Electronic Supporting Information

Rational Synthesis of An Exceptionally Stable Zn(II) Metal-Organic Framework for Highly Selective and Sensitive Detection of Picric Acid

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S1 Materials and Instrumentation

All chemicals were purchased from commercial sources and used without further treatment: zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, Energy Chemical, 99%), 4'-(1H-tetrazol-5-yl)-[1,1'-biphenyl]-3,5-dicarboxylic acid (TZBPDC, Jinan Henghua Sci. & Tec. Co., Ltd., 99%), dimethyl formamide (DMF, Energy Chemical, 99.5%), dimethyl sulfoxide(Aladdin Industrial Inc., 99%), *n*-hexane (Sinopharm Chemical Reagent Co., Ltd., 99%), ethanol (CH_3CH_2OH, Sinopharm Chemical Reagent Co., Ltd., 99.7%), 2,4,6-trinitrophenol (picric acid, Sinopharm Chemical Reagent Co., Ltd., 70%), nitrobenzene (Sinopharm Chemical Reagent Co., Ltd., AR), 2,4-dinitrotoluene (Aladdin Industrial Inc., 99%), 2,6-dinitrotoluene (Aladdin Industrial Inc., 99%), 2,4,6-trinitrotoluene (Aladdin Industrial Inc., 1.00 ± 0.02mg/mL methanol solution), 1,3-dinitrobenzene (Aladdin Industrial Inc., CP). De-ionized water with the specific resistance of 18.25 MΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration (Cleaned Water Treatment Co., Ltd., Hefei). Powder X-ray diffraction patterns (PXRD) were collected on a Japan Rigaku SmartLab™ rotation anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.54 Å). Thermogravimetric analysis (TGA) was carried out on a Shimadzu DTG-60H thermogravimetric analyzer at a ramp rate of 10 °C min^{-1} under nitrogen. The contents of C, H and N were measured by using a VarioELIII Elemental analyzer. Fluorescent emission spectra were obtained on a LS-55 fluorescence spectrometer made by PerkinElmer.

S2 Experimental Section

2.1 Synthesis of USTC-7 single crystals

The single crystals of **USTC-7** were synthesized as follows: a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (30.5 mg, 0.10 mmol) and 4'-(1H-tetrazol-5-yl)-[1,1'-biphenyl]-3,5-dicarboxylic acid (H_3TZBPDC) (12.7 mg, 0.041 mmol) was dissolved in N,N-dimethylformamide (DMF, 1 mL), de-ionized water (1 mL) and dimethyl sulfoxide (DMSO, 350 μL) at room temperature in a 5 mL glass vial. Then the vial was placed in a preheated oven at 85 °C for 3 days. After cooling down to room temperature, colorless rhombic single crystals were obtained. Anal. Calcd for $C_{15}H_7N_4O_7Zn_2$: C, 37.07; H, 1.45; N, 11.52%; Found: C, 37.12; H, 1.42; N, 12.41%.

2.2 Synthesis of USTC-7 powder

The **USTC-7** powder was synthesized as follows: a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (416 mg, 1.40 mmol) and 4'-(1H-tetrazol-5-yl)-[1,1'-biphenyl]-3,5-dicarboxylic acid (H_3TZBPDC) (200 mg, 0.645 mmol) was dissolved in DMF (10 mL) and de-ionized water (10 mL) at room temperature in a 50 mL Teflon reactor. Then the Teflon reactor was placed into a steel autoclave and put into a preheated oven at 85 °C for 48 h. The resulting pale yellow powder was filtrated, then washed by DMF for three times and CH_2Cl_2 for three times. The product was dried at 50 °C in vacuum.

2.3 Fluorescence measurement

To obtain a stable suspension, the **USTC-7** sample was finely ground and immersed in different solvents by ultrasonication treatment for 2 h. Then it was made into a 0.125 mg/mL suspension. Finally, the stable suspensions of **USTC-7** in different

solvents, including H_2O, DMF, $CHCl_3$, C_2H_5OH and CH_3CN, were used for the fluorescence investigation at room temperature. The excitation and emission slit widths were set to 15.0 and 10.0 nm, respectively.

S3 X-ray Crystallography

Suitable single crystals of **USTC-7** were selected and mounted onto the end of a thin glass fiber using Fomblin oil. Single crystal X-ray diffraction data were recorded on a Bruker SMART APEXII CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. Determinations of the crystal system, orientation matrix, and cell dimensions were performed according to the established procedures. Absorption corrections were applied using multi-scan technique. The structure was solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program.[1] Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters and hydrogen atoms were placed geometrically and refined using the riding model. During the final stages of refinement, the residual Q peaks probably correspond to highly disordered solvent molecules were removed by SQUEEZE program.[2] Data collection and structure refinement parameters and crystallographic data for **USTC-7** is given in Table S1. Selected bond lengths and bond angles are given in Table S2.

Table. S1 Summary of crystallographic data for **USTC-7**.

Compound	**USTC-7**
Empirical formula	$C_{15}H_7N_4O_7Zn_2$
F_W	486.03
Color	Colorless
Crystal system	Orthorhombic
Space group	*Cmcm*
a (Å)	10.267(5)
b (Å)	32.086(5)
c (Å)	6.955(5)
α (°)	90.000(5)
β (°)	90.000(5)
γ (°)	90.000(5)
V (Å^3)	2291(2)
Z	4
$D_{calcd.}$ (g cm^{-3})	1.409
μ (mm^{-1})	2.144
F(000)	1076
Reflections collected	8940
Independent reflections	1551 [R(int)=0.0338]
Observed data [$I > 2\sigma(I)$]	1342
Data/restraints/parameters	1551/221/100
GOF on F^2	1.108
R_1,[a] w R_2[b] [$I > 2\sigma(I)$]	0.0530, 0.1538
R_1,[a] w R_2[b] (all data)	0.0598, 0.1588

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

Table. S2 Selected bond lengths (Å) and bond angles (deg) for USCT-7.

Zn(1)-O(3)	2.110(3)	Zn(2)-O(2)	1.983(5)
Zn(1)-N(1)#4	2.111(4)	Zn(2)-O(3)	2.035(6)
Zn(1)-O(1W)	2.159(7)	Zn(2)-N(2)#5	2.385(4)
O(3)#1-Zn(1)-O(3)#2	25.4(3)	N(1)#4-Zn(1)-O(1W)#1	90.000(5)
O(3)#1-Zn(1)-O(3)	180.0(2)	O(2)-Zn(2)-O(2)#3	112.4(5)
O(3)#2-Zn(1)-O(3)	154.6(3)	O(2)-Zn(2)-O(3)#3	137.0(3)
O(3)#1-Zn(1)-N(1)#4	88.82(16)	O(2)-Zn(2)-O(3)	110.6(3)
O(3)-Zn(1)-N(1)#4	91.18(16)	O(3)#3-Zn(2)-O(3)	26.4(4)
N(1)#4-Zn(1)-N(1)#5	180.00(9)	O(2)-Zn(2)-N(2)#5	90.28(5)
O(3)#1-Zn(1)-O(1W)#1	77.28(17)	O(3)-Zn(2)-N(2)#5	89.51(8)
O(3)#2-Zn(1)-O(1W)#1	102.72(17)	N(2)#5-Zn(2)-N(2)#6	178.99(17)

Symmetry codes: #1 –x+1, –y+1, –z+1; #2 x, –y+1, –z+1; #3 –x+1, y, z; #4 x+1/2, y+1/2, z; #5 –x+1/2, –y+1/2, –z+1; #6 –x+1/2, –y+1/2, z–1/2.

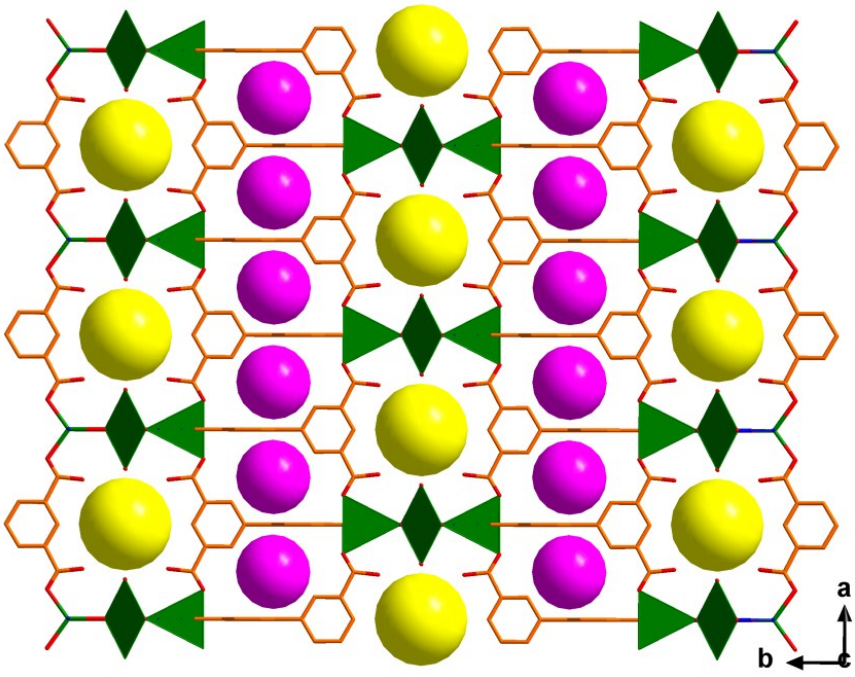
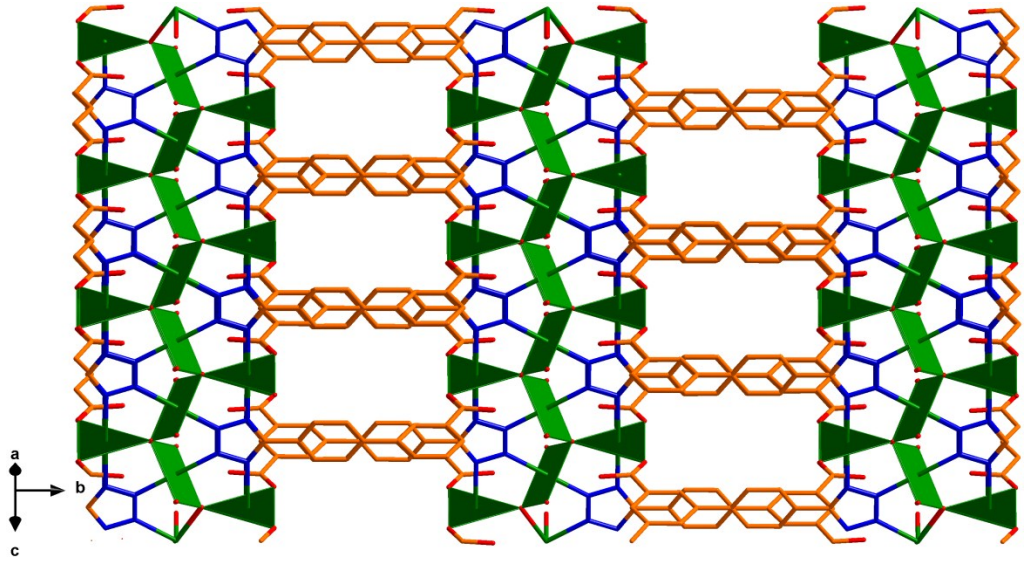
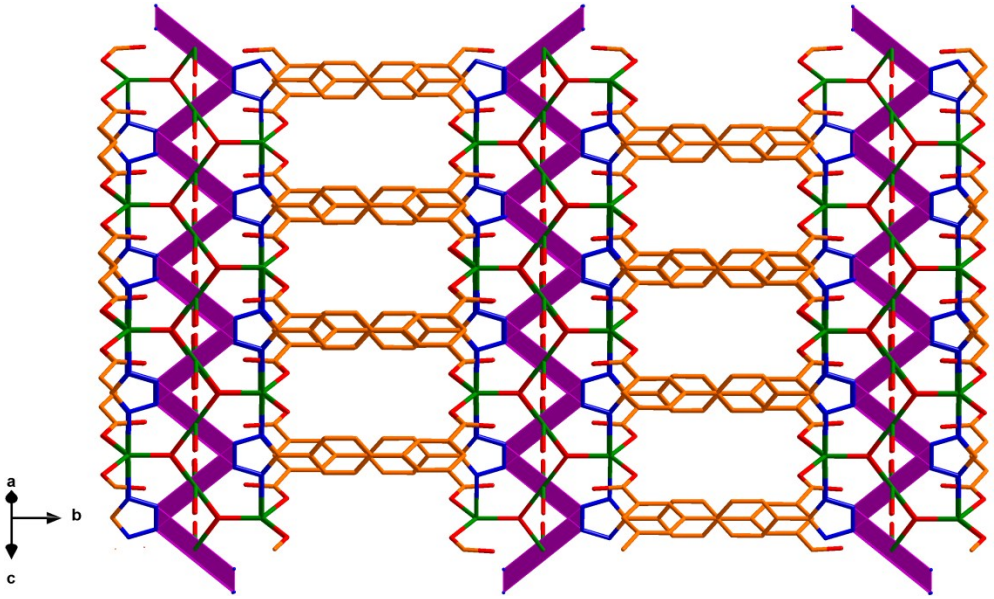


Fig. S1 View of the two channels of **USTC-7** along *c*-axis. The small and big channels are highlighted with pink and yellow tubes, respectively. The ZnO_3 or ZnO_4 polyhedra are shaded in olive green.



(a)



(b)

Fig. S2 View of **USTC-7** from the special direction to show the interconnection between the ligands and Zn-O/N slabs involving Zn-N and μ_3-OH-Zn bonds. The ZnO_3 or ZnO_4 polyhedra are shaded in olive green, and the ZnN_4 polyhedra are shaded in purple.

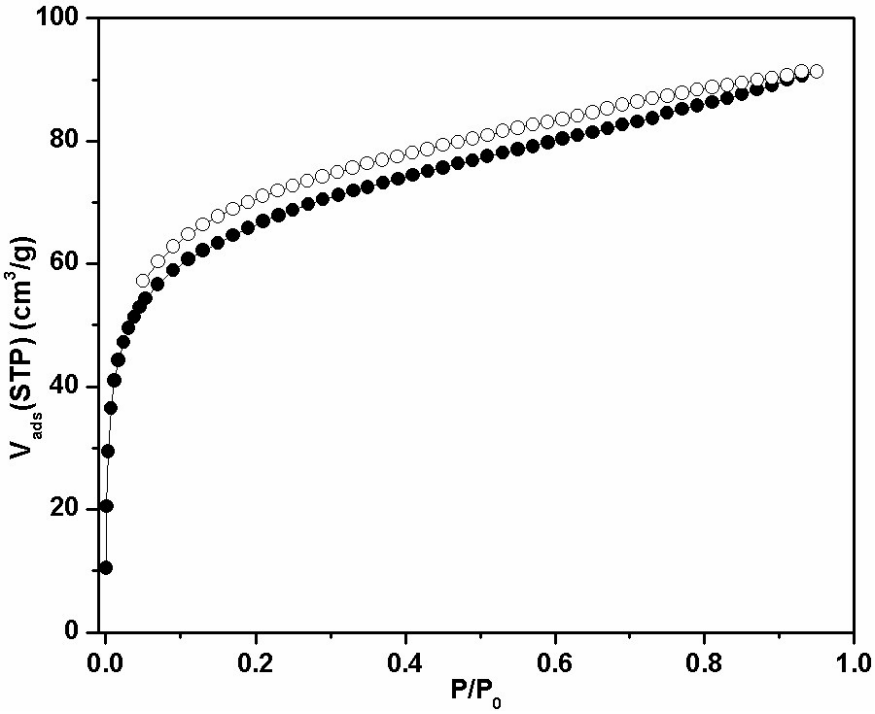


Fig. S3 CO_2 sorption isotherm for **USTC-7** at 195 K.

S4 Thermogravimetric analysis

Thermogravimetric (TG) analysis of **USTC-7** shows a significant weight loss of ~8.6% in the range of 50-250 ˚C, which could be attributed to the loss of free H_2O molecules in the pores of the MOF and the coordinated water molecules (calcd. 7.4%). Following that, the de-solvated framework started to collapse from 250 ˚C (Fig. S3).

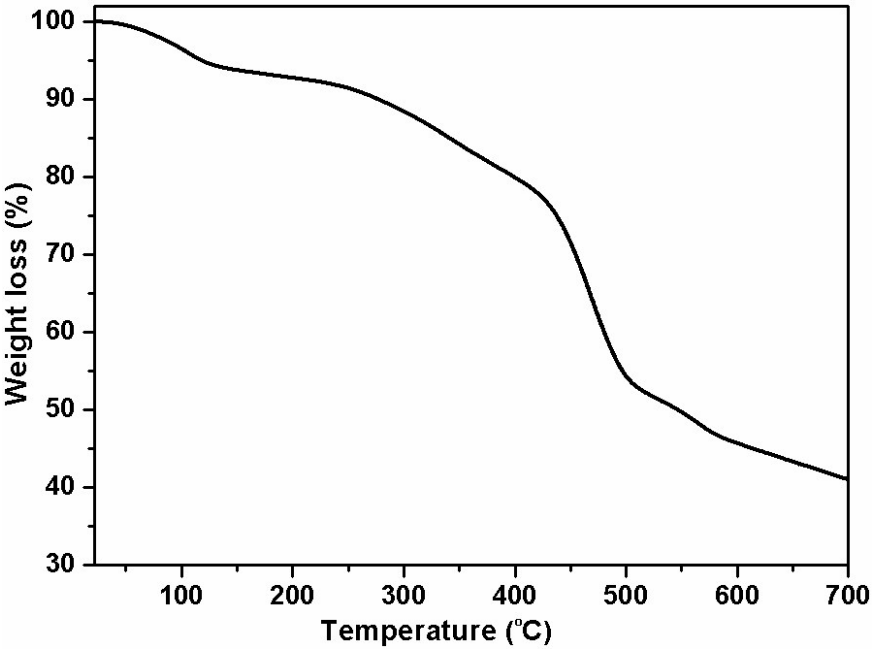


Fig. S4 TG Plot of **USTC-7** in N_2 atmosphere.

S5 Fluorescence measurements

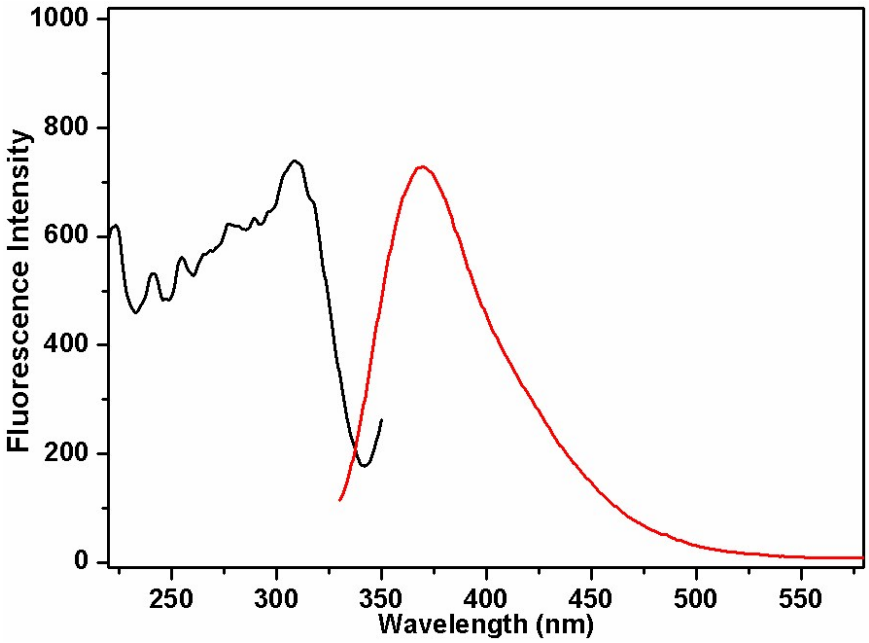


Fig. S5 Solid state excitation (black, λ_{em} = 370 nm) and emission (red, λ_{ex} = 309 nm) spectrum of **USTC-7**.

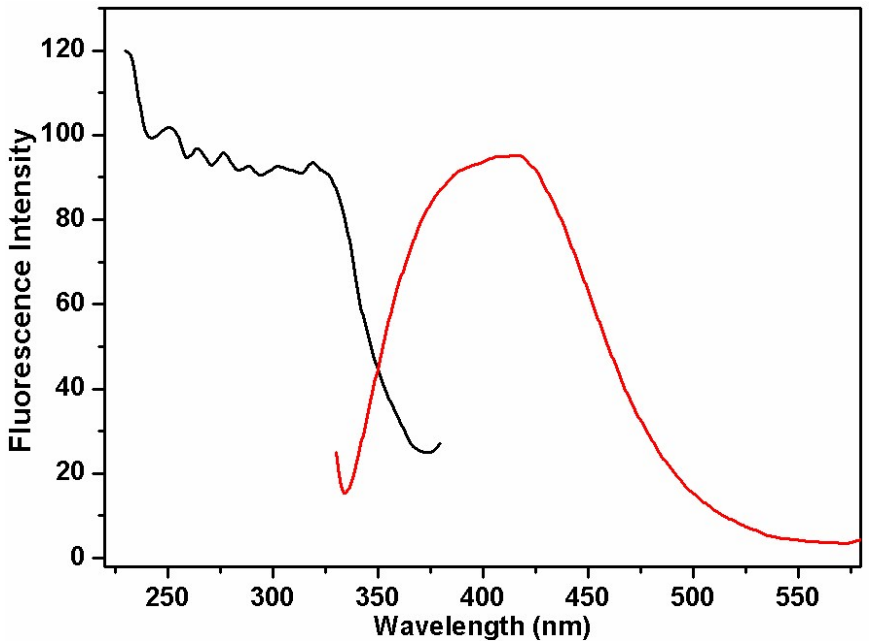


Fig. S6 Solid state excitation (black, λ_{em} = 409 nm) and emission (red, λ_{ex} = 319 nm) spectrum of H_3TZBPDC.

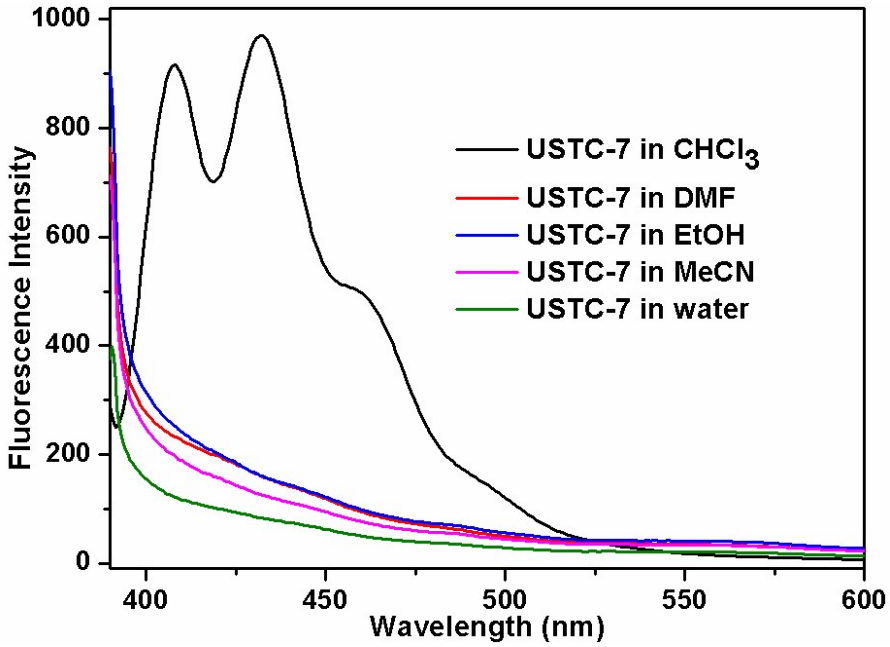


Fig. S7 Emission spectra of **USTC-7** (λ_{ex} = 370 nm) dispersed in different solvents.

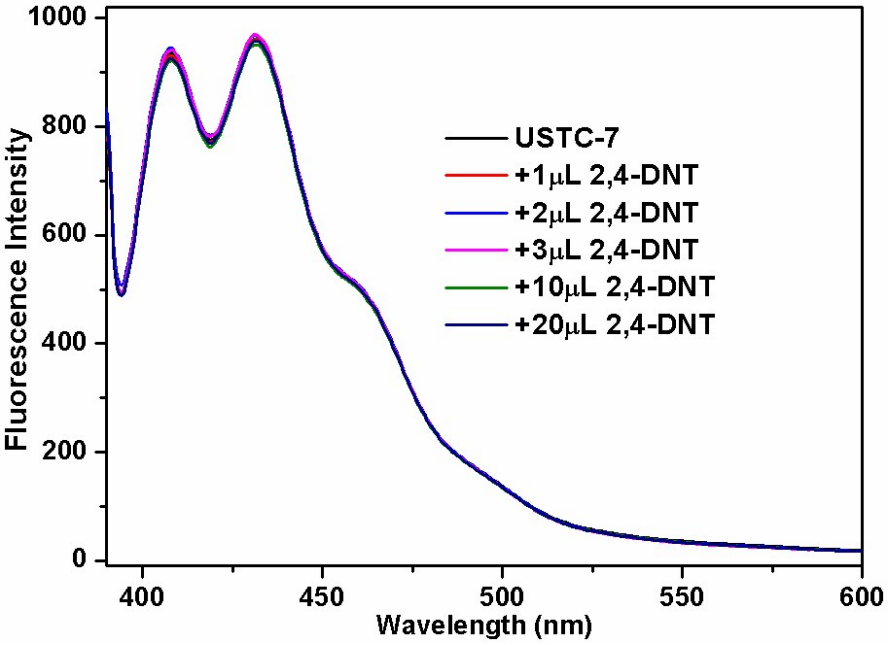


Fig. S8 Emission spectra of **USTC-7** suspension (λ_{ex} = 370 nm) upon incremental addition of 2,4-DNT (5 mM).

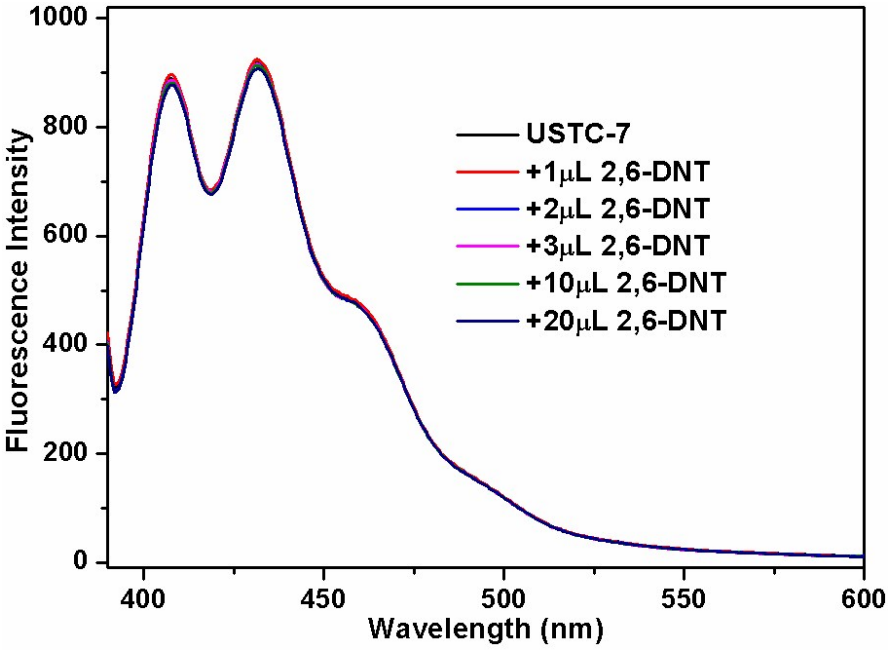


Fig. S9 Emission spectra of **USTC-7** suspension (λ_{ex} = 370 nm) upon incremental addition of 2,6-DNT (5 mM).

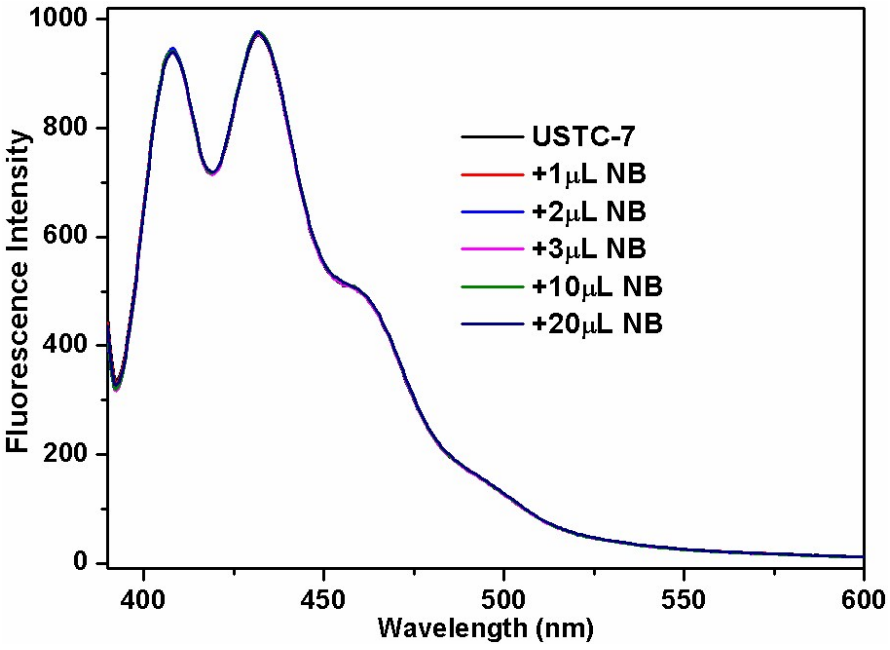


Fig. S10 Emission spectra of **USTC-7** suspension (λ_{ex} = 370 nm) upon incremental addition of NB (5 mM).

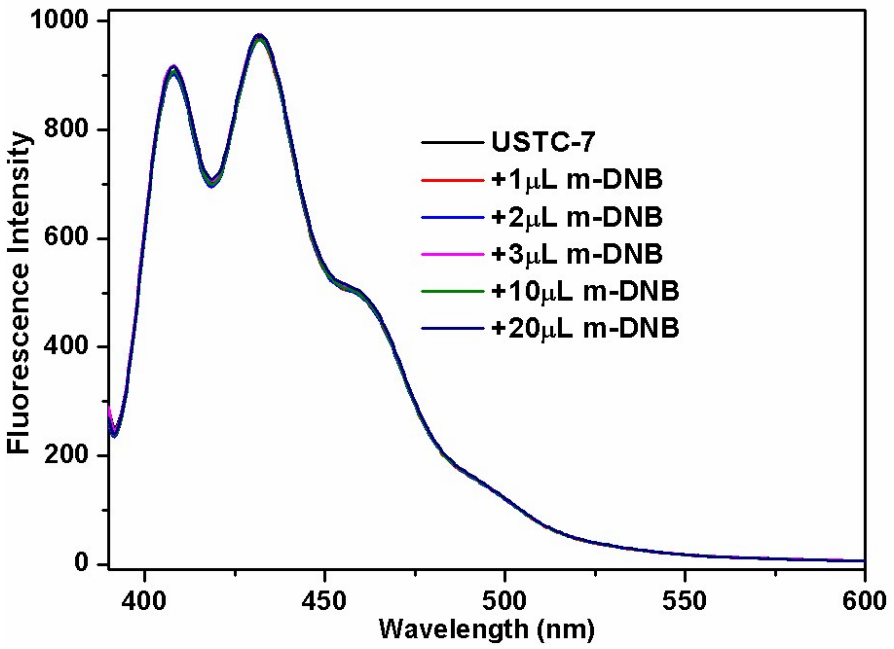


Fig. S11 Emission spectra of **USTC-7** suspension (λ_{ex} = 370 nm) upon incremental addition of m-DNB (5 mM).

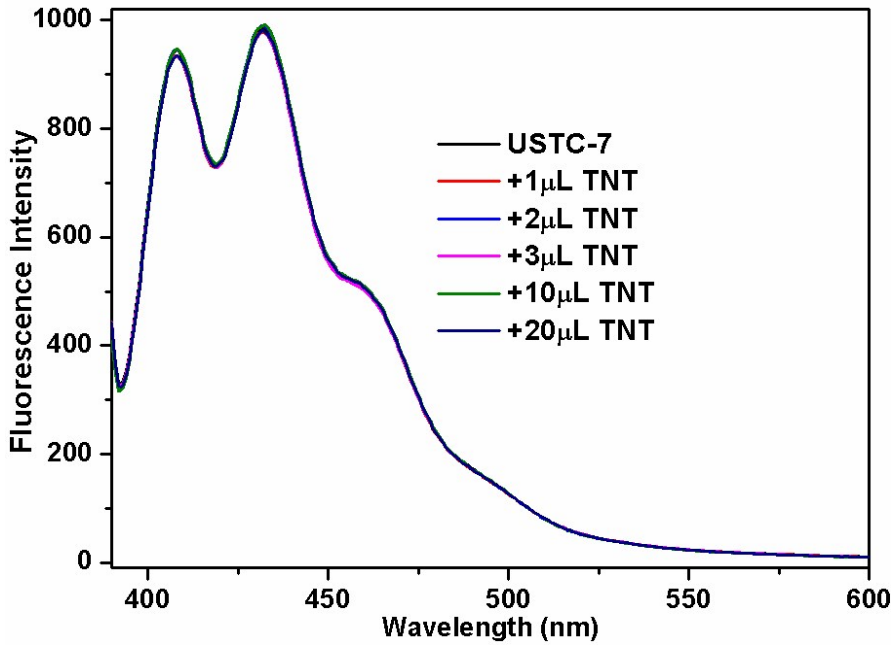


Fig. S12 Emission spectra of **USTC-7** suspension (λ_{ex} = 370 nm) upon incremental addition of TNT (5 mM).

S6 Standard deviation and detection limit calculation

To calculate the standard deviation and detection limit of this detection method, **USTC-7** with fine particles was made into a 0.125 mg/mL suspension. Then, PA solution (1-20 μL, 5 mM) was added into the suspension and the fluorescent intensities were recorded. Standard deviation (σ) was calculated from five blank tests of **USTC-7** suspension and the detection limit was calculated via the formula: 3σ/m (m: the slope of the linear region).

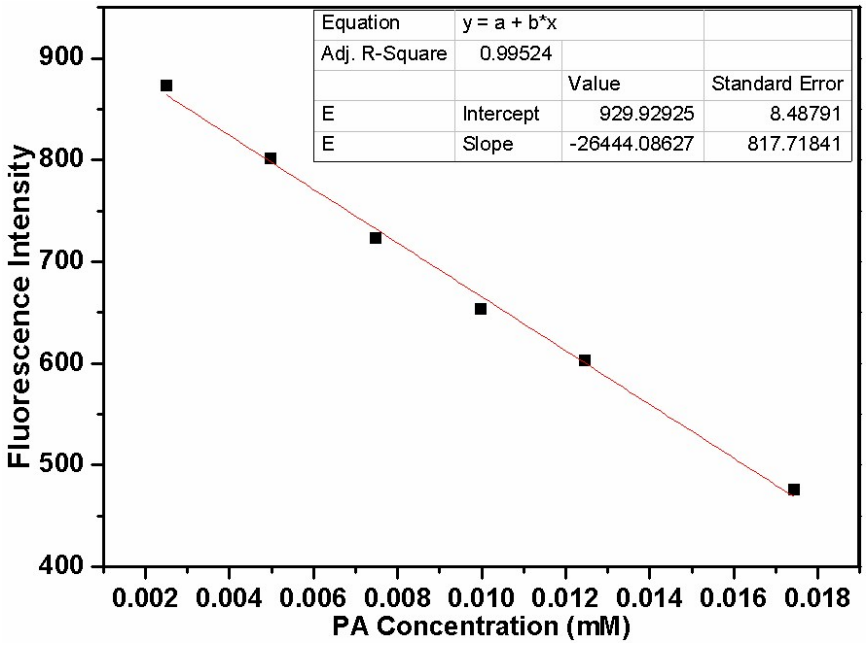


Fig. S13 Linear region of fluorescence intensity of **USTC-7** suspension (λ_{ex} = 370 nm) upon incremental addition of PA (5 mM) at λ_{em} = 432 nm.

Table S3. Standard deviation calculation.

	Fluorescence intensity
Test 1	958.55
Test 2	942.10
Test 3	953.23
Test 4	941.24
Test 5	948.87
Standard Deviation (σ)	7.36

Table S4. Detection limit calculation.

Slope (m)	26444.09 mM^{-1}
Detection limit (3σ/m)	0.000278 mM

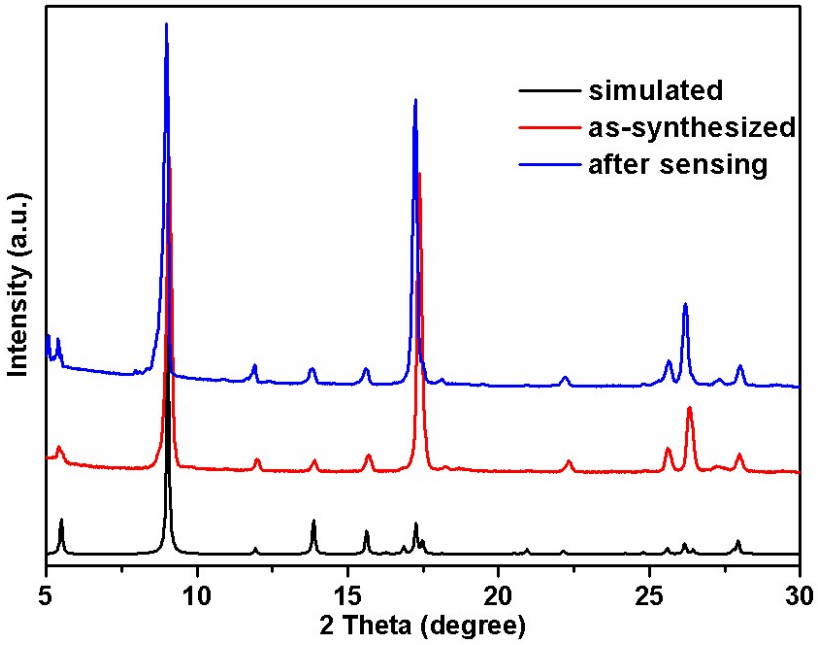


Fig. S14 Powder XRD profiles of **USTC-7** after fluorescence sensing.

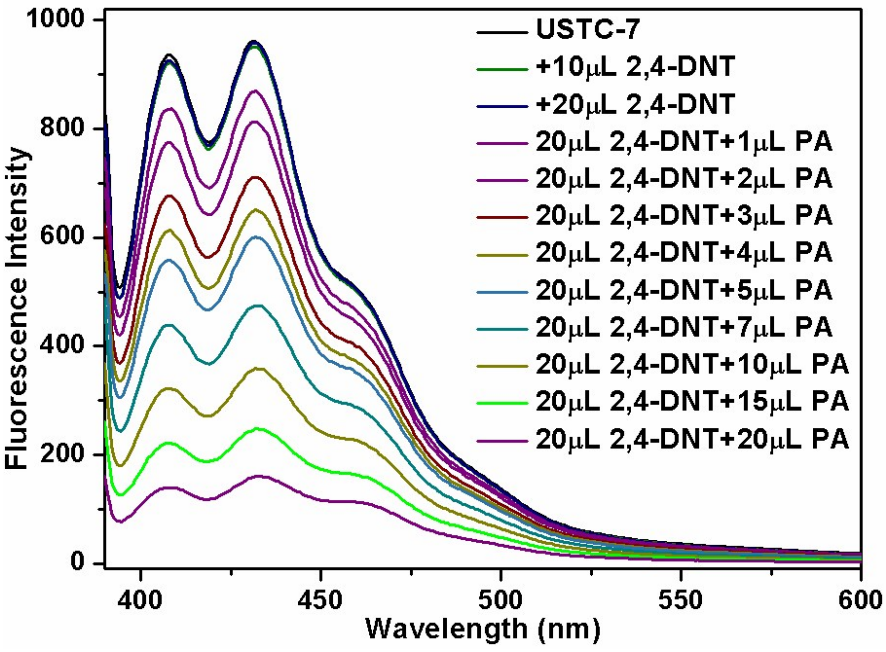


Fig. S15 Emission spectra of **USTC-7** suspension (λ_{ex} = 370 nm) upon the addition of 2,4-DNT followed by PA.

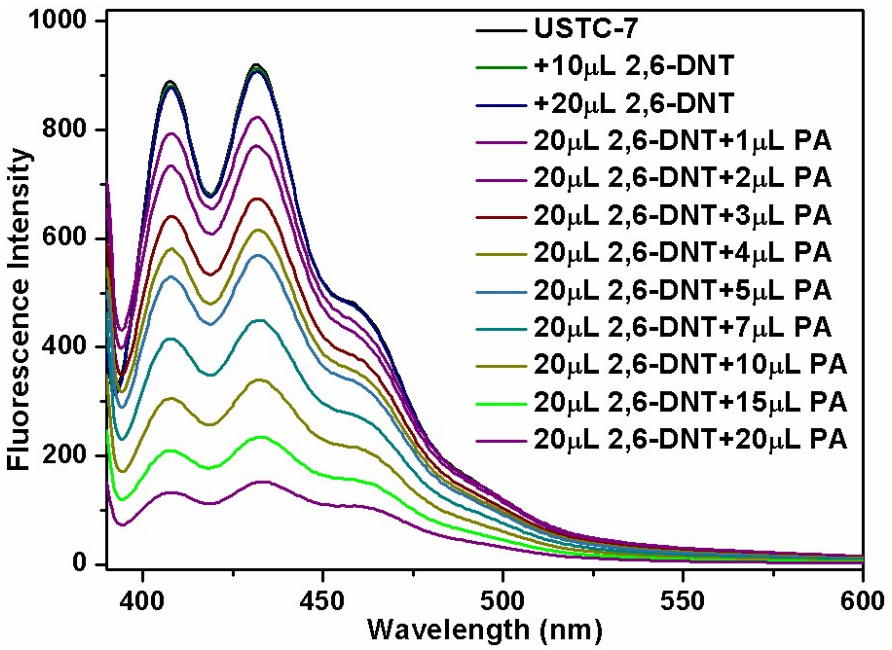


Fig. S16 Emission spectra of **USTC-7** suspension (λ_{ex} = 370 nm) upon the addition of 2,6-DNT followed by PA.

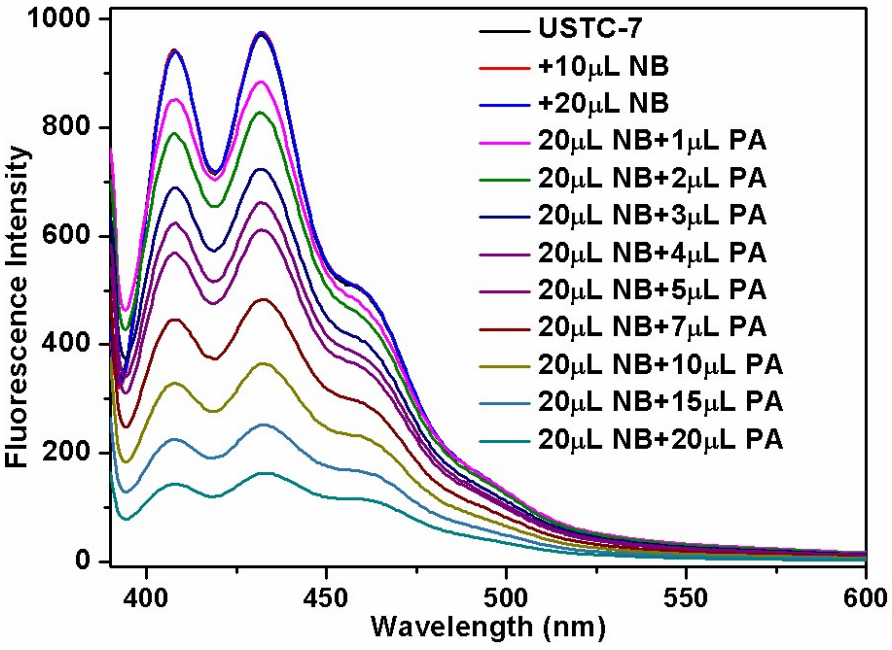


Fig. S17 Emission spectra of **USTC-7** suspension (λ_{ex} = 370 nm) upon the addition of NB followed by PA.

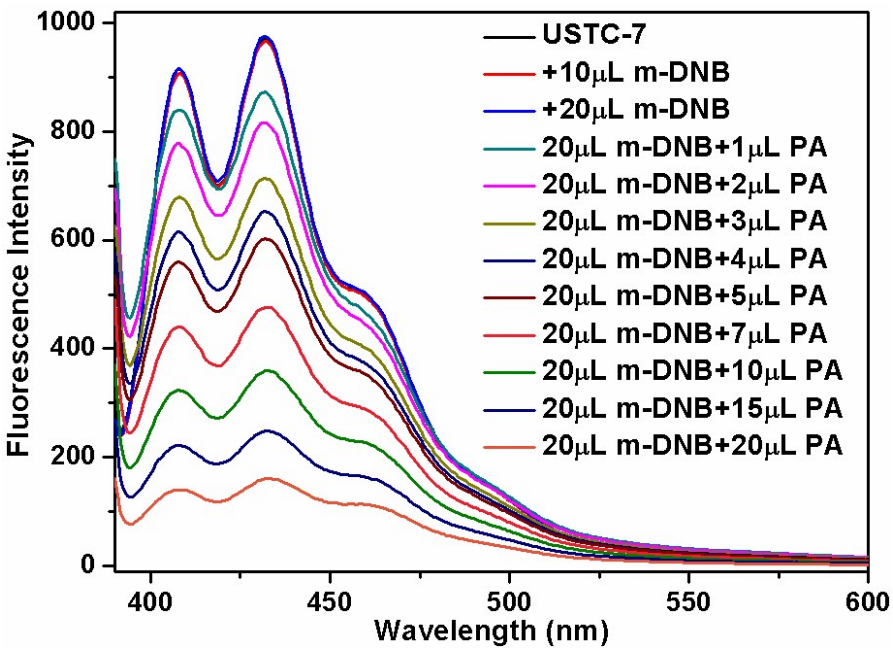


Fig. S18 Emission spectra of **USTC-7** suspension (λ_{ex} = 370 nm) upon the addition of m-DNB followed by PA.

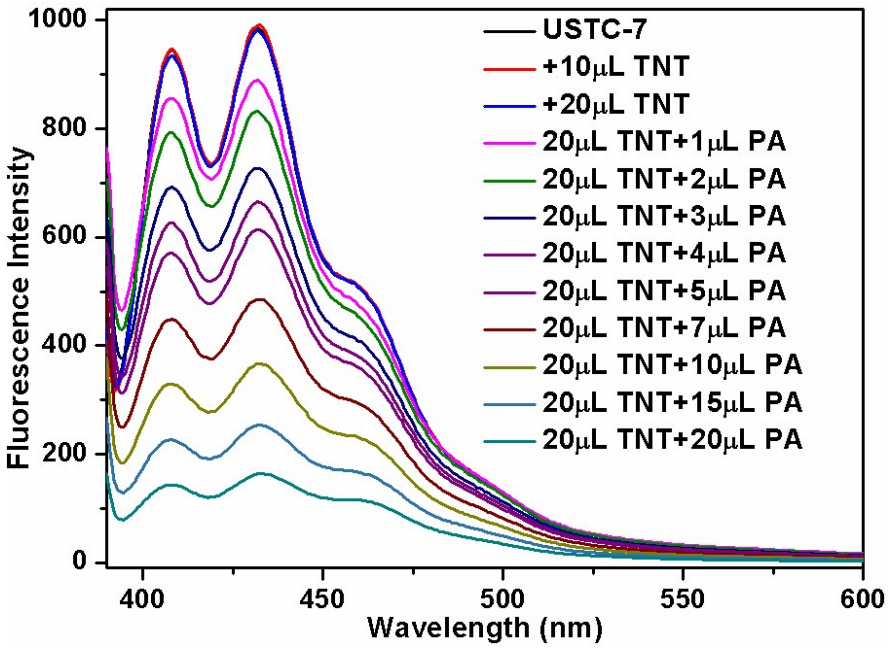


Fig. S19 Emission spectra of **USTC-7** suspension (λ_{ex} = 370 nm) upon the addition of TNT followed by PA.

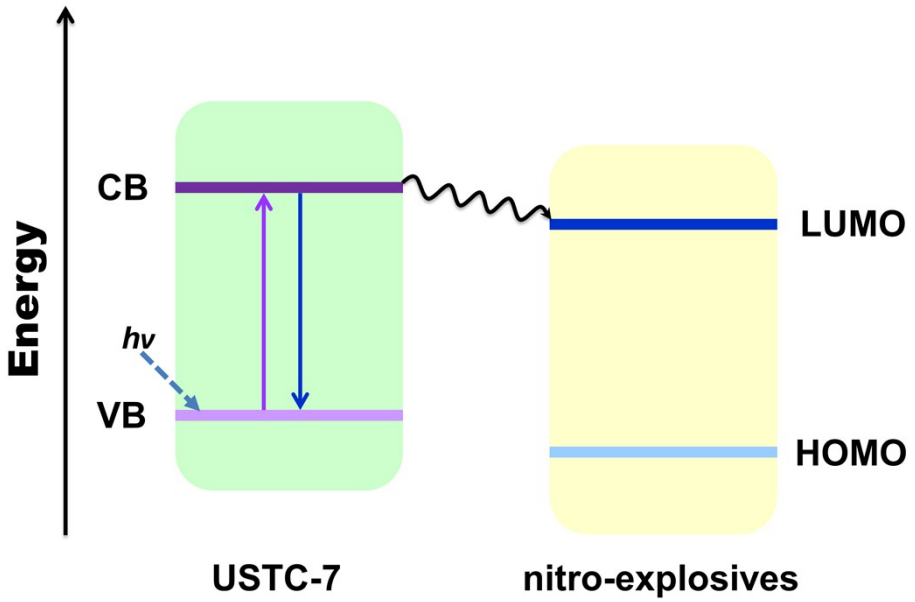


Fig. S20 Schematic illustration of the electron transfer process between **USTC-7** and nitro-explosives.

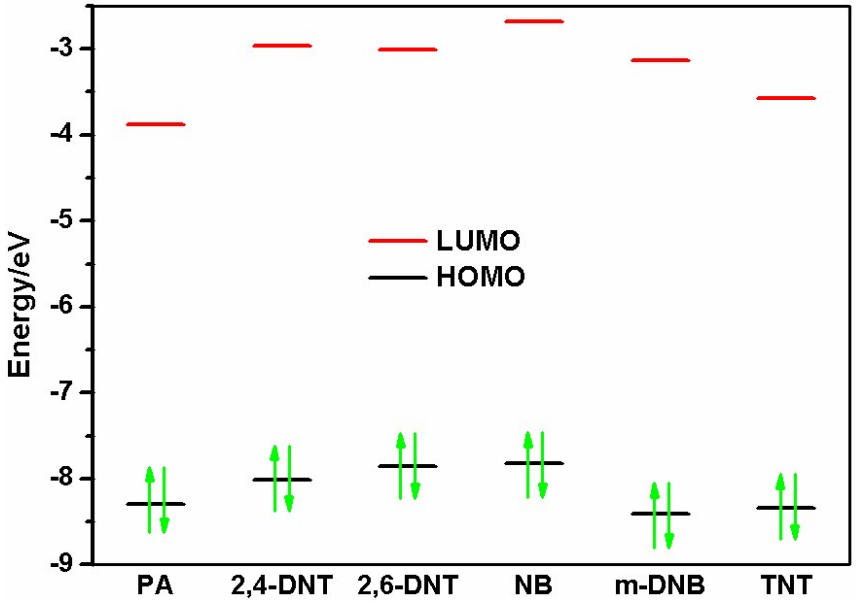


Fig. S21 HOMO and LUMO energies of the investigated nitro analytes. The data are based on the reported results.[3]

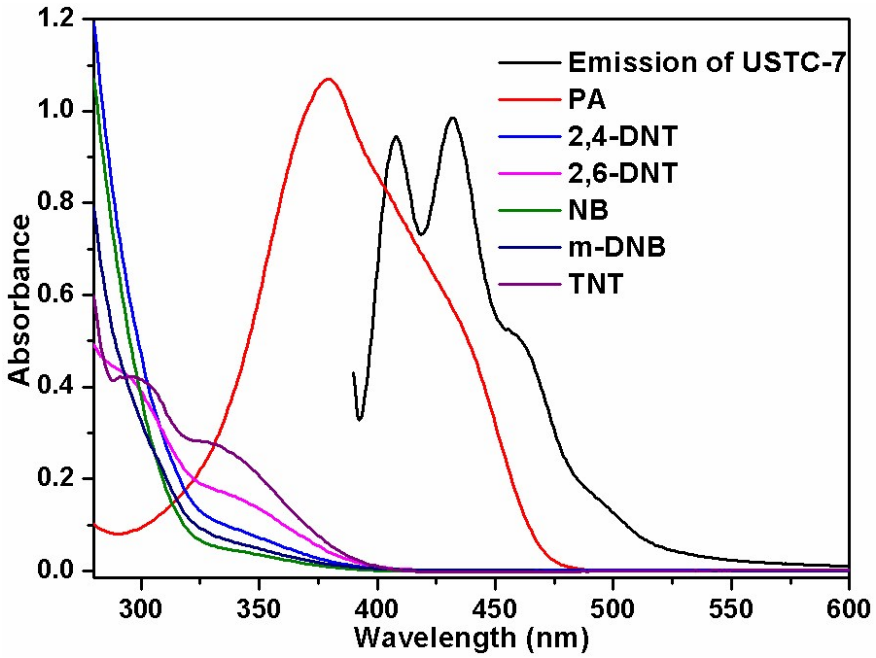


Fig. S22 Spectral overlap between the emission spectrum of **USTC-7** (λ_{ex} = 309 nm) and the absorption spectra of nitro analytes investigated.

Table S5. HOMO and LUMO energies of different nitro analytes. The data are based on the reported results.[3]

Analytes	**HOMO (eV)**	**LUMO (eV)**	**Band gap (eV)**
PA	-8.292	-3.875	4.417
2,4-DNT	-8.014	-2.961	5.053
2,6-DNT	-7.859	-3.012	4.847
NB	-7.820	-2.684	5.136
m-DNB	-8.412	-3.135	5.277
TNT	-8.335	-3.573	4.762

References

1 (a) G. M. Sheldrick, *SHELXS-97*, *Programs for X-ray Crystal Structure Solution*, University of Göttingen: Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXL-97*, *Programs for X-ray Crystal Structure Refinement*, University of Göttingen: Göttingen, Germany, 1997.

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3 (a) S. Mukherjee, A. V. Desai, B. Manna, A. I. Inamdar and S. K. Ghosh, *Cryst. Growth Des.*, 2015, **15**, 4627; (b) S. Sanda, S. Parshamoni, S. Biswas and S. Konar, *Chem. Commun.*, 2015, **51**, 6576.