

Supporting Information for

A colorimetric and fluorescent chemosensor for the detection of an explosive —2,4,6-trinitrophenol (TNP)

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1. General information and methods.

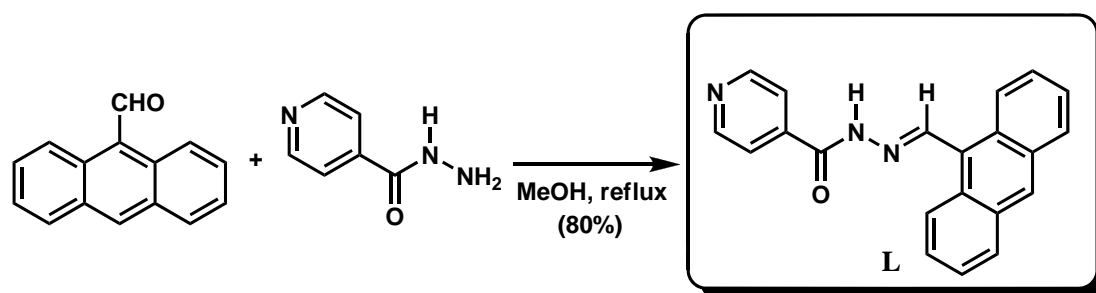
The commercially available chemicals were used without further purification. All of the solvents used were of analytical reagent grade. C, N and H were determined using an Elementar Vario EL. Melting points were determined on a Kofler apparatus. X-Ray powder diffraction (XRPD) patterns were obtained on a Rigaku D/Max-II X-ray diffractometer in the 5-70° 2 θ range with graphite-monochromatized Cu-K α radiation. IR spectra were recorded on Nicolet FT-170SX instrument using KBr discs in the 400-4000 cm⁻¹ region. ¹H and ¹³C NMR spectra were measured on a Bruker Avance III 400 spectrometer in *d*₆-DMSO solution with TMS as internal standard. ESI-MS were determined on a Bruker esquire 6000 spectrometer.

The X-ray diffraction data of **L** and **L·TNP** were collected on a Bruker APEX-II CCD diffractometer operating at 50 KV and 30 mA using graphite-monochromated Mo-K α radiation source ($\lambda = 0.71073 \text{ \AA}$). An empirical absorption correction based on the comparison of redundant and equivalent reflections was applied using SADABS. The structures were solved with direct methods and refined with full-matrix least squares on F^2 using the *SHELXTL-97* and *SHELXTL-97* program package,¹ respectively. All non-hydrogen atoms were subjected to anisotropic refinement, and all hydrogen atoms were added in idealized positions and refined isotropically.

TNT, RDX and HMX were purchased from AccuStandard[®], Inc.

Caution! TNP, TNT, DNT, RDX, HMX and other nitroaromatics should be used with extreme care using the best safety shield due to its high explosion and should be handled only in small quantities.

2. Synthesis and characterization of **L** and **L**·TNP.



Scheme S1 Synthetic procedure for **L**.

Preparation of **L:** The solution of isonicotinohydrazide (1.37 g, 10 mmol) in methanol (30 mL) was added to a solution of anthracene-9-carbaldehyde (2.06 g, 10 mmol) in methanol (40 mL). The reaction mixture was refluxed for 8 h at 70 °C and the yellow precipitates were obtained. The resulting yellow solid was filtered and washed with methanol and diethyl ether, and then dried over vacuum to yield **L** as a yellow solid. Yield: 2.60 g, 80%. m.p.: 273-275 °C. Elemental analysis calcd (%) for C₂₁H₁₅N₃O: C 77.52, H 4.65, N 12.91; found: C 77.50, H 4.60, N 12.88. ¹H NMR (*d*₆-DMSO, 400 MHz): δ (*E/Z* = 10:1) (*E* isomer) 12.29 (s, 1H, -NH), 9.68 (s, 1H, -N=CH), 8.85 (d, *J* = 6.0 Hz, 2H, *Py*), 8.75 (s, 1H, *Ar*), 8.74 (d, *J* = 8.0 Hz, 2H, *Ar*), 8.17 (d, *J* = 8.4 Hz, 2H, *Ar*), 7.93 (d, *J* = 6.0 Hz, 2H, *Py*), 7.67 (t, *J* = 7.4 Hz, 2H, *Ar*), 7.59 (t, *J* = 7.4 Hz, 2H, *Ar*) ppm. (*Z* isomer) 12.16 (s, 1H, -NH), 9.35 (s, 1H, -N=CH), 8.68 (s, 1H, *Ar*), 8.46 (d, *J* = 6.0 Hz, 2H, *Py*), 8.11 (d, *J* = 5.6 Hz, 2H, *Py*), 7.89 (d, *J* = 9.2 Hz, 2H, *Ar*), 7.57–7.50 (m, 4H, *Ar*) ppm, other signals are inseparable. ¹³C NMR (*d*₆-DMSO, 100 MHz): δ (*E* isomer) 161.5, 150.4 (2C), 148.3, 140.4, 130.8 (2C), 129.9, 129.7 (2C), 129.0 (2C), 127.2 (2C), 125.5 (3C), 124.7 (2C), 121.5 (2C) ppm. (*Z* isomer) 168.4, 149.6, 149.5, 143.9, 127.0, 126.9, 124.4, 122.5 ppm, other signals are inseparable. ESI-MS: *m/z* 326.2. [M+H]⁺. IR (KBr, ν): 3431 (br), 3195 (m), 3048 (m), 1654 (s), 1591 (m), 1544 (s), 1409 (m), 1365 (m), 1292 (s), 1212 (w), 1159 (w), 1067 (m), 968 (w), 882 (w), 842 (m), 788 (w), 734 (s), 683 (m), 603 (w) cm⁻¹.

Synthesis of **L·TNP:** A ethanol (0.5% DMF, v/v) solution (5 mL) of **L** (32.5 mg, 0.10 mmol) was added to a ethanol solution (10 mL) of picric acid (22.9 mg, 0.10 mmol) at ambient temperature. The solution was stirred for 10 min and an orange precipitate

appeared. Then the precipitation was filtered, washed with ethanol, and dried under *vacuum*. This precipitation was dissolved in DMF (20 mL) and stirred then filtered. After a few days orange block crystals were obtained by slow evaporation of solvent at room temperature. Yield: 37.9 mg, 62%. m.p.: 228-229 °C. Elemental analysis calcd (%) for C₂₇H₁₈N₆O₈: C 58.49, H 3.24, N 15.16; found: C 58.55, H 3.24, N 15.22. IR (KBr, ν): 3431 (br), 3204 (w), 3089 (m), 2572 (br), 2125 (w), 1632 (s), 1600 (m), 1562 (s), 1499 (m), 1436 (m), 1363 (m), 1336 (s), 1272 (s), 1231 (m), 1160 (m), 1079(m), 1000 (m), 903 (w), 837(w), 788(w),743 (m), 709(w), 609 (w) cm⁻¹.

References

- [1] (a) G. M. Sheldrick, *SHELXL-97*, Program for the Solution of Crystal Structures; University of Göttingen: Göttingen, Germany, **1997**. (b) G. M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, **1997**.
- [2] Dennis, W. H., Jr.; Rosenblatt, W. G.; Blucher, D. H.; Coon, C. L. *J. Chem. Eng. Data* **1975**, *20*, 202–203.

3. Linear concentration range of TNP in DMF.

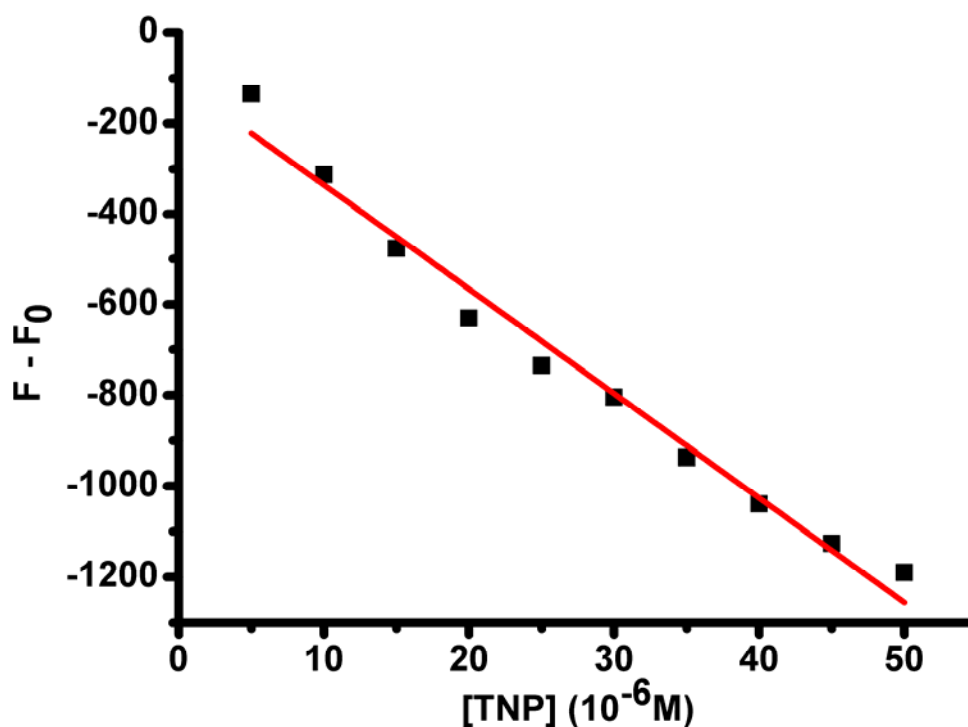


Fig. S1 Linear concentration range of TNP (L: 50.0 μ M) in DMF ($\lambda_{\text{ex}} = 419$ nm).

The corresponding quantitative analytical data (linear concentration range, RSD, LOD, LOQ) were determined using a reported procedure (C. Tong, G. Xiang, *J. Lumin.*, 2007, **126**, 575–580. C. Tong, G. Xiang, *J. Lumin.*, 2007, **126**, 575–580; and ref. 8b).

The result of the analysis as follows:

$$\text{Linear Equation: } Y = -105.7333 - 23.0133 \times X \quad R = 0.9787$$

$$S = 23.0133 \times 10^6 \quad \delta = \sqrt{\frac{\sum (F_0 - \bar{F}_0)^2}{N-1}} = 3.3025 \quad (N = 10) \quad K = 3$$

$$\text{LOD} = K \times \delta / S = 4.30 \times 10^{-7} \text{ M}$$

$$\text{LOQ} = 3\text{LOD} = 1.29 \times 10^{-6} \text{ M}$$

$$\text{RSD} = \delta / F_0 \times 100\% = 0.186\%$$

F_0 is the fluorescence intensity of L.

4. UV-vis absorption spectra of L with TNP.

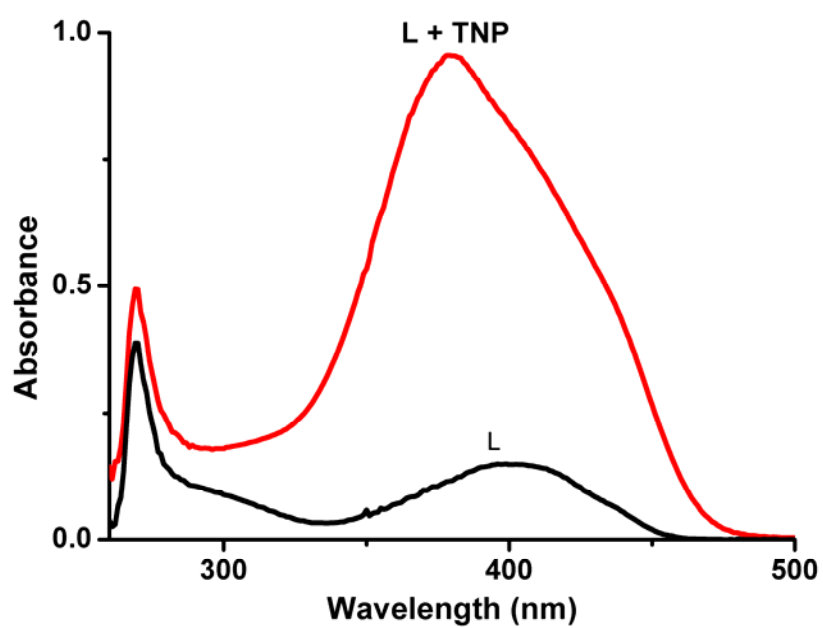


Fig. S2 UV-vis absorption spectra of **L** (50.0 μ M) with TNP (1.0 equiv) in DMF.

5. The image of L with TNP in ethanol (0.5% DMF, v/v).



Fig. S3 The image of L (9.0×10^{-4} M) with TNP (1.0×10^{-3} – 1.0×10^{-2} M) in ethanol (0.5% DMF, v/v).

6. Powder X-ray diffraction pattern of the precipitate.

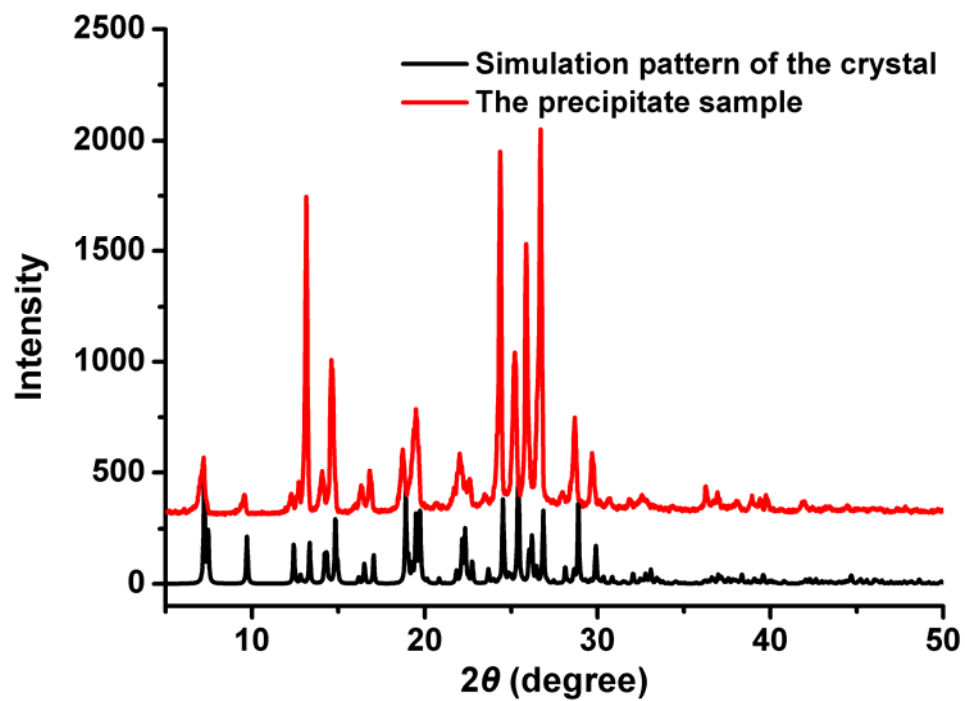


Fig. S4 Powder X-ray diffraction pattern of the precipitate.

7. Crystal data and structure refinement parameters for L·TNP.

Table S1 Crystal data and structure refinement parameters for L·TNP.

Empirical formula	C ₂₇ H ₁₈ N ₆ O ₈
Temperature/K	296(2)
<i>M</i>	554.47
Crystal system	Monoclinic
Space group	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> /Å	7.394(5)
<i>b</i> /Å	23.675(16)
<i>c</i> /Å	14.376(10)
<i>α</i> /°	90.00
<i>β</i> /°	97.916(8)
<i>γ</i> /°	90.00
<i>V</i> /Å ³	2493(3)
<i>Z</i>	4
<i>D_c</i> /kg m ⁻³	1.472
<i>μ</i> /mm ⁻¹	0.112
<i>F</i> (000)	1144
Crystal size/mm	0.37 × 0.35 × 0.32
<i>θ</i> Range for data collection/°	2.24-25.20
Index ranges, <i>hkl</i>	-6 ≤ <i>h</i> ≤ 8, -27 ≤ <i>k</i> ≤ 28, -17 ≤ <i>l</i> ≤ 16
Reflections collected/unique	11651/4404
Data/restraints/params	4404/0/371
Goodness-of-fit on <i>F</i> ²	1.052
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0584, <i>wR</i> 2 = 0.1214
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1228, <i>wR</i> 2 = 0.1495

8. The hydrogen-bonds data of L·TNP.

Table S2. Intermolecular hydrogen bonds data in L·TNP.

D-H...A	d(D-H)(Å)	d(H...A)(Å)	d(D...A)(Å)	<(DHA)(°)
C(1)-H(1)...O(3)	0.93	2.34	3.251(5)	166.9
C(17)-H(17)...O(3)	0.93	2.58	3.470(5)	160.3
C(13)-H(13)...O(4)	0.93	2.64	3.429(5)	143.0
C(5)-H(5)...O(4)	0.93	2.51	3.291(4)	141.0
C(11)-H(11)...O(5)	0.93	2.46	3.272(5)	145.4
C(20)-H(20)...O(6)	0.93	2.59	3.436(5)	152.1
C(4)-H(4)...O(7)	0.93	2.50	3.249(4)	138.0
C(4)-H(4)...O(8)	0.93	2.33	3.042(4)	133.5
N(2)-H(2A)...O(8)	0.86	1.99	2.840(3)	169.9
N(1)-H(1A)...O(1)	0.86	1.87	2.713(4)	165.0
N(1)-H(1A)...N(3)	0.86	2.63	3.089(4)	114.8

