

Supporting information

Rapid and sensitive detection of nitroaromatic explosives by new 3D lanthanide phosphonates

Ruibiao Fu*, Shengmin Hu, Xintao Wu

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou, Fujian, 350002 China

● Corresponding author. E-mail: furb@fjirsm.ac.cn

EXPERIMENTAL SECTION

General. The phosphonic acid (1,4- $C_6H_4(CH(OH)(PO_3H_2))_2$, H_4L) was synthesized according to similar method in previous literature (Scheme S1).¹ Other chemicals were obtained from commercial sources without further purification. Elemental analyses were conducted with a Vario EL III element analyzer. While metals content were tested using a Ultrimas ICP spectrometer. Infrared spectra were obtained on a VERTEX 70 FT-IR spectrometer. UV/Vis spectroscopy was performed with a Lambda35 spectrophotometer in the range of 250-600 nm. Luminescent emission and excitation spectra were recorded at room temperature with a model F-7000 fluorescence spectrophotometer. Luminescent spectra at 77 K and NIR luminescence were investigated in solid state with an Edinburgh model FLS980 fluorescence spectrometer. While the lifetime and the quantum yield were measured in solid state with an Edinburgh model FLS920 fluorescence spectrometer. The quantum yield was measured according to the published method.² Thermogravimetric analysis (TGA) was performed on a Netzsch STA449C instrument at a heating rate of 10 °C ·min⁻¹ from room temperature to 1000 °C (for solids **1-4**) or 900 °C (for solid **2-80**) under an air gas flow. Powder X-ray diffraction (XRD) patterns were acquired on a Ultima IV diffractometers using Cu-K α radiation in an ambient environment.

Synthesis of $[Eu_2(H_2L)_3(H_2O)_2] \cdot 21H_2O$ (1**).** A mixture of $Eu(NO_3)_3 \cdot 6H_2O$ (0.0724 g, 0.162 mmol) and H_4L (0.0622 g, 0.209 mmol) in 10.0 mL distilled water with the pH value adjusted to around 1.1, was sealed in a weighing bottle and heated at 55 °C for 312 h. After slow cooling to room temperature, colorless crystals were obtained as a homogenous phase based on powder XRD patterns. Yield: 0.0412 g (37 %). Anal. Calcd. for $C_{24}H_{76}O_{47}P_6Eu_2$: C 17.94, H 4.77 %. Found: C 18.54, H 4.53 %. IR (KBr pellet, cm⁻¹): 3387m(ν_{O-H}), 2923w(ν_{C-H}), 2852w(ν_{C-H}), 1638w, 1511w, 1384w, 1151s(ν_{P-O}), 1064s(ν_{P-O}), 922m, 740s, 591m, 484m.

Synthesis of [Tb₂(H₂L)₃(H₂O)₂]·**21H₂O (2).** A mixture of TbCl₃·6H₂O (0.0521 g, 0.140 mmol) and H₄L (0.0619 g, 0.208 mmol) in 10.0 mL distilled water with the pH value adjusted to around 1.1, was sealed in a weighing bottle and heated at 55 °C for 24 h. After slow cooling to room temperature, colorless crystals were obtained as a homogenous phase based on powder XRD patterns. Yield: 0.0346 g (31 %). Anal. Calcd. for C₂₄H₇₆O₄₇P₆Tb₂: C 17.79, H 4.73 %. Found: C 17.50, H 4.70 %. IR (KBr pellet, cm⁻¹): 3424m(ν_{O-H}), 2924w(ν_{C-H}), 2852w(ν_{C-H}), 1638w, 1510w, 1384w, 1157s(ν_{P-O}), 1069s(ν_{P-O}), 929m, 740s, 579m, 484m.

Synthesis of [Nd₂(H₂L)₃(H₂O)₂]·**21H₂O (3).** A mixture of Nd(NO₃)₃·6H₂O (0.1263 g, 0.288 mmol) and H₄L (0.0561 g, 0.197 mmol) in 10.0 mL distilled water, was sealed in a weighing bottle and stood at room temperature for 24 h. Light purple crystals were obtained as a homogenous phase based on powder XRD patterns. Yield: 0.0245 g (23 %). Anal. Calcd. for C₂₄H₇₆O₄₇P₆Nd₂: C 18.12, H 4.81 %. Found: C 17.78, H 4.66 %. IR (KBr pellet, cm⁻¹): 3384m(ν_{O-H}), 2924w(ν_{C-H}), 2852w(ν_{C-H}), 1638w, 1511w, 1385w, 1154s(ν_{P-O}), 1065s(ν_{P-O}), 924m, 741s, 582m, 484m.

Synthesis of [La₂(H₂L)₃(H₂O)₂]·**21H₂O (4).** A mixture of La(NO₃)₃·6H₂O (0.0861 g, 0.199 mmol) and H₄L (0.0731 g, 0.245 mmol) in 10.0 mL distilled water with the pH value adjusted to around 1.5, was sealed in a weighing bottle and heated at 55 °C for 48 h. After slow cooling to room temperature, colorless crystals were obtained as a homogenous phase based on powder XRD patterns. Yield: 0.0515 g (40 %). Anal. Calcd. for C₂₄H₇₆O₄₇P₆La₂: C 18.24, H 4.85 %. Found: C 18.55, H 4.69 %. IR (KBr pellet, cm⁻¹): 3398m(ν_{O-H}), 2926w(ν_{C-H}), 2855w(ν_{C-H}), 1639w, 1511w, 1301w, 1142s(ν_{P-O}), 1070s(ν_{P-O}), 919m, 740s, 588m, 484m.

Synthesis of [Tb_{0.8}La_{1.2}(H₂L)₃(H₂O)₂]·**21H₂O (5).** A mixture of La(NO₃)₃·6H₂O (0.0822 g, 0.190 mmol), Tb(NO₃)₃·6H₂O (0.0084 g, 0.019 mmol) and H₄L (0.0735 g, 0.2468 mmol) in 10.0 mL distilled water with the pH value adjusted to around 1.5, was sealed in a weighing bottle and heated at 55 °C for 48 h. After slow cooling to room temperature, colorless crystals were obtained as a homogenous phase based on powder XRD patterns. Anal. Calcd. for C₂₄H₇₆O₄₇P₆Tb_{0.8}La_{1.2}: C 18.06, H 4.80 %. Found: C 18.39, H 4.65 %. The molar ratio of Tb/La is confirmed by ICP.

Heating Treatment: Solid **2-80** denotes that polycrystalline of **2** has been heated at 80 °C for 6 h under an air atmosphere, and then naturally cooled to room temperature. The formula of solid **2-80** is [Tb₂(H₂L)₃(H₂O)₂]**·**9H₂O. Anal. Calcd. for C₂₄H₅₂O₃₅P₆Tb₂: C 20.53, H 3.73 %. Found: C 20.54, H 4.17 %.

Caution! Nitroaromatic explosives should be handled carefully in small quantities with necessary precaution.

Luminescent quenching experiment. Solid **2** is previously ground. For the experiment of sensing solvents, 5.0 mg powder of solid **2** was dispersed in 2.00 mL of ethanol, methanol, water, acetonitrile, 2-propanol, dichloromethane, cyclohexane,

tetrahydrofuran, and acetone. Solid **2** behaves stable in ethanol. Moreover, ethanol has no significant absorption band around 265 nm. On the other hand, nitroaromatic explosives can dissolve in ethanol. Therefore, ethanol is selected as the solvent for the experiment of sensing nitroaromatic explosives. In typical experimental setup, 5.00 or 0.1 mg powder of solid **2** was dispersed in 2.00 mL ethanol to form a suspension. The luminescence was measured in-situ after the incremental addition of freshly prepared nitroaromatic explosives solution. Before each measurement, the quartz cuvette was shaken thoroughly. In addition, each measurement was performed twice, and the average value was used.

X-Ray crystallography. X-ray data for compounds **1**, **3** and **4** were collected at 293(2) K on a Rigaku Mercury CCD/AFC diffractometer using graphite-monochromated Mo K α radiation ($\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$). Data of compounds **1**, **3** and **4** were reduced with CrystalClear v1.3. Their structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXTL-97.³ Except for two free water molecules (O21 and O24), all non-hydrogen atoms were treated anisotropically. Hydrogen atoms that bonded to carbon atoms, as well as hydrogen atoms of hydroxyl, phosphonate group, and coordinated water molecule were generated geometrically. While no attempts were performed to locate hydrogen atoms of lattice water molecules. Crystallographic data for compounds **1**, **3** and **4** are summarized in Table S1. Selected bond lengths and angles for compound **1** are listed in Tables S2. Hydrogen bond lengths and angles for compound **1** are listed in Table S3. CCDC 1509694 (**1**), 1509695 (**3**) and 1509696 (**4**).

Table S1. Crystal data and refinement details for compounds **1**, **3** and **4**.

| Compounds | 1 | 3 | 4 |
|--|--|--|--|
| Formula | C ₂₄ H ₇₆ O ₄₇ P ₆ Eu ₂ | C ₂₄ H ₇₆ O ₄₇ P ₆ Nd ₂ | C ₂₄ H ₇₆ O ₄₇ P ₆ La ₂ |
| FW | 1606.59 | 1591.15 | 1580.49 |
| Space group | P-1 | P-1 | P-1 |
| <i>a</i> (Å) | 10.390(5) | 10.3912(10) | 10.35(2) |
| <i>b</i> (Å) | 11.803(6) | 11.8723(4) | 11.94(3) |
| <i>c</i> (Å) | 11.934(6) | 11.8790(8) | 12.75(3) |
| α (deg) | 82.967(10) | 82.379(10) | 104.97(4) |
| β (deg) | 81.366(11) | 87.725(12) | 90.47(2) |
| γ (deg) | 87.884(9) | 81.666(8) | 93.06(3) |
| <i>V</i> (Å ³) | 1435.7(13) | 1436.89(18) | 1520(6) |
| <i>Z</i> | 1 | 1 | 1 |
| <i>T</i> (K) | 293(2) | 293(2) | 293(2) |
| Measured/unique/ observed reflections | 17943 / 6503 / 5512 | 17803/6586/6064 | 18003/6881/5283 |
| <i>D</i> _{calcd} (g cm ³) | 1.858 | 1.839 | 1.727 |
| μ (mm ⁻¹) | 2.446 | 2.068 | 1.653 |
| <i>GOF</i> on F ² | 1.082 | 1.049 | 1.185 |
| <i>R</i> _{int} | 0.0500 | 0.0305 | 0.0787 |
| <i>R</i> 1 ^a [<i>I</i> > 2σ(<i>I</i>)] | 0.0480 | 0.0350 | 0.1099 |
| <i>wR</i> 2 ^b [<i>all data</i>] | 0.1124 | 0.0949 | 0.3244 |

^a $R1 = \sum(|F_o| - |F_c|) / \sum |F_o|$. ^b $wR2 = \{\sum w [(F_o^2 - F_c^2)] / \sum w [(F_o^2)^2]\}^{0.5}$

Table S2. Selected bond lengths (Å) and angles (°) for **1**.

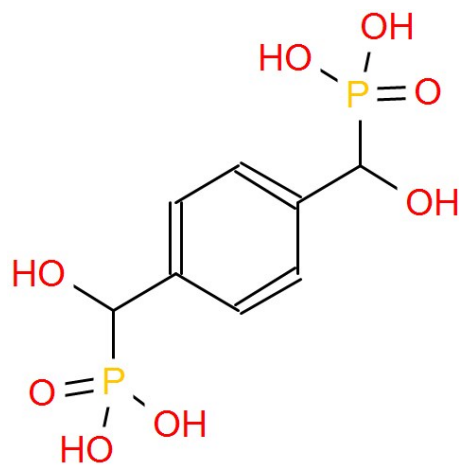
| | | | |
|--|------------|--------------------------------|------------|
| Eu(1)-O(1) | 2.307(4) | Eu(1)-O(9) ^a | 2.354(4) |
| Eu(1)-O(5) ^b | 2.365(4) | Eu(1)-O(10) | 2.387(4) |
| Eu(1)-O(6) | 2.458(4) | Eu(1)-O(12) | 2.508(4) |
| Eu(1)-O(8) | 2.551(4) | Eu(1)-O(13) | 2.419(4) |
| O(1)-Eu(1)-O(5) ^b | 99.09(15) | O(6)-Eu(1)-O(9) ^a | 132.22(13) |
| O(1)-Eu(1)-O(6) | 74.67(14) | O(6)-Eu(1)-O(10) | 140.49(14) |
| O(1)-Eu(1)-O(8) | 139.08(14) | O(6)-Eu(1)-O(12) | 133.32(12) |
| O(1)-Eu(1)-O(9) ^a | 153.00(14) | O(6)-Eu(1)-O(13) | 78.35(14) |
| O(1)-Eu(1)-O(10) | 81.65(14) | O(8)-Eu(1)-O(9) ^a | 67.74(13) |
| O(1)-Eu(1)-O(12) | 77.05(15) | O(8)-Eu(1)-O(10) | 125.07(13) |
| O(1)-Eu(1)-O(13) | 89.78(17) | O(8)-Eu(1)-O(12) | 138.29(14) |
| O(5) ^b -Eu(1)-O(6) | 78.74(13) | O(8)-Eu(1)-O(13) | 74.55(16) |
| O(5) ^b -Eu(1)-O(8) | 81.73(14) | O(9) ^a -Eu(1)-O(10) | 76.57(14) |
| O(5) ^b -Eu(1)-O(9) ^a | 86.39(14) | O(9) ^a -Eu(1)-O(12) | 80.17(14) |
| O(5) ^b -Eu(1)-O(10) | 136.86(13) | O(9) ^a -Eu(1)-O(13) | 97.58(16) |
| O(5) ^b -Eu(1)-O(12) | 69.97(13) | O(10)-Eu(1)-O(12) | 68.23(13) |
| O(5) ^b -Eu(1)-O(13) | 152.22(15) | O(10)-Eu(1)-O(13) | 70.29(14) |
| O(6)-Eu(1)-O(8) | 65.32(12) | O(12)-Eu(1)-O(13) | 137.80(14) |

Symmetry codes: a - x, - y, - z; b - x, - y + 1, - z.

Table S3. Hydrogen bond lengths (Å) and angles (°) for **1**.

| D-H...A | D-H | H...A | D...A | D-H...A |
|--------------------------|------|-------|-----------|---------|
| O2-H1...O24 ^c | 0.82 | 1.88 | 2.681(15) | 166.4 |
| O4-H2...O22 ^d | 0.82 | 1.93 | 2.733(17) | 167.2 |
| O7-H3...O15 | 0.82 | 1.83 | 2.642(9) | 172.0 |
| O8-H4...O14 | 0.85 | 2.00 | 2.818(9) | 161.2 |
| O11-H5...O16 | 0.82 | 1.91 | 2.729(12) | 171.7 |
| O12-H6...O23 | 0.85 | 2.01 | 2.806(8) | 156.4 |
| O13-H16...O15 | 0.85 | 1.92 | 2.763(9) | 168.3 |
| O13-H17...O17 | 0.85 | 1.94 | 2.747(12) | 158.4 |

Symmetry codes: c x - 1, y, z; d - x, - y + 1, - z + 1.



Scheme S1 Structure of H₄L.

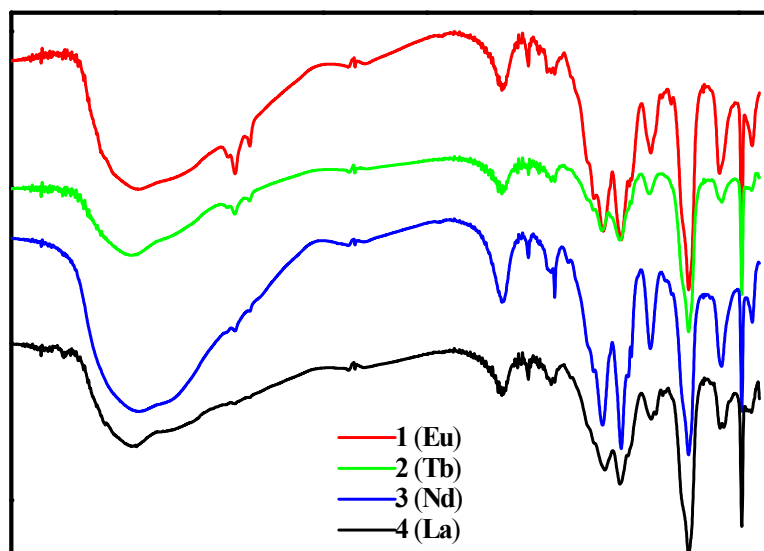


Figure S1. IR spectra of solids 1-4.

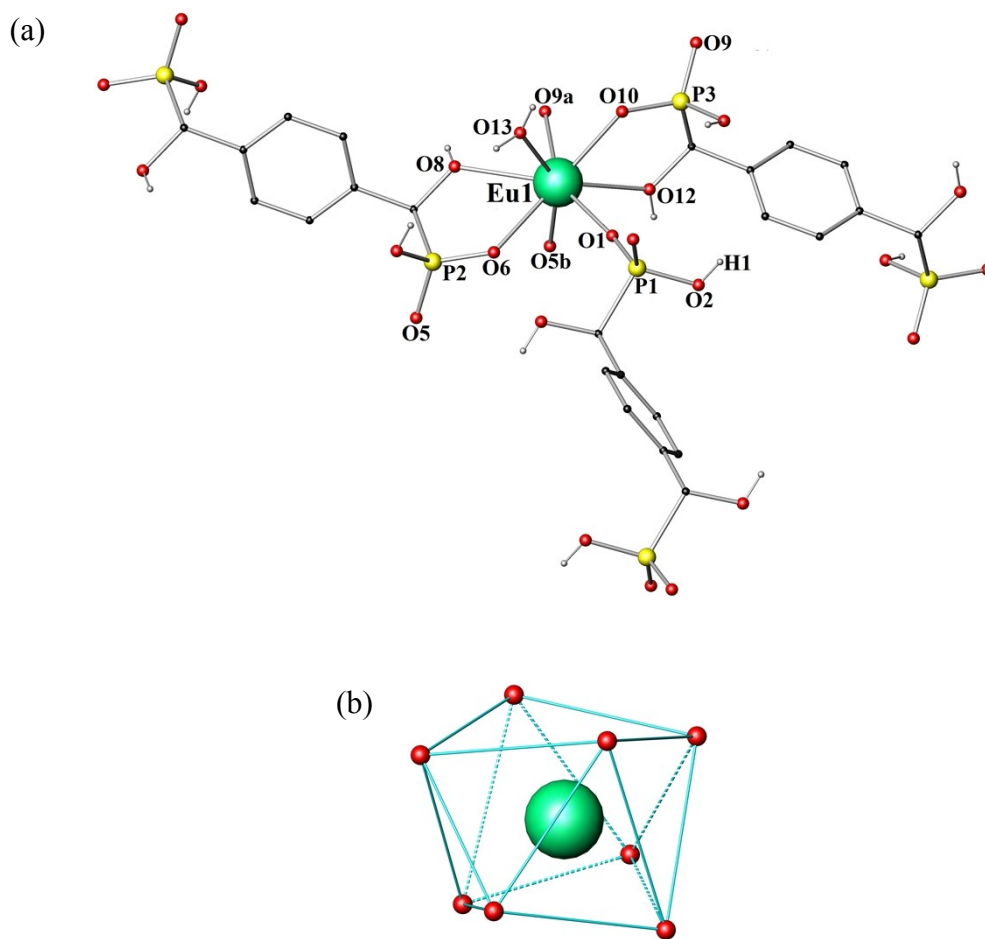


Figure S2. Ball-stick view of (a) the coordination environment of Eu(III) atom and (b) the distorted $[\text{EuO}_8]$ square antiprism geometry in **1**. Unrelated atoms are omitted for clarity. Symmetry codes: a - x, - y, - z; b - x, - y + 1, - z.

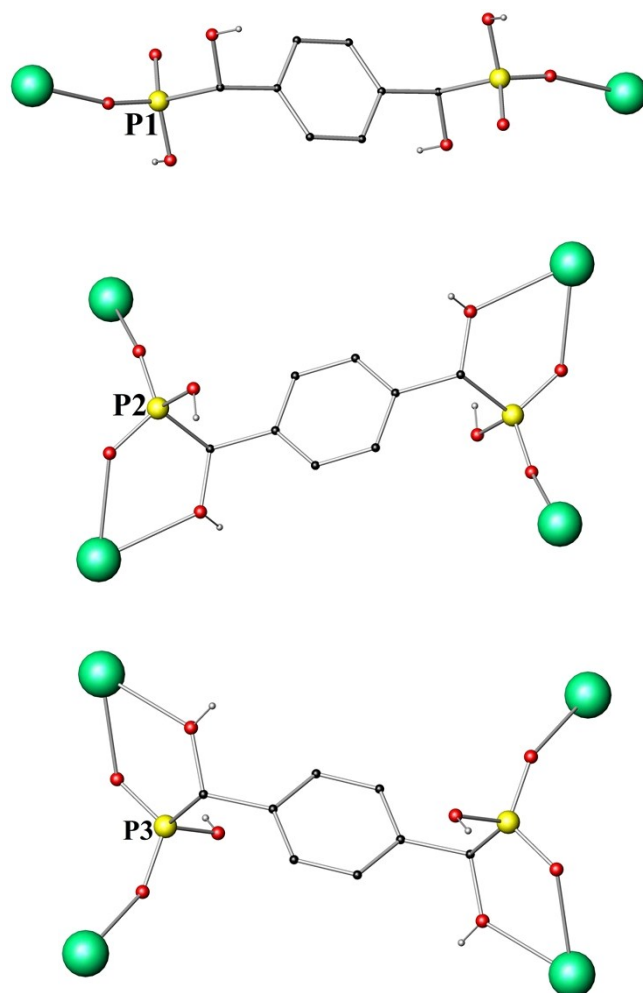


Figure S3. Coordination modes of H_2L^{2-} anions in **1**. Unrelated atoms are omitted for clarity.

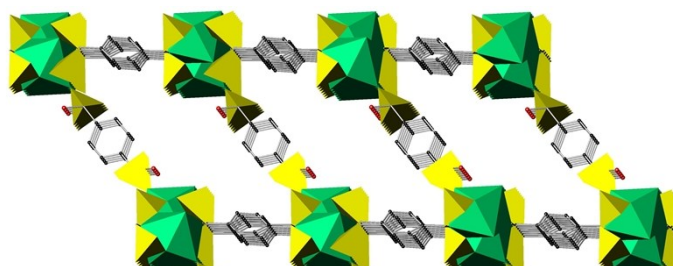


Figure S4. Polyhedral view of the 3D structure down *b* axis in **1**. [EuO₈]: green square antiprism; [PCO₃]: yellow tetrahedron. Unrelated atoms are omitted for clarity.

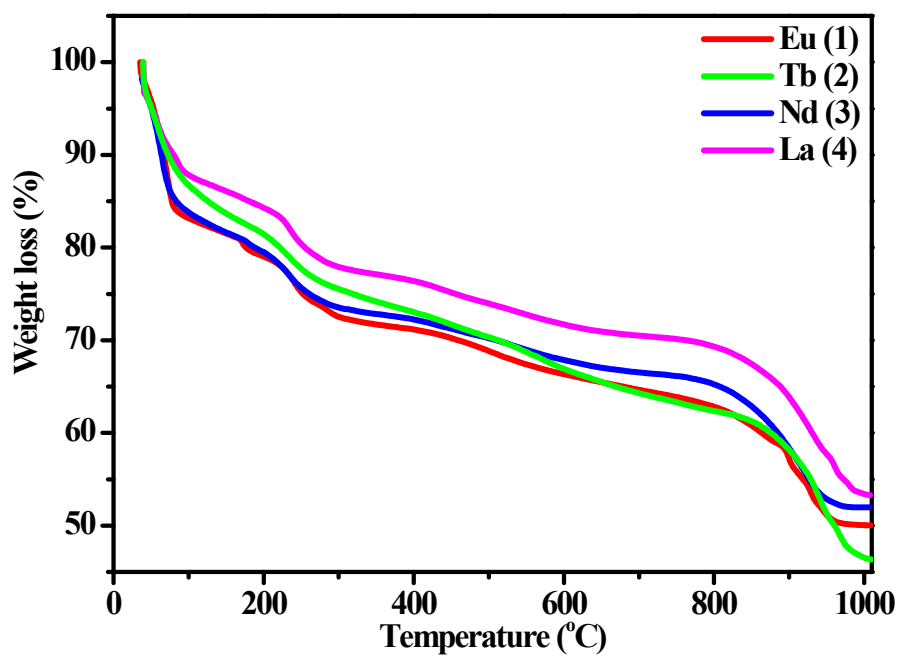


Figure S5. TGA curves of compounds 1-4.

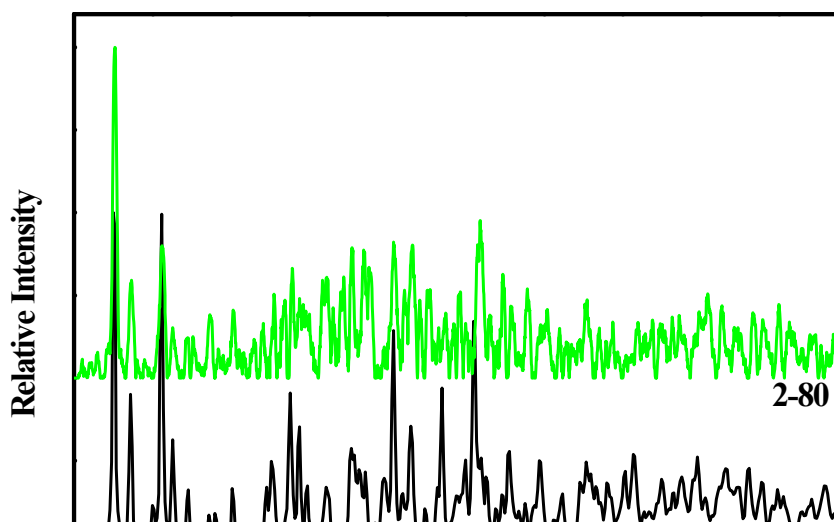


Figure S6. PXRD patterns of compound **1** simulated from single-crystal X-ray data, and experimental data of solid **2-80**.

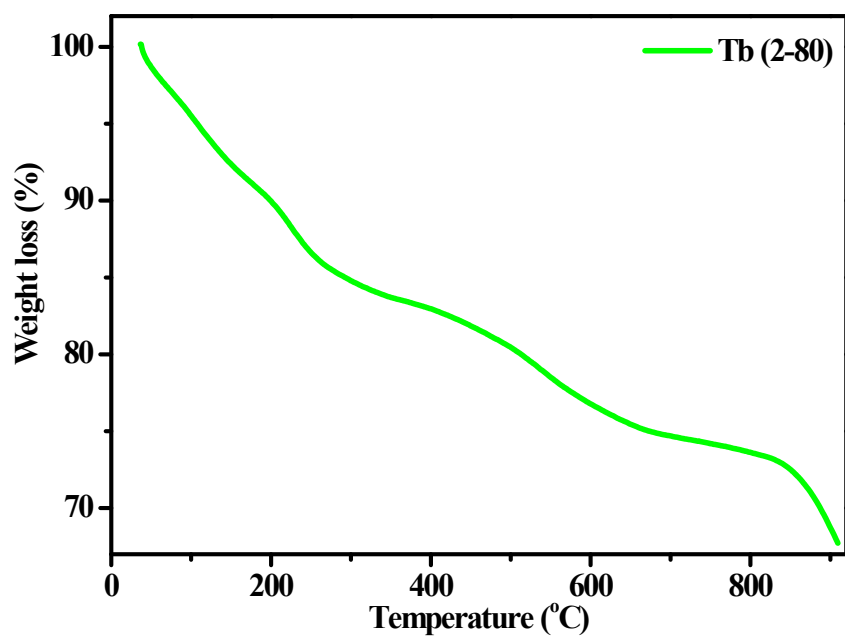


Figure S7. TGA curve of compound **2-80**.

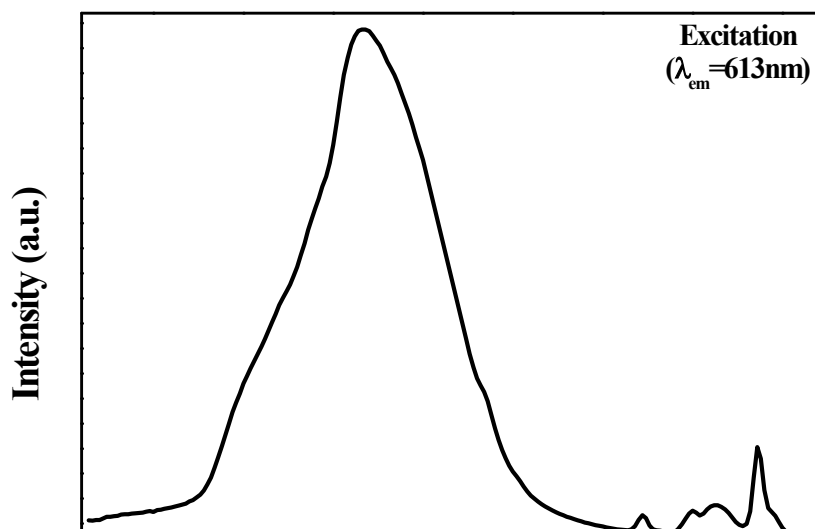


Figure S8. Excitation spectrum for compound **1** at an ambient temperature.

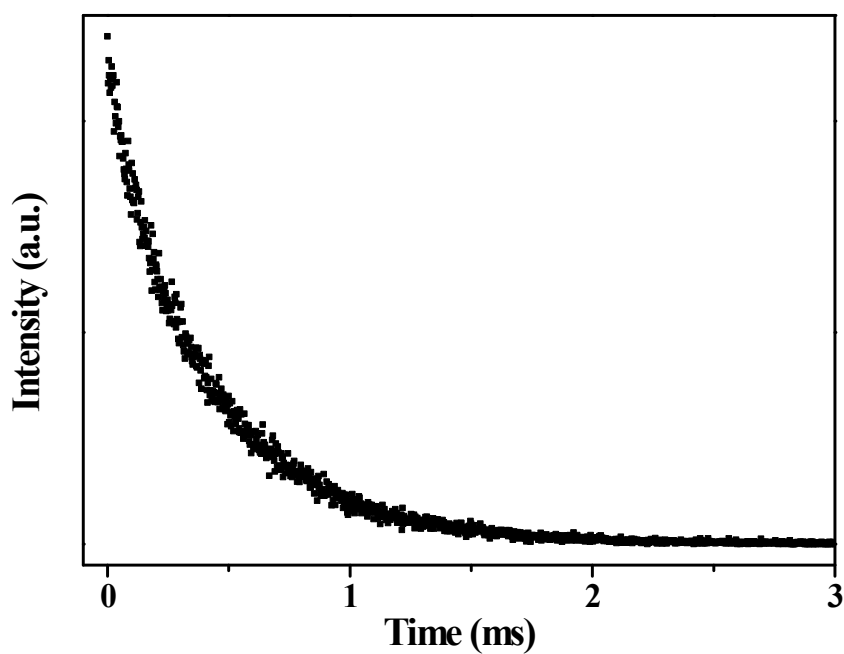


Figure S9. Luminescent intensity as a function of time for compound **1** at 298 K (λ_{ex} , λ_{em} = 283, 613 nm).

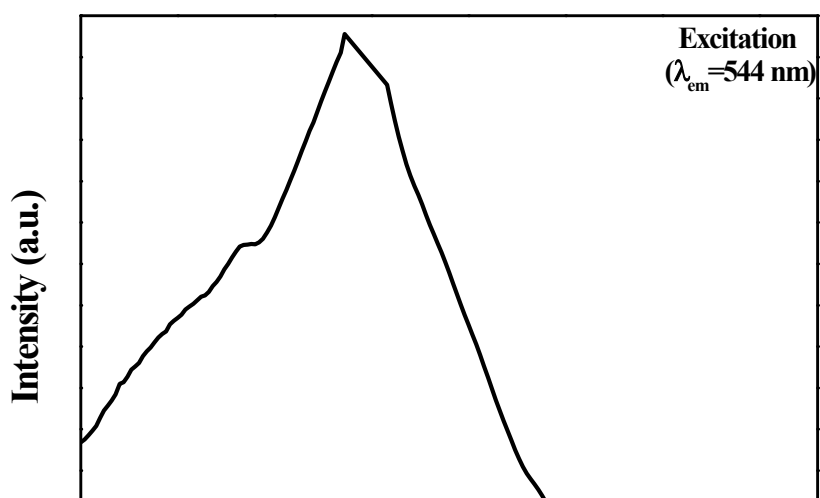


Figure S10. Excitation spectrum for compound **2** at an ambient temperature.

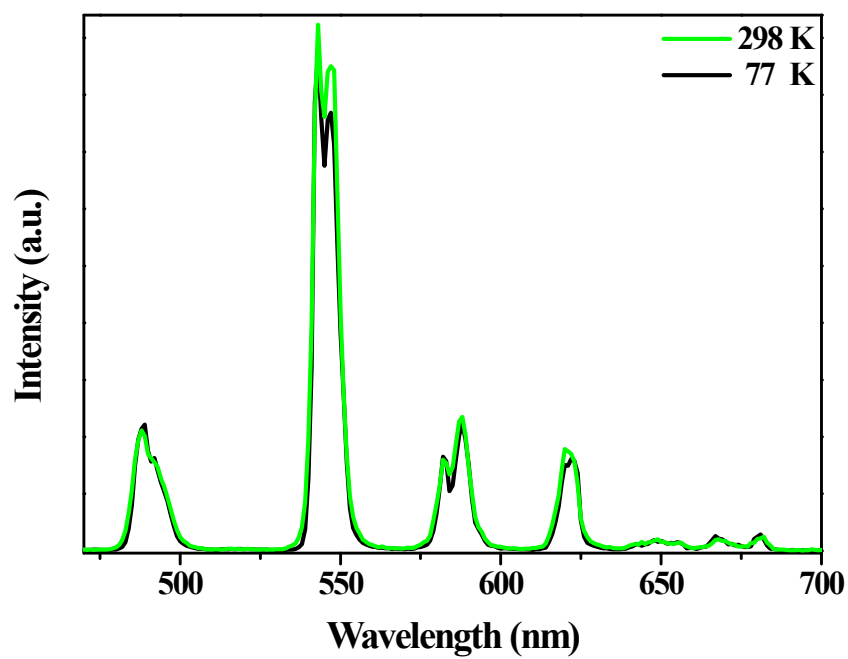


Figure S11. Relative emission intensities for compound **2** at 298 and 77 K under 265 nm excitation.

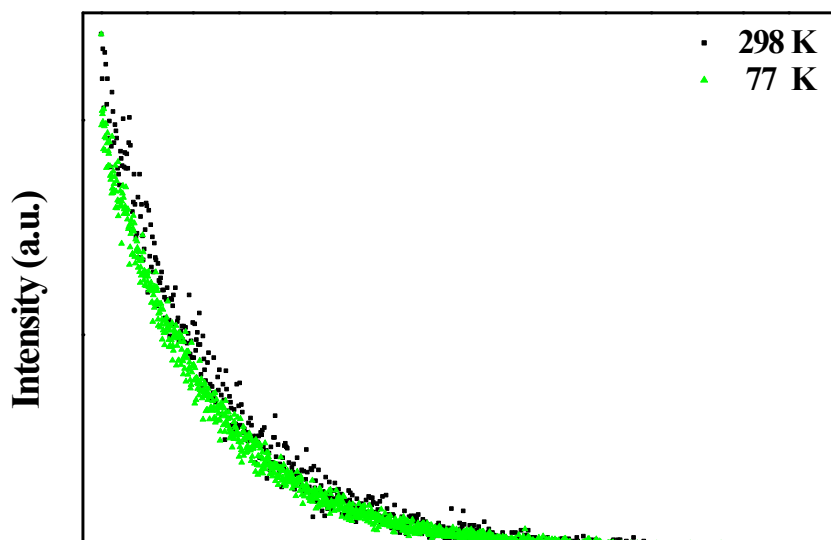


Figure S12. Luminescent intensity as a function of time for compound **2** at 298 and 77 K.

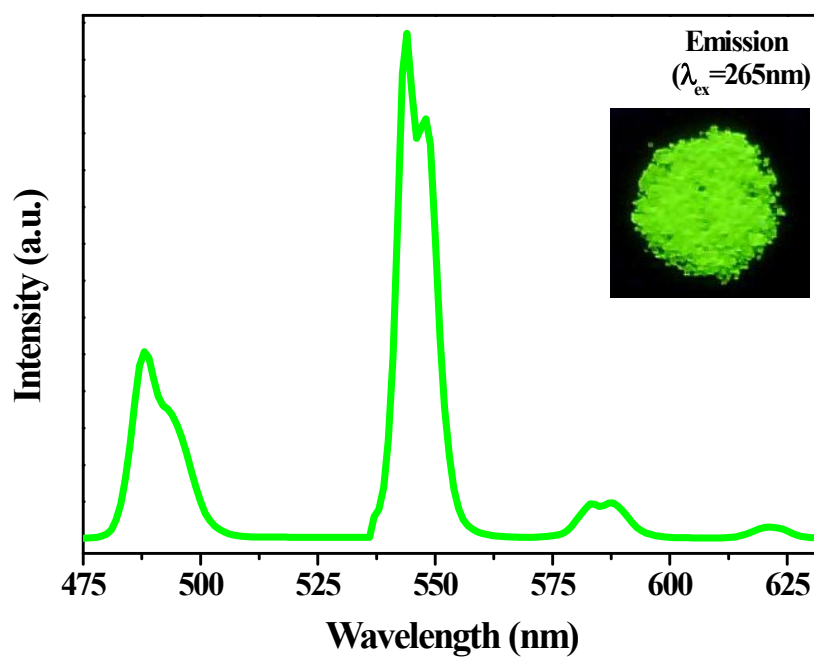


Figure S13. Emission spectrum for compound **2-80** at an ambient temperature upon 265 nm excitation. Inset: photograph of compound **2-80** under an UV lamp at 254 nm.

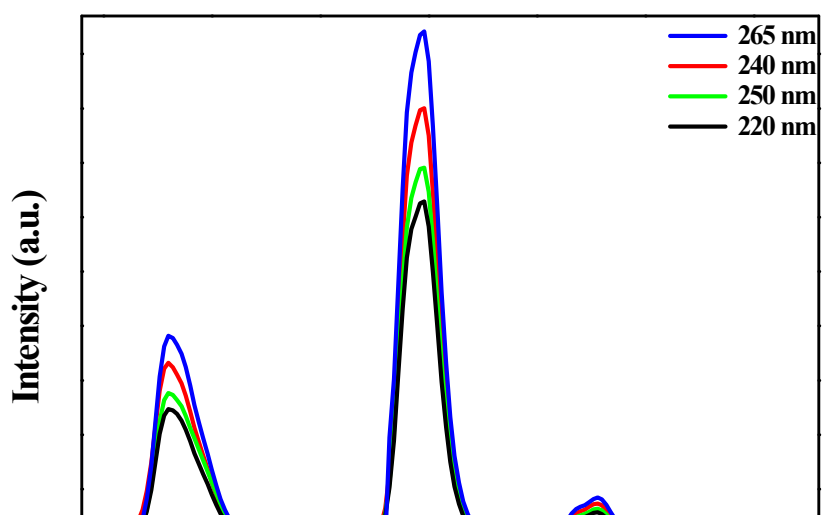


Figure S14 Luminescent emission spectra of the suspension of solid **2** in 2-propanol under different wavelengths of excited light. .

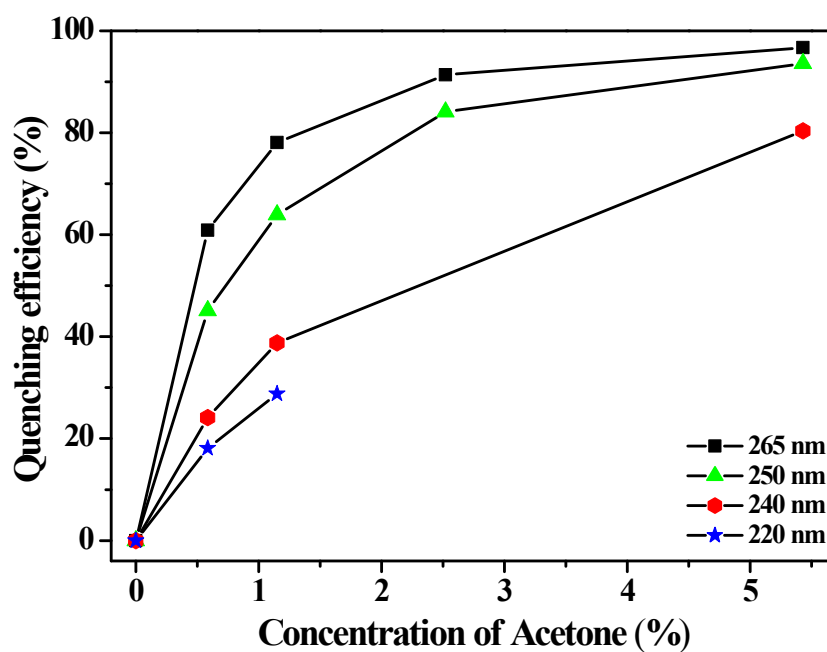


Figure S15. Luminescent quenching efficiencies of the suspension of solid **2** in 2-propanol upon incremental addition of acetone under different wavelengths of excited light.

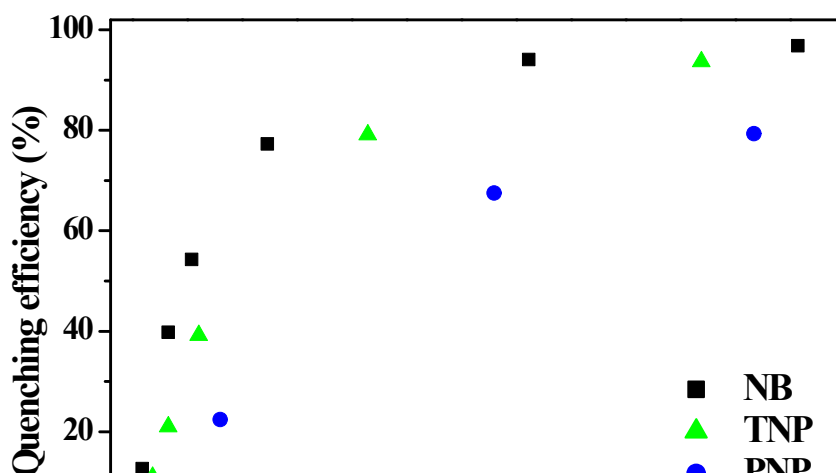


Figure S16. The trends of quenching efficiency for the suspension of solid **2** in ethanol with a concentration of $2.5 \text{ mg}\cdot\text{mL}^{-1}$ upon incremental additions of NB, TNP, and PNP when excited at 265 nm.

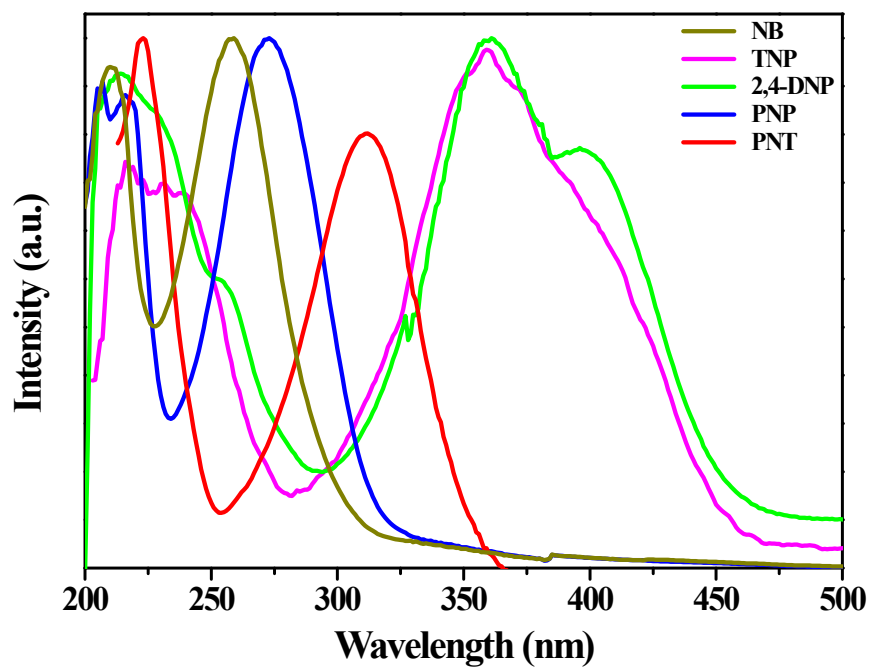


Figure S17. UV-Vis absorption spectra of NB, TNP, 2,4-DNP, PNP, and PNT in ethanol.

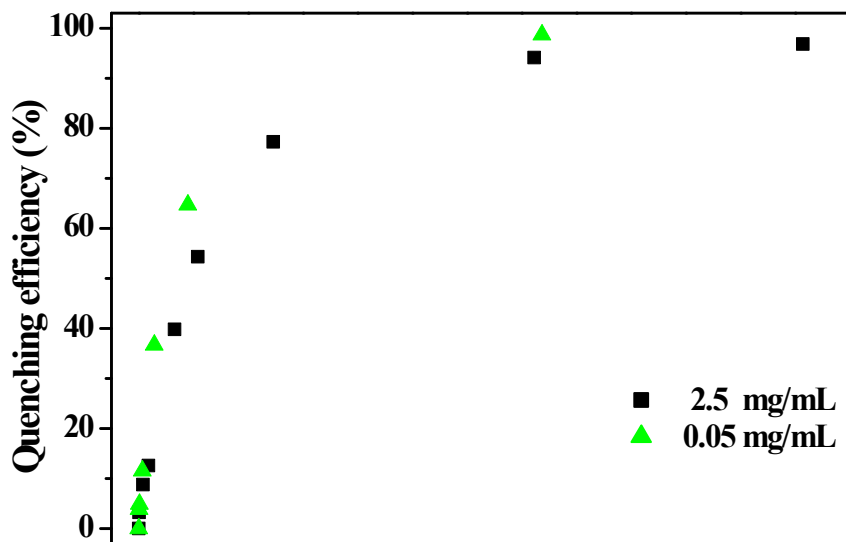


Figure S18. The trends of quenching efficiency for the suspension of solid **2** in ethanol with concentrations of 2.5 and 0.05 mg·mL⁻¹ upon incremental addition of NB when excited at 265 and 260 nm, respectively.

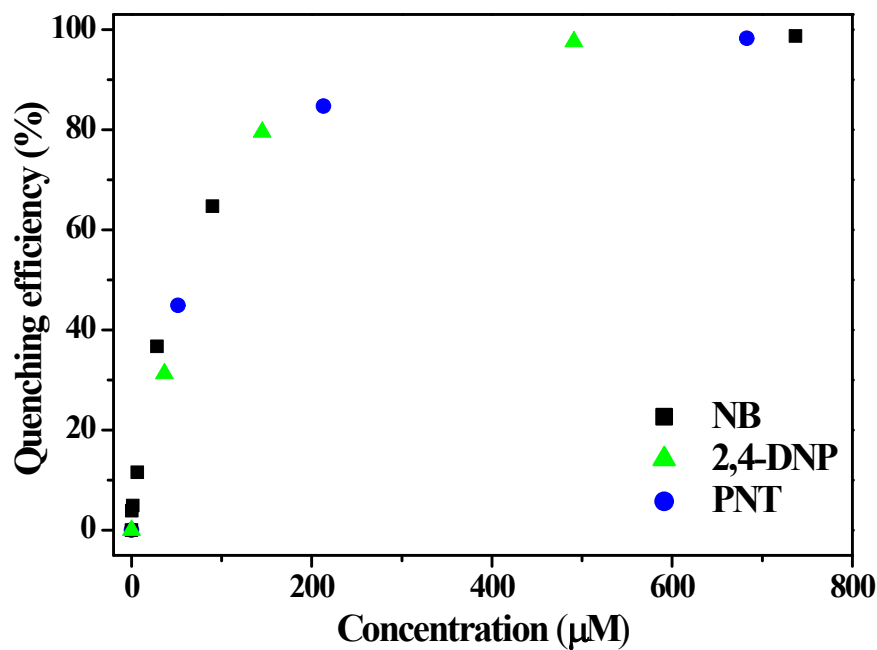


Figure S19. The trends of quenching efficiency for the suspension of solid **2** in ethanol with a concentration of 0.05 mg·mL⁻¹ upon incremental additions of NB, 2,4-DNP, and PNT when excited at 260 nm.

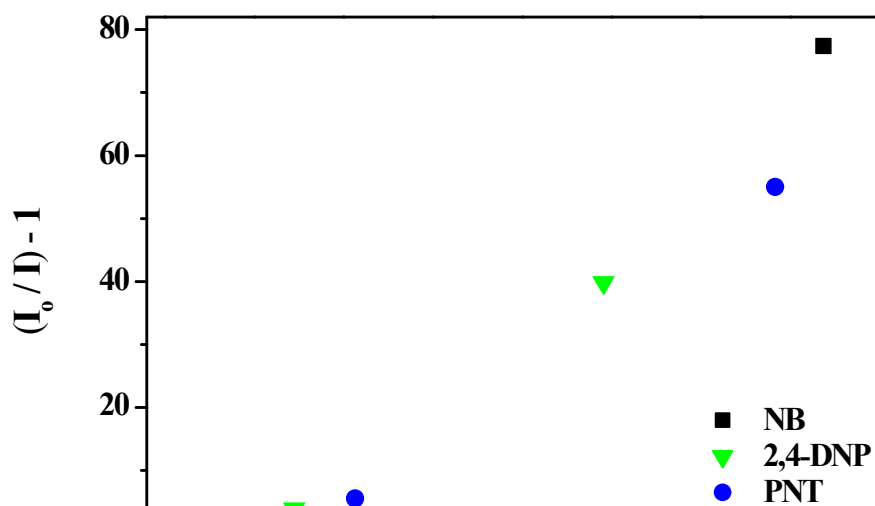


Figure S20. Corresponding Stern-Volmer plots for the suspension of solid **2** in ethanol with a concentration of $0.05 \text{ mg}\cdot\text{mL}^{-1}$ upon incremental additions of NB, 2,4-DNP, and PNT with the emission wavelength fixed at 545 nm

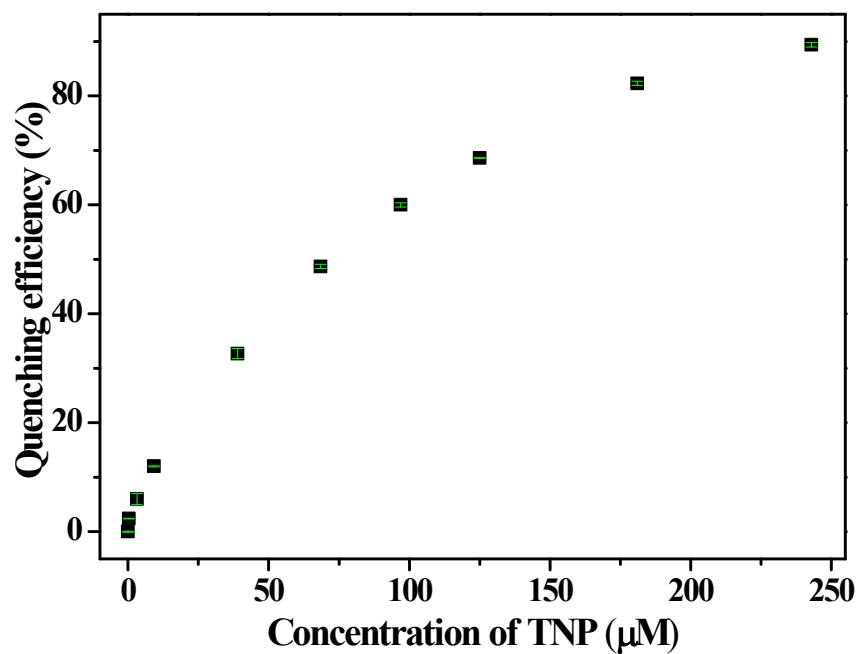


Figure S21. The trend of quenching efficiency for the suspension of solid **2** in water with a concentration of $0.05 \text{ mg}\cdot\text{mL}^{-1}$ upon incremental additions of TNP when excited at 260 nm.

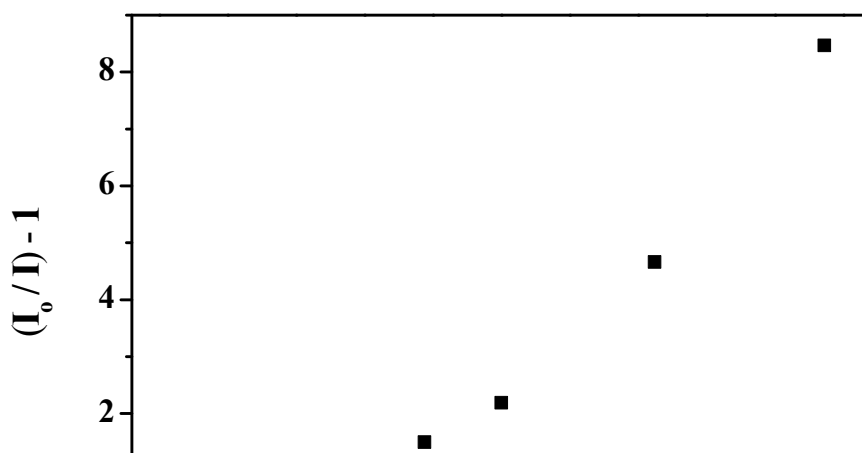


Figure S22. The Stern-Volmer plot for the suspension of solid **2** in water with a concentration of $0.05 \text{ mg}\cdot\text{mL}^{-1}$ upon incremental additions of TNP with the emission wavelength fixed at 545 nm

References

- (1) B. Boduszek, *Tetrahedron* 1996, 52, 12483-12494.
- (2) J. C. de Mello, H. F. Wittmann, R. Friend, *Adv. Mater.* 1997, 9, 230-232.
- (3) G. M. Sheldrick, SHELXT 97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.