

<Supporting Information>

**An DHPA-Containing Metal-Organic Octahedron Responding
to a Photoreaction in a Fluorescent Enhancement Manner for
Detecting of High Explosive RDX**

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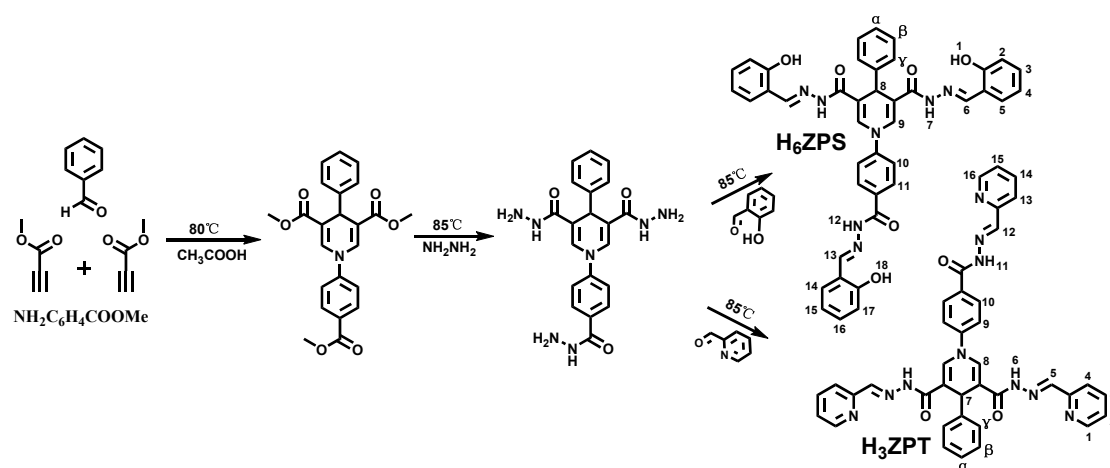
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1. Experimental Section.

1.1 Materials and Methods. All the chemicals and solvents were of reagent grade quality obtained from commercial sources and used without further purification. The solutions of explosives were cyclotrimethylene trinitramine (RDX) and pentaerythritol tetranitrate (PETN), 2,4,6-trinitrotoluene (TNT), 2,6-dinitrotoluene (DNT), 2-nitrotoluene (NT), 1,4-dinitrobenzene (DNB), nitrobenzene (NB), 4-nitrophenol (NP) and picric acid (PA). The elemental analyses of C, H and N were performed on a vario EL III elemental analyzer. ^1H NMR spectra were measured on a BRUKER 400M spectrometer. ESI mass spectra were carried out on a HPLC-Q-ToF MS spectrometer using acetonitrile as mobile phase. *Uv-vis* spectra were measured on a HP 8453 spectrometer. The fluorescent spectra were measured on EDINBURGH FS920.

1.2 Preparation

Scheme S1 The synthetic routes of the H_6ZPS and H_3ZPT .



Synthesis of dimethyl 1-(4-(methoxycarbonyl)phenyl)-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate^{S1}

Methyl propiolate (1.68g, 20mmol), benzaldehyde (1.06g, 10mmol), and methyl 4-aminobenzoate (1.51g, 10mmol) in glacial acetic acid (2.0 mL) were heated at 80 °C for 30 min. After cooling, the mixture was poured into water (20 mL) and stirred for 1 h. The product was filtered and washed with Et_2O (3×30 mL) to give pure dimethyl 1-(4-(methoxycarbonyl)phenyl)-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate, which was recrystallized by ethanol. Yield: 2.26g, 55.5%. ^1H NMR (400 MHz, CDCl_3 , ppm):

δ 8.13 (d, 2H), 7.75 (s, 2H), 7.36 (d, 2H), 7.34 (d, 2H), 7.27 (t, 2H), 7.18 (t, 1H), 4.97 (s, 1H), 3.95 (s, 3H), 3.67 (s, 6H).

Synthesis of 1-(4-(hydrazinecarbonyl)phenyl)-4-phenyl-1,4-dihydropyridine-3,5-dicarbohydrazide

A mixture solution of 80% hydrazine hydrate (50ml) and dimethyl 1-(4-(methoxycarbonyl) phenyl)-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (4.07g, 10mmol) was stirred at 85°C over 12 h. The white precipitate was formed, which was collected by filtration, washed with methanol and dried in vacuum. Yield: 2.51g, 61.5%. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 9.91 (s, 1H), 9.30 (s, 2H), 8.05 (d, 2H), 7.74 (s, 2H), 7.69 (d, 2H), 7.35 (m, 4H), 7.25 (t, 1H), 5.27 (s, 1H), 4.47 (s, 6H).

Synthesis of H₆ZPS

1-(4-(hydrazinecarbonyl)phenyl)-4-phenyl-1,4-dihydropyridine-3,5-dicarbohydrazide (4.07g, 10mmol) was added to a ethanol solution (50 mL) containing salicylaldehyde (2.69g, 22mmol). After 5 drops of acetic acid was added, the mixture was heated at 85°C under magnetic stirring for 12 h according to the reference.^{S2} The yellow solid was collected by filtration, washed with methanol and dried in vacuum. Yield: 5.91g, 82.1%. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 12.13 (s, 1H₁₂), 11.63 (s, 2H₇), 11.27 (s, 1H₁₈), 11.18 (s, 2H₁), 8.68 (s, 1H₁₃), 8.44 (s, 2H₆), 8.13 (d, 2H₁₀), 7.88 (s, 2H₉), 7.78 (d, 2H_γ), 7.56 (d, 1H₁₄), 7.47 (d, 2H₁₁), 7.23~7.36 (m, 6H_{15,16,17,α,2,}), 7.16 (t, 2H_β), 6.93 (t, 2H₃), 6.88 (t, 4H_{4,5}), 5.32 (s, 1H₈). Anal calc. for C₄₁H₃₃N₇O₆: H 4.62, C 68.42, N 13.62 %. Found: H 4.78, C 67.75, N 13.29 %. ESI-MS calcd for C₄₁H₃₃N₇O₆ 719.25, found 718.24 [M-H]⁻, 754.22 [M+Cl]⁻.

Synthesis of H₃ZPT

1-(4-(hydrazinecarbonyl)phenyl)-4-phenyl-1,4-dihydropyridine-3,5-dicarbohydrazide (4.07g, 10mmol) was added to a ethanol solution (50 mL) containing 2-pyridyl aldehyde (2.35g, 22mmol). After 5 drops of acetic acid was added, the mixture was heated at 85°C under magnetic stirring for 12 h according to the reference.^{S2} The yellow solid was collected by filtration, washed with methanol and dried in vacuum. Yield: 5.66g, 83.9%. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 12.07 (s, 2H₁₁), 11.59 (s, 2H₆), 8.63 (d, 2H₁), 8.58 (d, 1H₁₆), 8.53 (s, 1H₁₂), 8.27 (s, 2H₅), 8.12 (m, 2H₁₀),

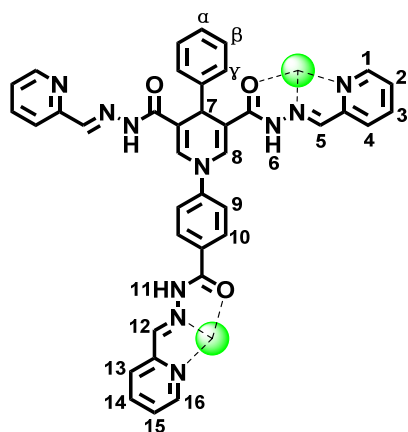
7.99 (m, 1H₁₅), 7.89~7.82 (m, 6H_{3,4,13,14}), 7.78 (m, 2H₂), 7.43 (m, 1H_α), 7.39~7.29 (m, 4H_{β,γ}), 7.26 (t, 2H₈), 7.14 (t, 2H₉), 5.37 (s, 1H₇). Anal calc. for C₃₈H₃₀N₁₀O₃: H 4.48, C 67.64, N 20.76 %. Found: H 4.66, C 67.89, N 20.22 %. ESI-MS calcd for C₃₈H₃₀N₁₀O₃ 674.25, found 675.2 [M+H]⁺, 697.3 [M+Na]⁺.

Preparation of Ce–ZPS

A solution of Ce(NO₃)₃·6H₂O (0.0434 g, 0.1 mmol), H₆ZPS ligand (0.072 g, 0.1 mmol) and KOH (0.0168 g, 0.3 mmol) in DMF/CH₃OH (9:1 v/v) solution (20 mL) was stirred for 5 h at room temperature. Then the solution was left for two weeks at room temperature to give X-ray quality black block crystals. Anal calc. for Ce₄(C₄₁H₂₉N₇O₆)₄·C₃H₇ON: H 3.55, C 57.37, N 11.62%. Found: H 4.03, C 56.95, N 11.51%. Yield: 57%. ESI-MS: *m/z*: 1710.24 [Ce₄(H₂ZPS)₂(HZPS)₂]²⁻, 1741.73 [Ce₄(H₂ZPS)₂(HZPS)₂·2CH₃OH]²⁻ and 1773.23 [Ce₄(H₂ZPS)₂(HZPS)₂·4CH₃OH]²⁻.

Synthesis of Zn–ZPT

Zn(NO₃)₂·6H₂O (29.7 mg, 0.10 mmol) and H₃ZPT (47.2 mg, 0.07 mmol) were dissolved in CH₃OH/CH₂Cl₃ (1:1 in volume) to give a red solution. After addition of NaClO₄, yellow precipitates formed were isolated and dried under vacuum. Yield: 68%. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 12.16 (s, 2H₁₁), 11.82 (s, 2H₆), 8.63 (d, 2H₁), 8.58 (d, 1H₁₆), 8.54 (s, 1H₁₂), 8.29 (s, 2H₅), 8.14 (m, 2H₁₀), 8.00 (m, 1H₁₅), 7.90 (m, 6H_{3,4,13,14}), 7.80 (m, 2H₂), 7.44 (m, 1H_α), 7.36 (m, 4H_{β,γ}), 7.29 (t, 2H₈), 7.18 (t, 2H₉), 5.37 (s, 1H₇). Anal calc. for Zn₆(C₁₅₂H₁₁₂N₄₀O₁₂)(ClO₄)₃·NO₃: H 3.28, C 53.02, N 16.68 %. Found: H 3.12, C 53.12, N 16.15 %. ESI-MS: *m/z*: 1027.51 [Zn₆(HZPT)₃(ZPT)]³⁺.



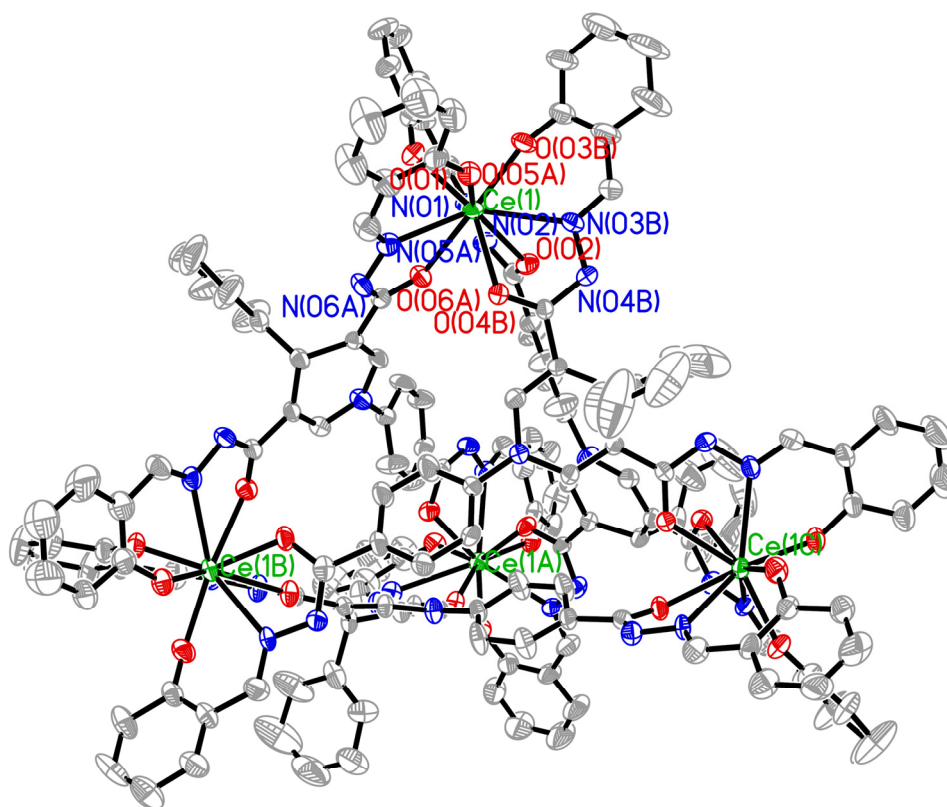
¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 12.16 (s, 2H₁₁), 11.82 (s, 2H₆), 8.63 (d, 2H₁), 8.58 (d, 1H₁₆), 8.54 (s, 1H₁₂), 8.29 (s, 2H₅), 8.14 (m, 2H₁₀), 8.00 (m, 1H₁₅), 7.90 (m, 6H_{3,4,13,14}), 7.80 (m, 2H₂), 7.44 (m, 1H_α), 7.36 (m, 4H_{β,γ}), 7.29 (t, 2H₈), 7.18 (t, 2H₉), 5.37 (s, 1H₇).

2. Crystallography:

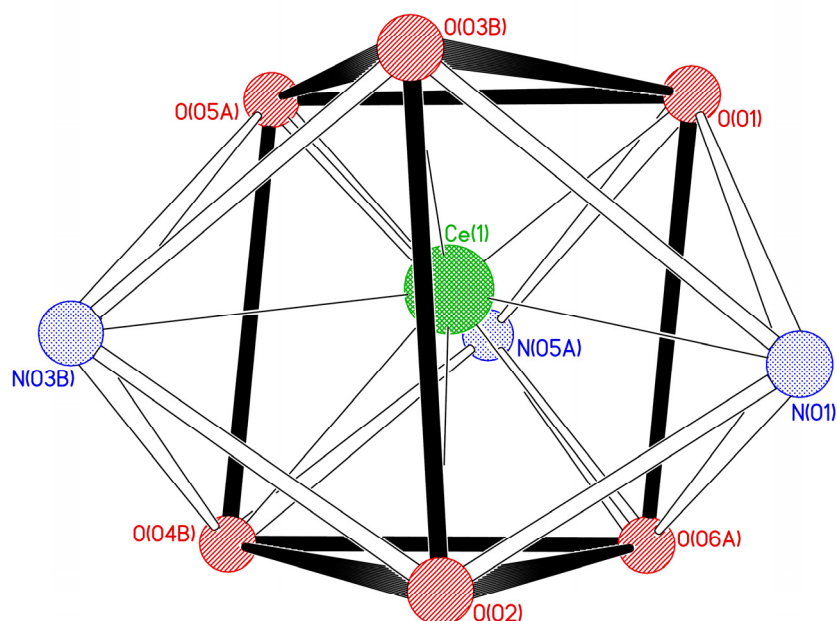
Intensities of the Ce–ZPS were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo-K α ($\lambda = 0.71073 \text{ \AA}$) using the SMART and SAINT programs. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL *version* 5.1. The SQUEEZE subroutine in PLATON^{S3} was used with the cycle number being 4.

In the structural refinement of Ce–ZPS, except the solvent water molecules and methanol molecules, the non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones and the solvent DMF molecules were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. To assist the stability of refinements, one benzene ring in the ligands and solvent DMF molecule were restrained as idealized regular polygons and thermal parameters on adjacent atoms in the solvent DMF molecule were restrained to be similar.

2.1 Figure S1 An ORTEP plot of the molecular tetrahedron Ce–ZPS, showing 30% probability displacement ellipsoids of non-hydrogen atoms. Hydrogen atoms are omitted for clarity. Symmetry code A: $-x+5/2, -y+5/2, z$; B: $-y+5/2, x, -z+1/2$.



2.2 Figure S2 The coordination configuration of the Ce(1). Symmetry code A: $-x+5/2, -y+5/2, z$; B: $-y+5/2, x, -z+1/2$.



2.3 Table S1 Selective bond distance (Å) in Ce-ZPS.

	bond distance (Å)		bond distance (Å)
Ce(1)-O(01)	2.201(6)	C(24)-O(04)	1.218(9)
Ce(1)-O(02)	2.451(6)	C(24)-N(04)	1.354(10)
Ce(1)-N(01)	2.664(7)	C(23)-N(03)	1.276(11)
Ce(1)-O(03B)	2.217(6)	C(17)-O(03)	1.295(11)
Ce(1)-O(04B)	2.474(6)	C(16)-N(07)	1.393(10)
Ce(1)-N(03B)	2.661(7)	C(15)-N(07)	1.395(10)
Ce(1)-O(05A)	2.181(6)	C(12)-N(07)	1.434(10)
Ce(1)-O(06A)	2.409(6)	C(08)-O(02)	1.264(10)
Ce(1)-N(05A)	2.631(7)	C(08)-N(02)	1.318(11)
O(05)-C(41)	1.331(11)	C(07)-N(01)	1.315(11)
N(05)-C(35)	1.276(11)	C(01)-O(01)	1.331(10)
N(05)-N(06)	1.375(9)	N(03)-N(04)	1.402(9)
C(34)-O(06)	1.271(9)	N(01)-N(02)	1.350(9)
C(34)-N(06)	1.304(10)		

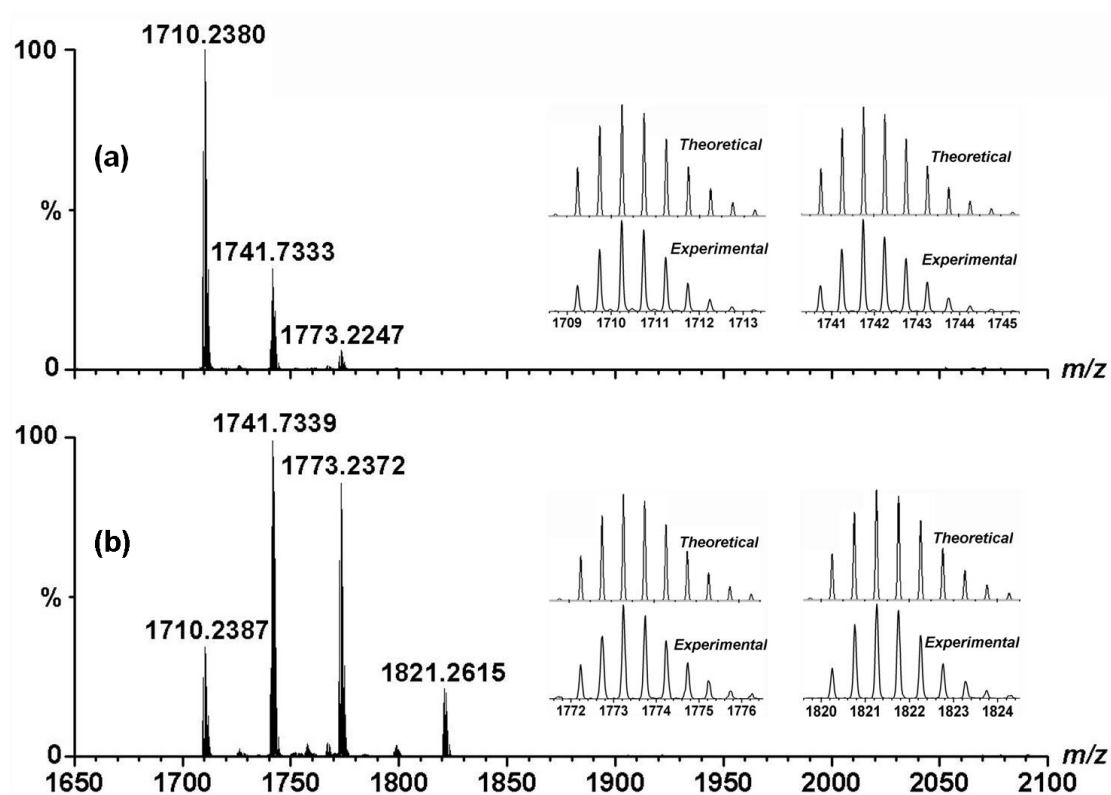
Symmetry code: $-x+5/2, -y+5/2, z$; B: $-y+5/2, x, -z+1/2$

2.4 Table S2 Selective bond angle (°) in Ce–ZPS.

	bond angle (°)		bond angle (°)
O(05A)-Ce(1)-O(01)	87.2(2)	O(05A)-Ce(1)-O(06A)	130.5(2)
O(05A)-Ce(1)-O(03B)	84.8(2)	O(01)-Ce(1)-O(06A)	87.4(2)
O(01)-Ce(1)-O(03B)	80.5(2)	O(03B)-Ce(1)-O(06A)	142.2(2)
O(05A)-Ce(1)-O(02)	142.8(2)	O(01)-Ce(1)-O(02)	127.8(2)
O(03B)-Ce(1)-O(02)	88.9(2)	O(06A)-Ce(1)-O(02)	70.7(2)
O(05A)-Ce(1)-O(04B)	86.9(2)	O(01)-Ce(1)-O(04B)	149.9(2)
O(03B)-Ce(1)-O(04B)	128.2(2)	O(06A)-Ce(1)-O(04B)	74.3(2)
O(02)-Ce(1)-O(04B)	68.7(2)	O(05A)-Ce(1)-N(05A)	69.6(2)
O(01)-Ce(1)-N(05A)	77.8(2)	O(03B)-Ce(1)-N(05A)	146.9(2)
O(06A)-Ce(1)-N(05A)	61.1(2)	O(02)-Ce(1)-N(05A)	124.2(2)
O(04B)-Ce(1)-N(05A)	72.5(2)	O(05A)-Ce(1)-N(03B)	77.8(2)
O(01)-Ce(1)-N(03B)	145.9(2)	O(03B)-Ce(1)-N(03B)	67.9(2)
O(06A)-Ce(1)-N(03B)	125.5(2)	O(02)-Ce(1)-N(03B)	65.9(2)
O(04B)-Ce(1)-N(03B)	60.4(2)	N(05A)-Ce(1)-N(03B)	123.3(2)
O(05A)-Ce(1)-N(01)	150.5(2)	O(01)-Ce(1)-N(01)	68.0(2)
O(03B)-Ce(1)-N(01)	75.8(2)	O(06A)-Ce(1)-N(01)	66.5(2)
O(02)-Ce(1)-N(01)	59.9(2)	O(04B)-Ce(1)-N(01)	122.6(2)
N(05A)-Ce(1)-N(01)	117.5(2)	N(03B)-Ce(1)-N(01)	113.9(2)

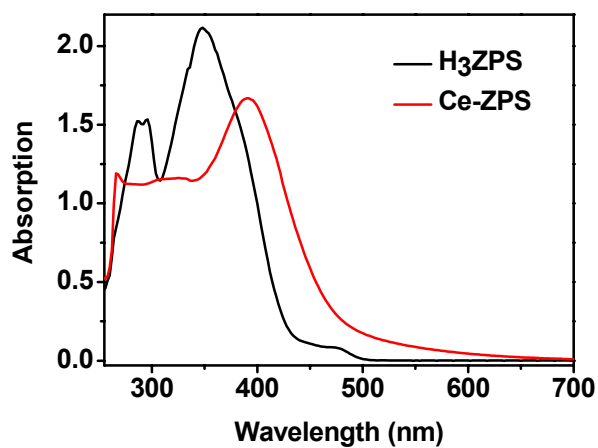
Symmetry code: $-x+5/2, -y+5/2, z$; B: $-y+5/2, x, -z+1/2$

3. Figure S3. ESI-MS of (a) Ce-ZPS (0.1mM) and (b) Ce-ZPS (0.1mM) upon addition of 1 equiv of RDX without illumination in DMF/CH₃CN solution. Inserts exhibit the measured and simulated isotopic patterns at 1710.24, 1741.73 (a) and 1773.23, 1821.26 (b).

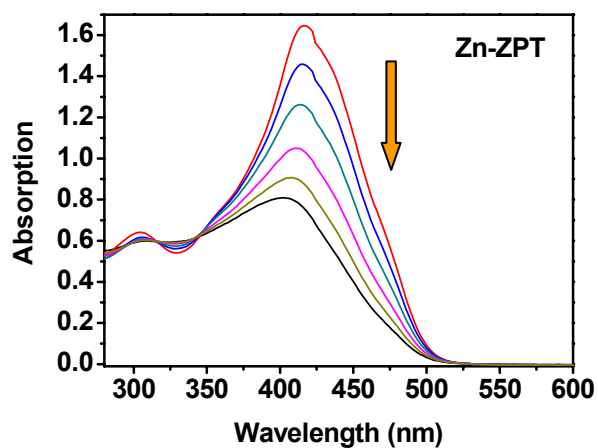
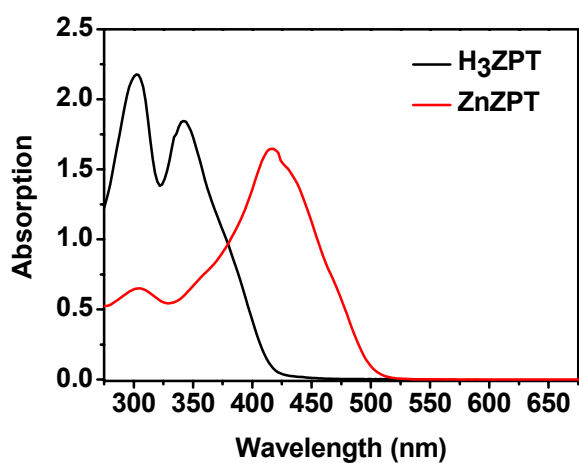


Peak	Value of m/z	Specie assigned
1	1710.2380	$[\text{Ce}_4(\text{H}_2\text{ZPS})_2(\text{HZPS})_2]^{2-}$
2	1741.7333	$[\text{Ce}_4(\text{H}_2\text{ZPS})_2(\text{HZPS})_2 \cdot 2\text{CH}_3\text{OH}]^{2-}$
3	1773.2247	$[\text{Ce}_4(\text{H}_2\text{ZPS})_2(\text{HZPS})_2 \cdot 4\text{CH}_3\text{OH}]^{2-}$
4	1821.2615	$[\text{Ce}_4(\text{H}_2\text{ZPS})_2(\text{HZPS})_2 \supset \text{RDX}]^{2-}$

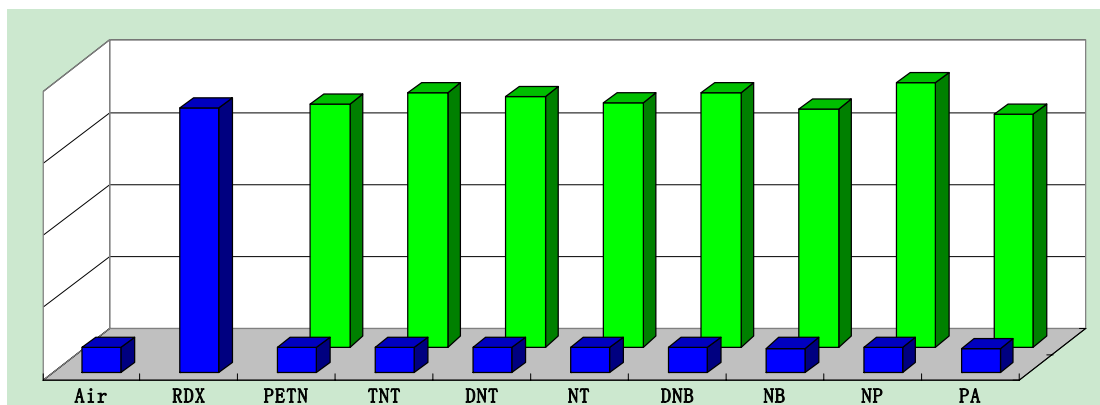
4. **Figure S4** Uv-vis absorption spectra of H₃ZPS (40 μM) and Ce-ZPS (10 μM) in DMF solution.



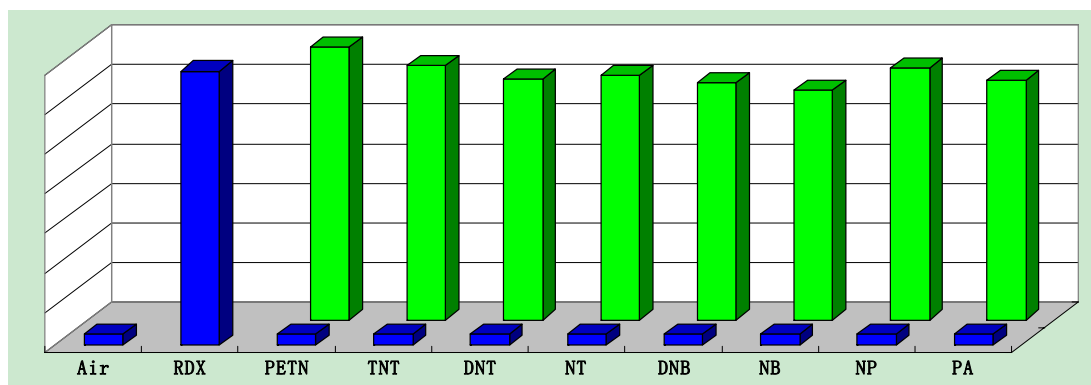
5. **Figure S5** Uv-vis absorption spectra of H₃ZPT (40 μM) and Zn-ZPT (10 μM) in DMF solution upon the addition of explosive RDX (1 μM) with increasing irradiation time (1 min intervals, 310 nm).



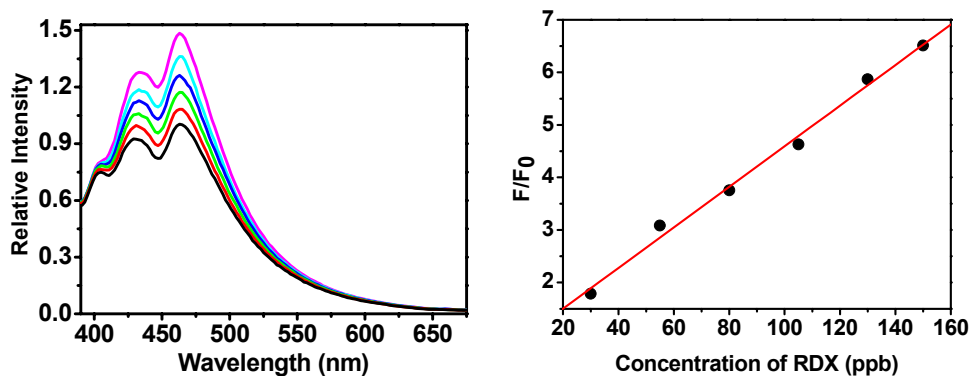
6. Figure S6 Fluorescence responses of solution containing Ce-ZPS (10 μM) to various explosives in DMF solution. The blue bars represent the integrated fluorescence in the presence of various explosives (10 μM). The green bars represent the fluorescence upon the addition of RDX (1 μM) to the above mentioned solution (except for RDX solution). The fluorescence was recorded at 465 nm after a 5 min irradiation with 310 nm light, excitation at 350 nm.



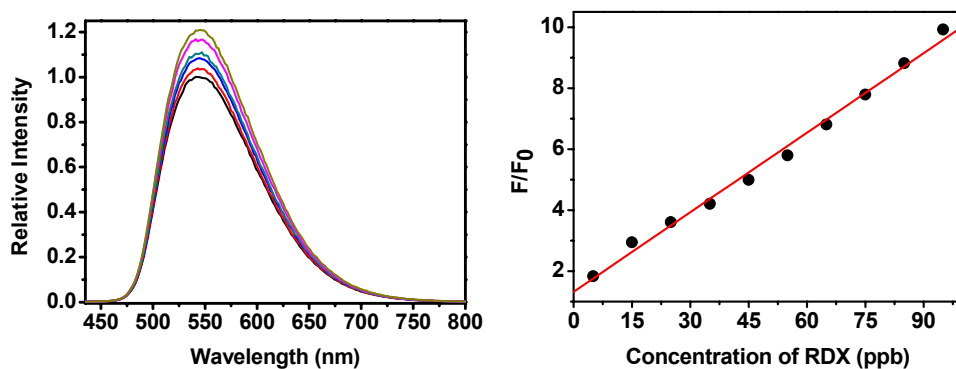
7. Figure S7 Fluorescence responses of solution containing Zn-ZPT (10 μM) to various explosives in DMF solution. The blue bars represent the integrated fluorescence in the presence of various explosives (10 μM). The green bars represent the fluorescence upon the addition of RDX (1 μM) to the above mentioned solution (except for RDX solution). The fluorescence was recorded at 545 nm after a 5 min irradiation with 310 nm light, excitation at 415 nm.



8. Figure S8 (left) Fluorescence intensity changes of Ce-ZPS (5 μM) in DMF solution upon additions of RDX (10 ppb) with increasing irradiation time with 310 nm light (1 min intervals). (right) Fluorescence intensity changes of Ce-ZPS (5 μM) in DMF solution upon additions of RDX (30-150 ppb). The fluorescence was recorded at 465 nm after 5 min irradiation with 310 nm light, excitation at 350 nm.



9. Figure S9 (left) Fluorescence intensity changes of Zn-ZPT (5 μM) in DMF solution upon additions of RDX (1 ppb) with increasing irradiation time with 310 nm light (1 min intervals). (right) Fluorescence intensity changes of Zn-ZPT (5 μM) in DMF solution upon additions of RDX (5-95 ppb). The fluorescence was recorded at 545 nm after 5 min irradiation with 310 nm light, excitation at 415 nm.



- S1 A. Mai, S. Valente, S. Meade, V. Carafa, M. Tardugno, A. Nebbioso, A. Galmozzi, N. Mitro, E. D. Fabiani, L. Altucci and A. Kazantsev, *J. Med. Chem.*, 2009, **52**, 5496–5504.
 S2 J. D. Ranford, J. J. Vittal, and Y. M. Wang, *Inorg. Chem.*, 1998, **37**, 1226–1231.
 S3 A. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.