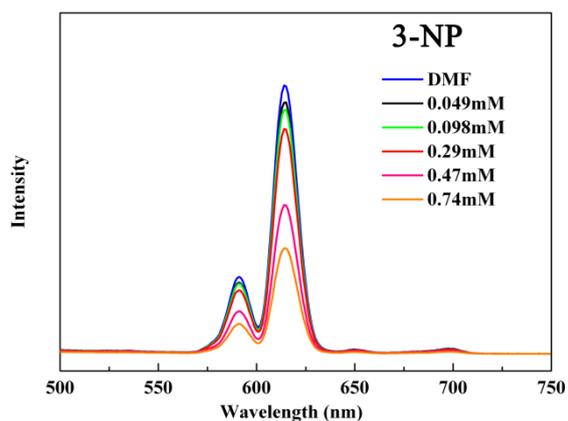


Fig. S18 Emission spectra of **2a** dispersed in DMF upon incremental addition of 3-NP solution in DMF.

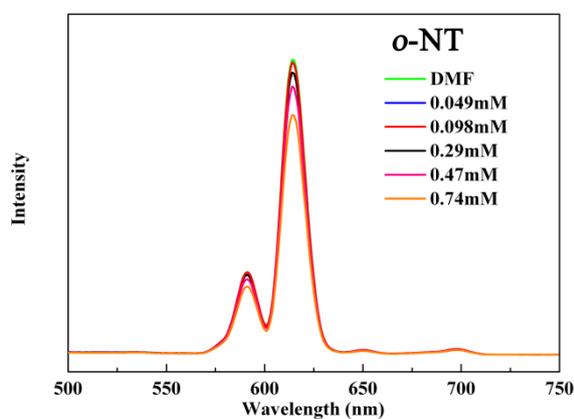


Fig. S19 Emission spectra of **2a** dispersed in DMF upon incremental addition of *o*-NT solution in DMF.

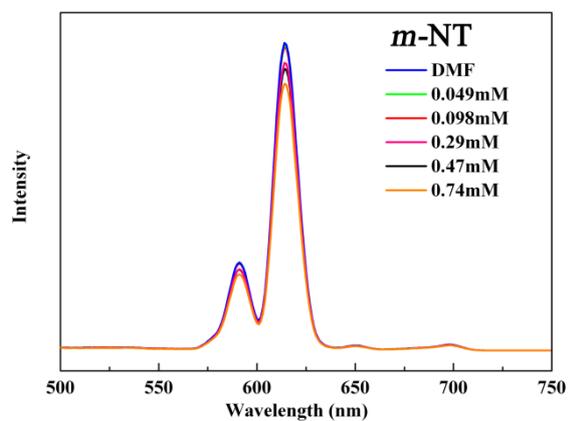


Fig. S20 Emission spectra of **2a** dispersed in DMF upon incremental addition of *m*-NT solution in DMF.

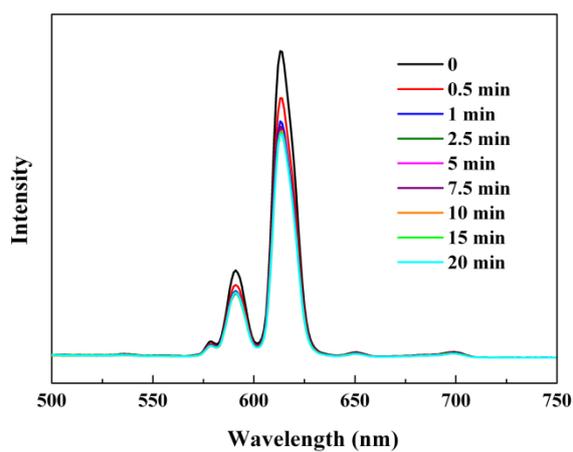


Fig. S21 Time-dependent emission spectra upon exposure of **2a** to TNP vapor.

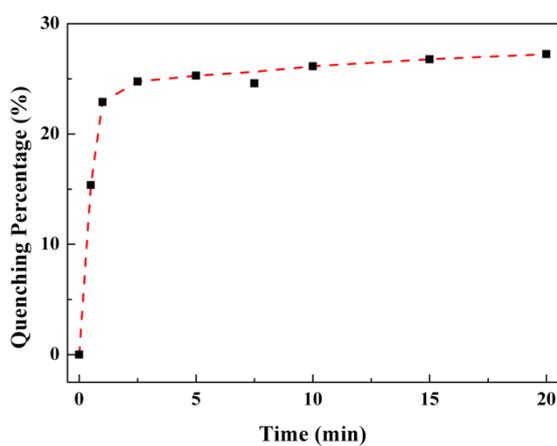


Fig. S22 Time-dependent fluorescence quenching percentage by TNP vapor.

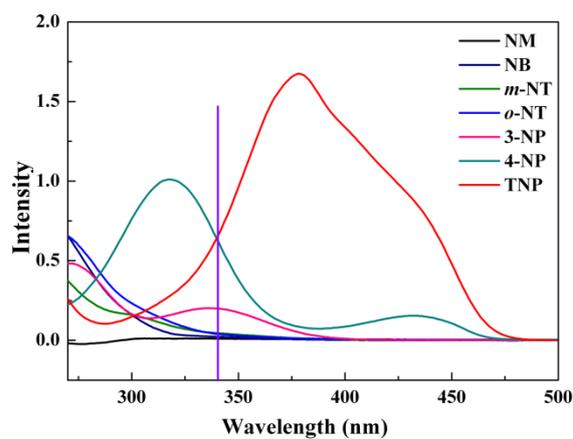


Fig. S23 The UV-vis absorption spectra of nitro compounds with the same concentration of analytes (0.1 mM, in DMF).

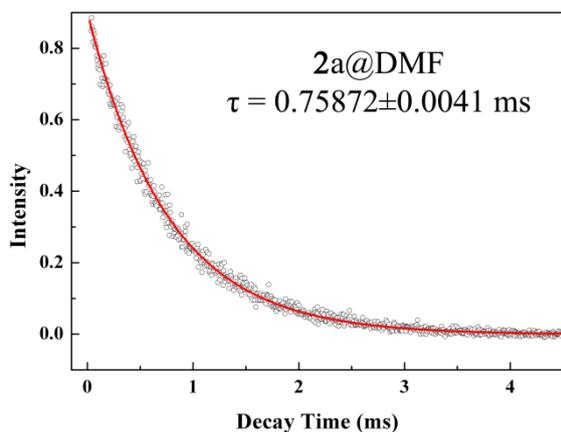


Fig. S24 Luminescence decay curve for the $^5D_0 \rightarrow ^7F_2$ (615 nm) emission of **2a** in DMF.

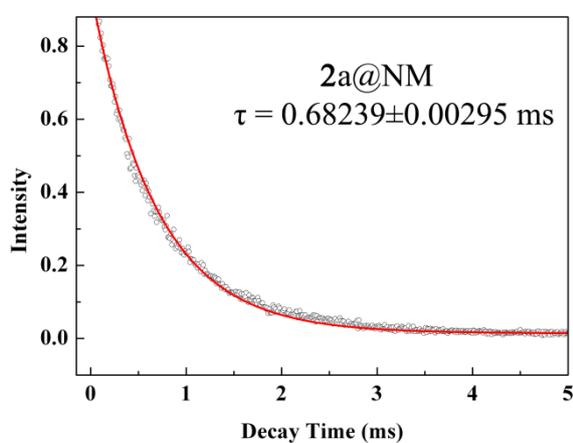


Fig. S25 Luminescence decay curve for the $^5D_0 \rightarrow ^7F_2$ (615 nm) emission of **2a@NM** in DMF.

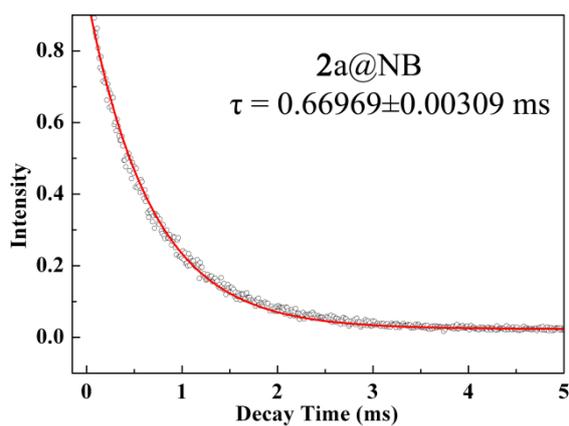


Fig. S26 Luminescence decay curve for the $^5D_0 \rightarrow ^7F_2$ (615 nm) emission of **2a@NB** in DMF.

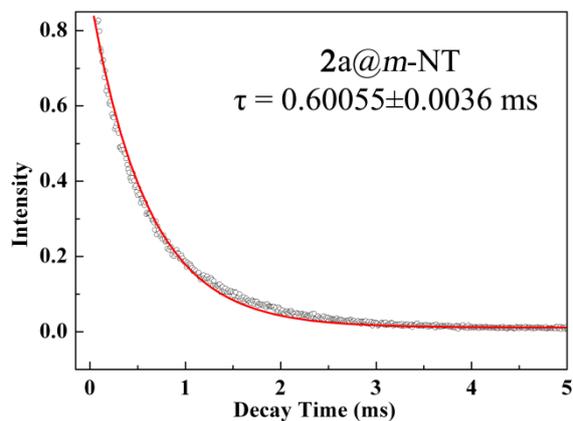


Fig. S27 Luminescence decay curve for the ${}^5D_0 \rightarrow {}^7F_2$ (615 nm) emission of **2a@m-NT** in DMF.

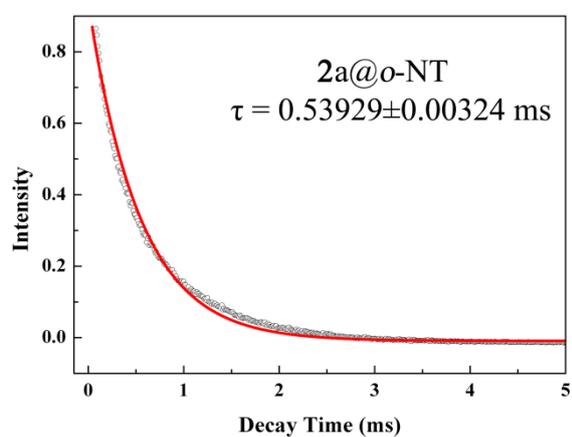


Fig. S28 Luminescence decay curve for the ${}^5D_0 \rightarrow {}^7F_2$ (615 nm) emission of **2a@o-NT** in DMF.

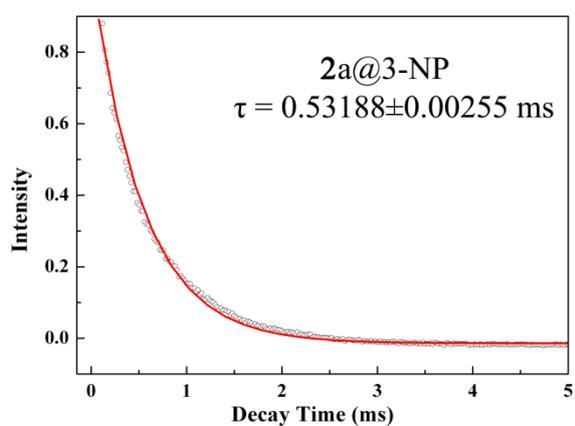


Fig. S29 Luminescence decay curve for the ${}^5D_0 \rightarrow {}^7F_2$ (615 nm) emission of **2a@3-NP** in DMF.

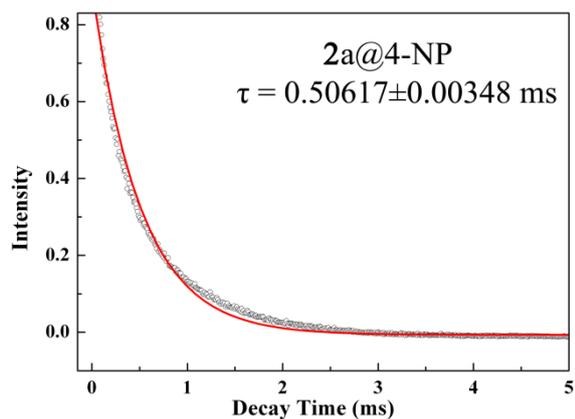


Fig. S30 Luminescence decay curve for the $^5D_0 \rightarrow ^7F_2$ (615 nm) emission of 2a@4-NP in DMF.

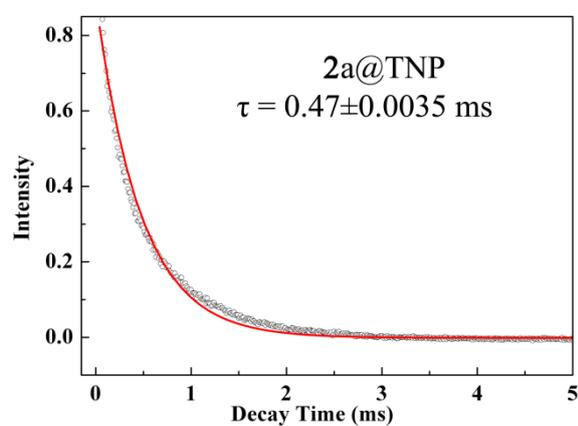


Fig. S31 Luminescence decay curve for the $^5D_0 \rightarrow ^7F_2$ (615 nm) emission of 2a@TNP in DMF.

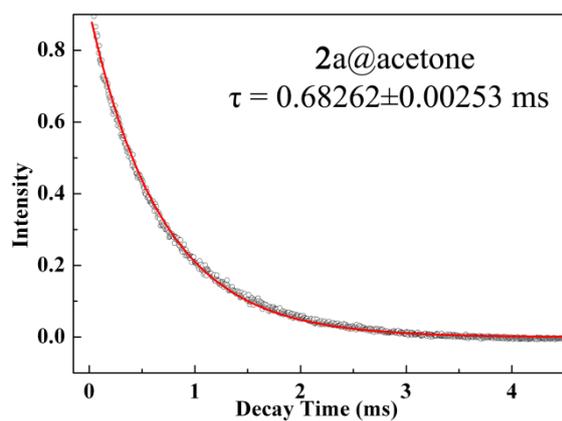


Fig. S32 Luminescence decay curve for the $^5D_0 \rightarrow ^7F_2$ (615 nm) emission of 2a in acetone.