Electronic Supplementary Material (ESI) for RSC Advances.

A metal–organic framework with a 9-phenylcarbazole moiety as a fluorescent tag for picric acid explosive detection: collaboration of electron transfer, hydrogen bonding and size matching

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Contents

1. Materials and Methods.

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. 9-Phenylcarbazole was purchased from Qingdao Frontierchem Co., Ltd., 4-Hydroxy-4'-nitrobiphenyl and 4-Aminophenol was purchased from J&K Scientific, Picric Acid and the other nitroaromatics were provided from Xiya Reagent Company (China).

The elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer. Mass spectra were carried out on a Bruker micro TOF mass spectrometer.

^{1}HNMR spectra were measured on a Bruker-400 spectrometer with Me_4Si as an internal standard.

X-Ray powder diffraction (XRD) patterns of the Zn−**PDA** was recorded on a Rigaku D/max-2400 X−ray powder diffractometer (Japan) using Cu Ka (l =1.5405 Å) radiation.

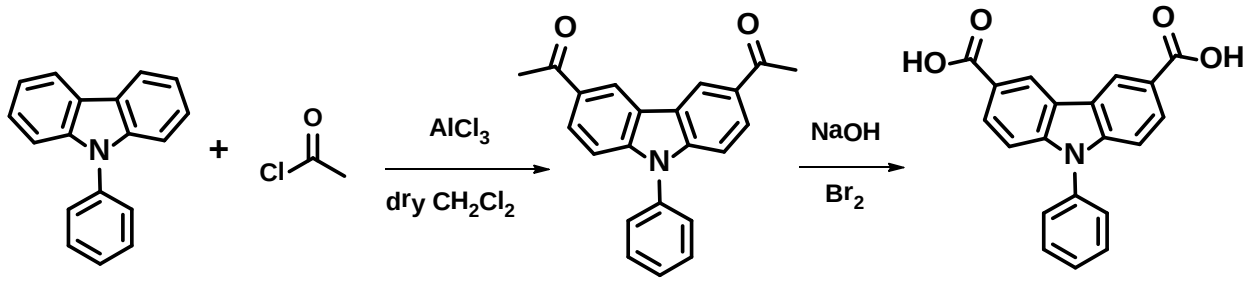
Thermogravimetric analysis (TGA) was carried out at a ramp rate of 5 °C/min in a nitrogen flow with a Mettler-Toledo TGA/SDTA851 instrument.

FT-IR spectra were recorded as KBr pellets on Bruker Optics TENSOR 27 FT-IR spectrophotometer.

The solution fluorescent spectra were measured on Hitachi F-4500. Both excitation and emission slit widths were 2.5 nm. The Zn−**PDA** emulsion was prepared by introducing 1 mg of Zn−**PDA** powder into 3.00 mL of ethanol, the intensity was recorded at 366 nm, excitation at 342 nm. For nitro-aromatic molecular detection, the high concentration stock solutions of related nitro-analysts (2.0×10^{-2} M) were prepared directly in ethanol solvents.

2. Syntheses and Reactions.

2.1 Synthesis of the H_2PDA ligand.



(a) Synthesis of 3,6-diacetyl 9-phenylcarbazole.

To the solution of 9-phenylcarbazole (2.0 g, 8.2 mmol) and 2.4 g (18.0 mmol) $AlCl_3$ in 100 mL dry CH_2Cl_2, 2.7 mL (28.28 mmol) acetyl chloride in 30 mL dry CH_2Cl_2 was added dropwisely. Then the reaction was carried out at room temperature for 12 hours and 100 mL water was added. The aqueous layer was further extracted with CH_2Cl_2 (3 × 150 mL); the combined organic layers were dried by Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was purified by flash column chromatography on silica gel (1: 10 hexanes–CH_2Cl_2) to afford a yellow solid (1.46 g, 54.3 %). ^{1}H NMR ($CDCl_3$, *ppm*): δ 9.16 (s, $2H_{Ar}$), 8.08 (d, J = 8.0 Hz, $2H_{Ar}$), 7.73 (d, J = 8.0 Hz, $2H_{Ar}$), 7.67-7.61 (m, $3H_{Ar}$), 7.42 (d, J = 8.0 Hz, $2H_{Ar}$), 2.72 (s, $6H_{\text{-}COCH_3}$).

(b) Synthesis of 9-phenylcarbazole-3,6-dicarboxylic acid.[S1]

3 mL Br_2 were added dropwisely to the solution of NaOH (7 g, 0.18 mol) in 30 mL water on ice-bath, and further stirred for 20 min. The solution were dumpage to a isobarically funnel and were added dropwisely to a solution of 3,6-diacetyl 9-phenylcarbazole (1.2 g, 3.6 mmol) in 30 mL 1,4-Dioxane on 45 ºC during 5 h. Then the mixture was put on ice-bath, saturated

hydroxylamine HCl was added to deoxidize excessive sub-bromo-sodium. The solution was acidified by muriatic acid and the solid product was filtered and dried under vacuum. The crude was recrystallized from acetic acid to afford pure products as a white solid. (1.0 g, 84.5 %). ^{1}H NMR (DMSO-*d*$_6$, *ppm*): δ 12.84 (s, 2H$_{COOH}$), 9.0 (s, 2H$_{Ar}$), 8.10 (d, *J* = 8.0 Hz, 2H$_{Ar}$), 7.76-7.63 (m, 5H$_{Ar}$), 7.44 (d, *J* = 8.0 Hz, 2H$_{Ar}$). ^{13}C NMR (DMSO-*d*$_6$, *ppm*): δ 167.7 (C$_{COOH}$), 143.5 (C$_{Ar}$), 135.9 (C$_{Ar}$), 130.5 (C$_{Ar}$), 128.7 (C$_{Ar}$), 128.3 (C$_{Ar}$), 127.1 (C$_{Ar}$), 123.6 (C$_{Ar}$), 123.0 (C$_{Ar}$), 122.5 (C$_{Ar}$), 109.9 (C$_{Ar}$). Anal calc. for $C_{20}H_{13}NO_4$: C 72.50, H 3.95, N 4.23 %; Found: C 72.52, H 3.94, N 4.22 %. TOF MS calcd for $C_{20}H_{13}NO_4$ 331.32, found 331.41.

2.2 Synthesis of Zn−PDA.

A mixture of 9-phenylcarbazole-3,6-dicarboxylic acid (H_2**PDA**) (40 mg, 62.5 mM) and $Zn(NO_3)_2 \cdot 6H_2O$ (75 mg,125 mM) were dissolved in dimethylformamide/methanol (9/1, 10 mL) in a screw capped vial. The resulting mixture was placed in an oven at 100 ºC for 3 days. Colorless crystals with block-shape were obtained after filtration. Yield: 75 %. Anal calc. for $C_{21}H_{11}NO_8Zn$: C 53.58, H 2.36, N 2.98%; Found: C 53.6, H 2.39, N 2.96%.

3. X-ray Crystallography (Single-crystal diffraction) and Characterizations.

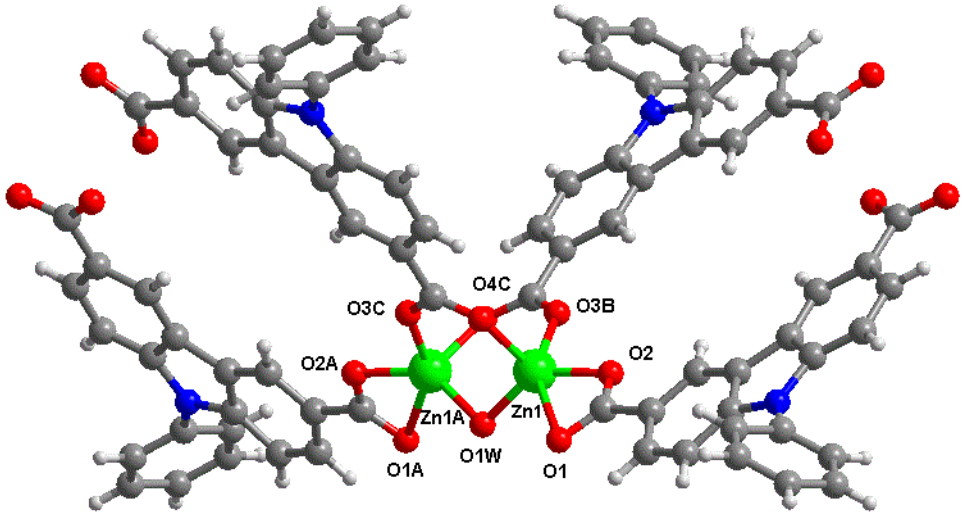
3.1 Crystal data of Zn−PDA:

$C_{21}H_{11}NO_8Zn$, M = 470.68, Monoclinic, space group *C*2/*c*, a = 25.951(3), b = 11.8662(14), c = 20.436(4) Å, α = 90.00, β = 125.847(6), γ = 90.00, V = 5101.1(13) $Å^3$, Z = 8, *D*c = 1.226 g cm^{-3}, μ(Mo-Kα) = 0.71073 mm^{-1}, *T* = 296(2) K. 4481 unique reflections [R_{int} = 0.0773]. Final R_1[with $I > 2\sigma(I)$] = 0.0758, wR_2(all data) = 0.2699, GOOF = 1.002. CCDC number: 1009908.

3.2 Crystallography:

Intensities were collected on a Bruker SMART APEX CCD diffractometer with graphitemonochromated Mo-Kα (λ = 0.71073 Å) using the SMART and SAINT programs. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL *version* 5.1. Non-hydrogen atoms of the ligand backbones were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at calculated positions and allowed to ride on the parent non-hydrogen atoms.

3.3 Figure S1 The coordination configuration of the Zn(1) centre in Zn−**PDA**. The asymmetric mode: A, 1-x, y, -1.5-z; B, 1.5 –x, 1.5-y, z; C, -0.5+x, 1.5-y, -0.5-z.

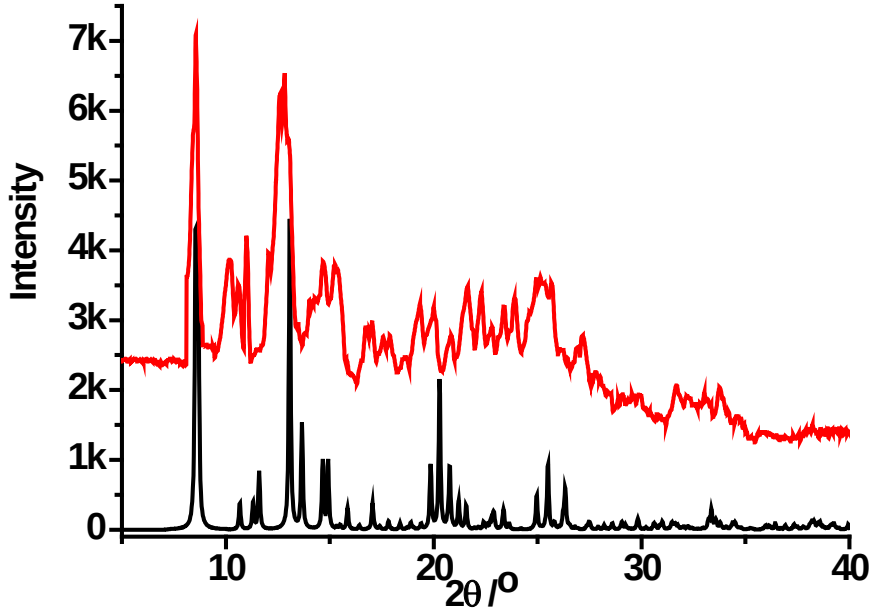


3.4 Selective bond distance (Å) and angle (°) in Zn−**PDA**.

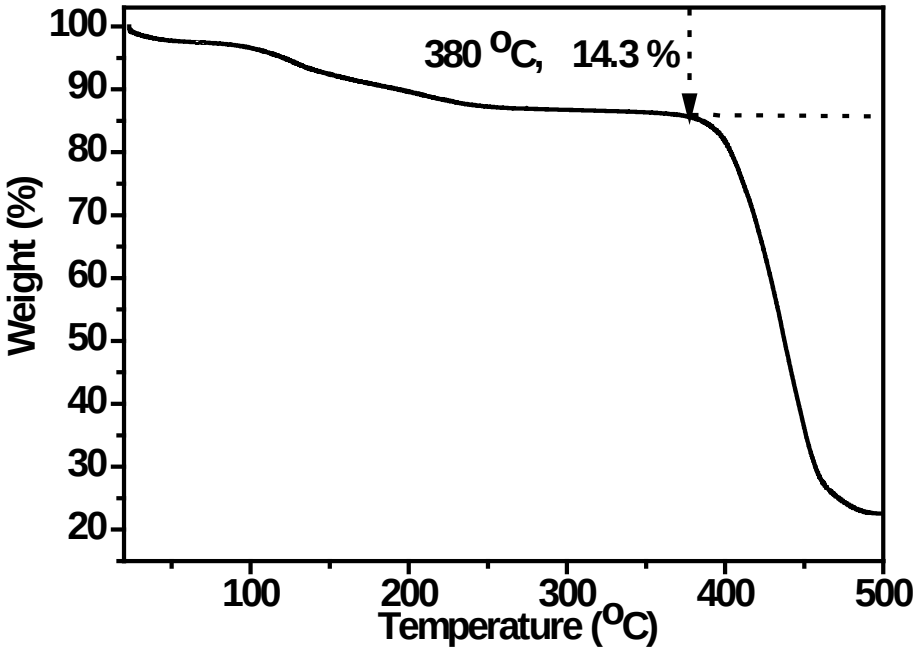
Selective bond distance (Å): Zn(1)−O(1W) 1.929(4), Zn(1)−O(2) 1.937(5), Zn(1)−O(3B) 1.994(4), Zn(1)−O(4C) 2.031(4).

Selective bond angle (°): O(1W)−Zn(1)−O(2) 138.5(2), O(1W)−Zn(1)−O(3B) 102.94(18), O(2)−Zn(1)−O(3B) 97.81(19), O(1W)−Zn(1)−O(4C) 104.63(16), O(2)−Zn(1)−O(4C) 106.95(19), O(3B)−Zn(1)−O(4C) 99.2(2).

3.5 Figure S2 PXRD patterns of the as-synthesized (red), the simulated from single X-ray crystal structure (black).

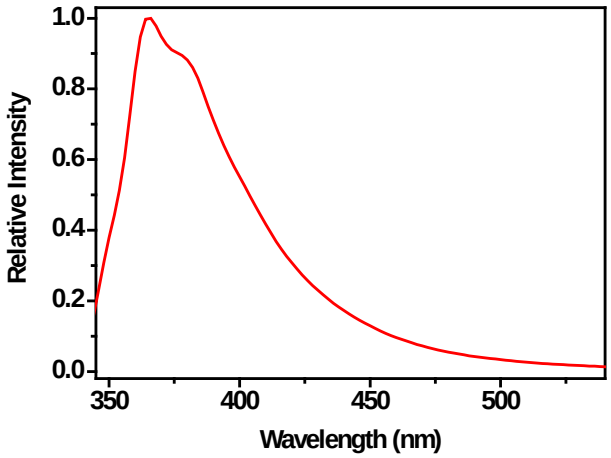


3.6 Figure S3 TGA traces of Zn−**PDA** ranging from room temperature to 500 °C

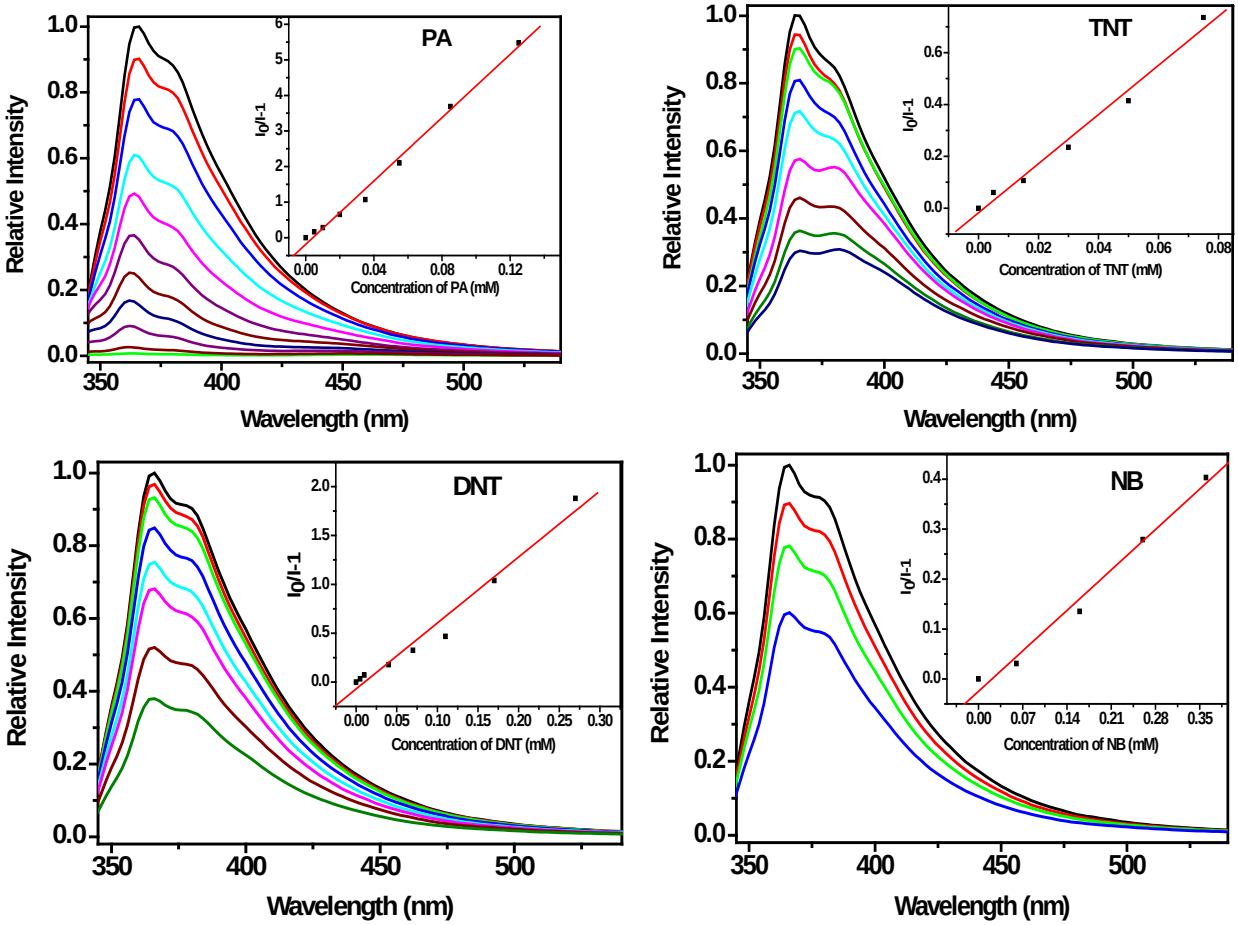


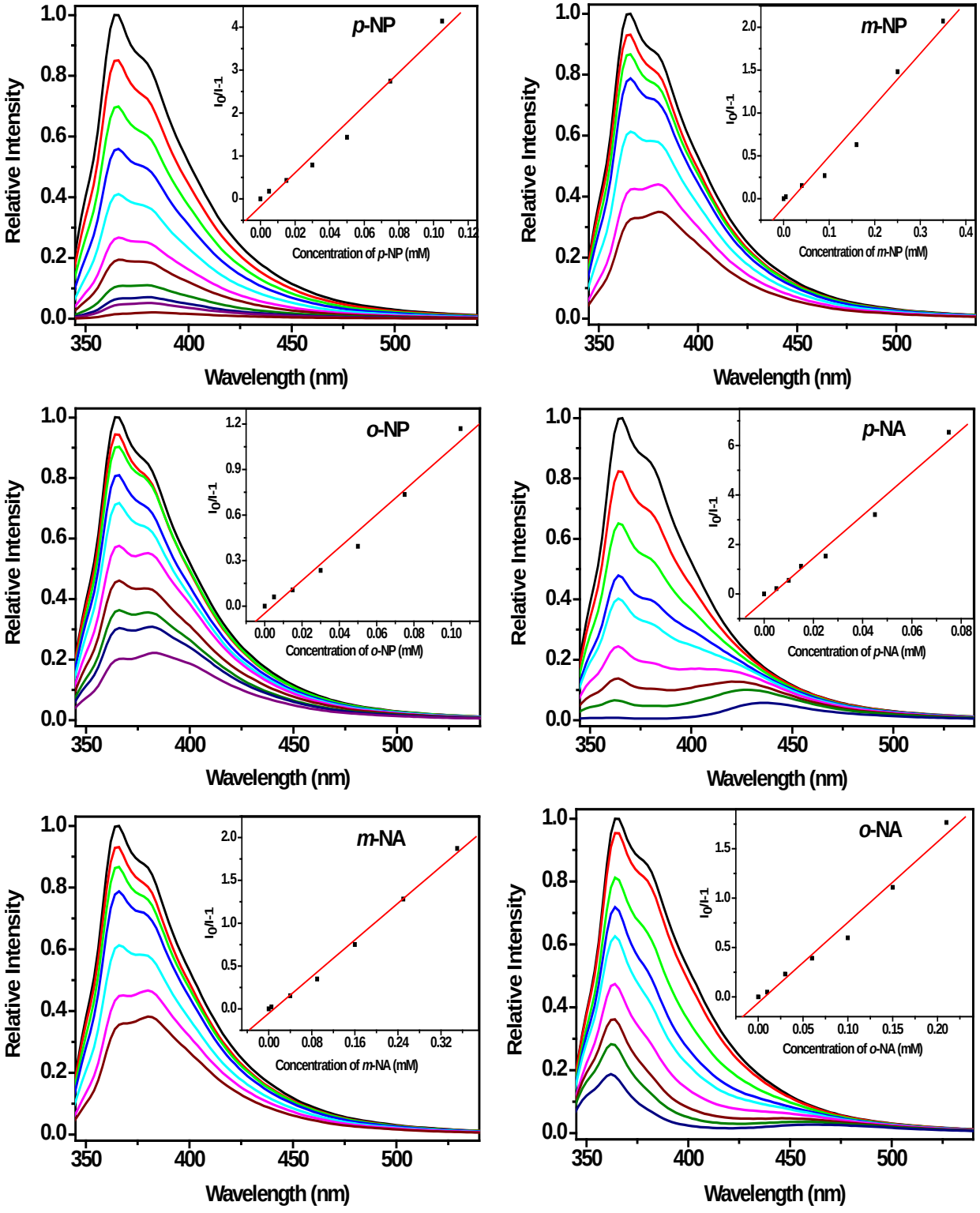
4. Studies on the nitro-explosives detection based on Zn−PDA.

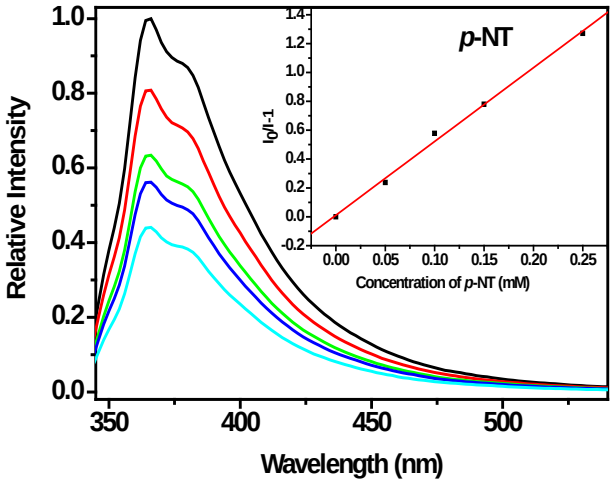
4.1 FigureS4 The PL spectra of 250 *ppm* Zn−**PDA** in ethanol solvent when excited at 342 nm.

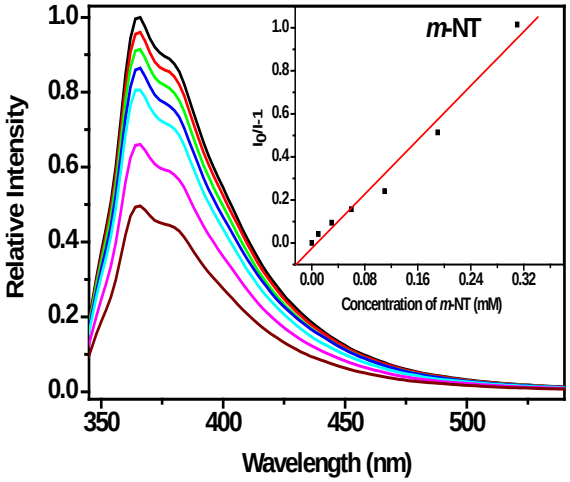


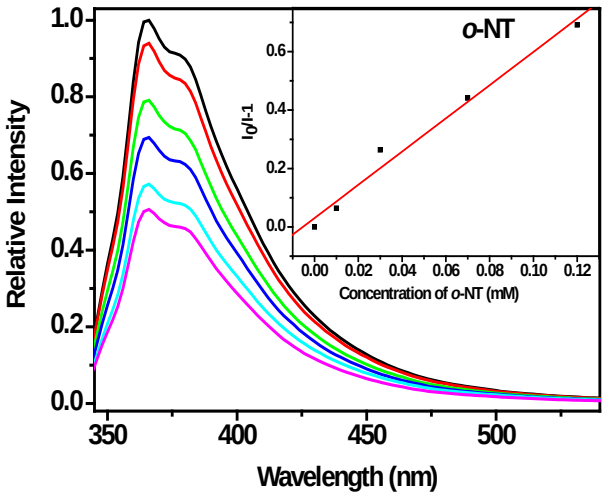
4.2 Figure S5 Families of various fluorescence spectra of 250 *ppm* Zn−**PDA** in ethanol solution upon the addition of 0.35 mM of different selected analytes.

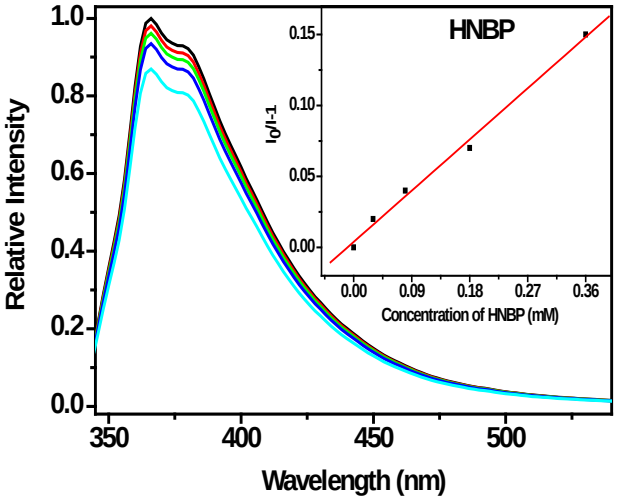


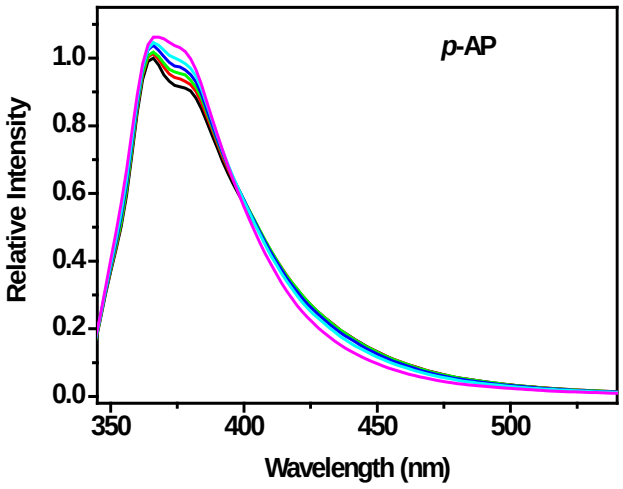

p-NP
Relative Intensity
Wavelength (nm)
I0/I-1
Concentration of p-NP (mM)
m-NP
Concentration of m-NP (mM)
o-NP
Concentration of o-NP (mM)
p-NA
Concentration of p-NA (mM)
m-NA
Concentration of m-NA (mM)
o-NA
Concentration of o-NA (mM)


p-NT
Relative Intensity
Wavelength (nm)
I0/I-1
Concentration of p-NT (mM)

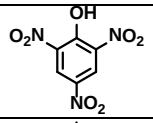
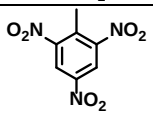
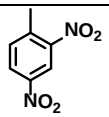
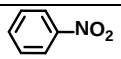
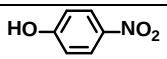
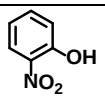
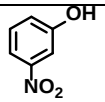
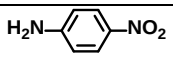
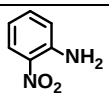
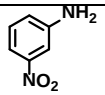
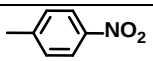
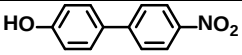
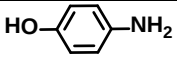

m-NT
Relative Intensity
Wavelength (nm)
I0/I-1
Concentration of m-NT (mM)


o-NT
Relative Intensity
Wavelength (nm)
I0/I-1
Concentration of o-NT (mM)

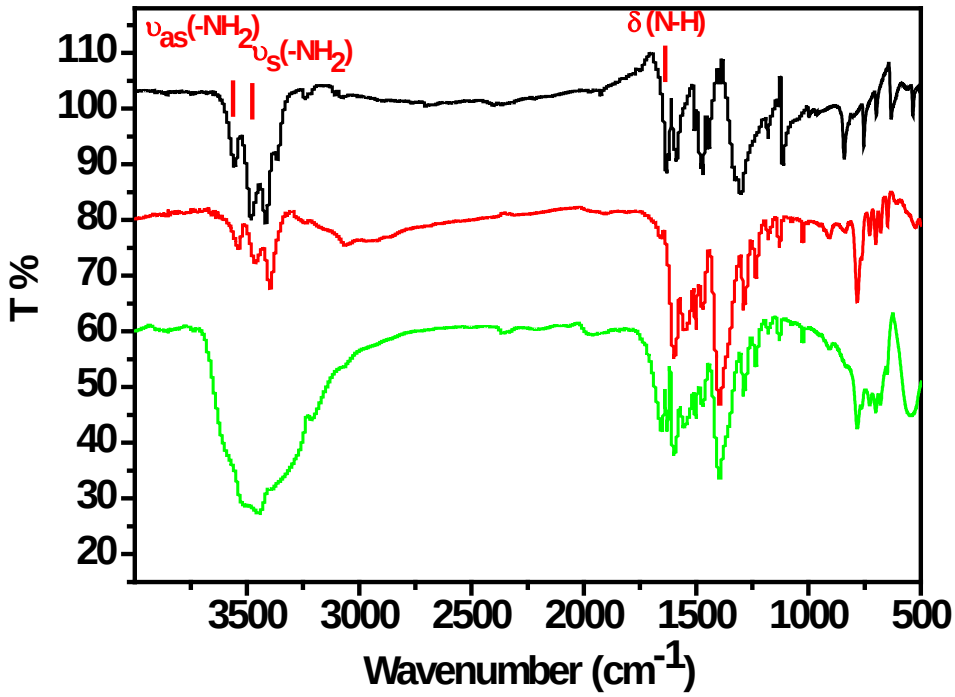

HNBP
Relative Intensity
Wavelength (nm)
I0/I-1
Concentration of HNBP (mM)


p-AP
Relative Intensity
Wavelength (nm)

4.3 Table S1 Summary of linear correlation coefficients (R), quenching constants (K_{sv}) for the Zn−**PDA** for the sensing of various nitroaromatics at room temperature.

Analysts	Molecular structure	R	K_{sv} (M^{-1})
Picric Acid (**PA**)		0.997	44501.8
2,4,6-Trinitrotoluene (**TNT**)		0.992	9482.7
2,4-dinitrotoluene (**DNT**)		0.992	6753.2
Nitrobenzene (**NB**)		0.993	1157.4
p-Nitrophenol (*p*-**NP**)		0.991	38973.8
o-Nitrophenol (*o*-**NP**)		0.991	10830.2
m-Nitrophenol (*m*-**NP**)		0.991	5997.6
p-Nitroaniline (*p*-**NA**)		0.992	43424.2
o-Nitroaniline (*o*-**NA**)		0.990	8141.2
m-Nitroaniline (*m*-**NA**)		0.996	5622.2
p-Nitrotoluene (*p*-**NT**)		0.998	5107.2
o-Nitrotoluene (*o*-**NT**)		0.990	5684.9
m-Nitrotoluene (*m*-**NT**)		0.990	3149.5
4-Hydroxy-4'-nitrobiphenyl (**HNBP**)		0.997	400.9
p-Aminophenol (*p*-**AP**)		-	-

4.4 Figure S6 FT-IR spectra of *p*-NA (top), Zn−**PDA** obtained after the absorption of *p*-NA (middle) and Zn−**PDA** (bottom).



Compounds	$\upsilon_{as}(-NH_2)$ (cm^{-1})[S2]	$\upsilon_{s}(-NH_2)$ (cm^{-1})	δ(N−H) (cm^{-1})
p-NA	3558.1	3481.2	1634.8
Zn−**PDA**⊃*p*-NA	3534.5	3468.4	1596.1

5. References.

S1. J.Wang, C. He, P. Y. Wu, J. Wang, C. Y. Duan, *J. Am. Chem. Soc*., 2011, **133**, 12402.

S2. U. Okwieka, K. H. Natkaniec, T. Misiaszek, W. Medycki, J. Baran and M. M. Szostak, *J. Chem. Phys.*, 2009, **131**, 144505.