Electronic Supplementary Material (ESI) for RSC Advances.

A stable 3D Cd(II) metal-organic framework for highly sensitive detection of Cu^{2+} ions and nitroaromatic explosives

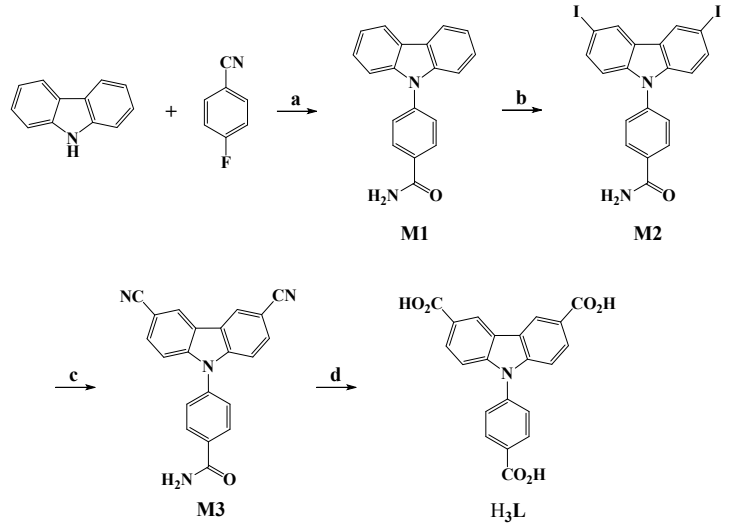
Jian-Long Du,*[a,b] Ju-Ping Gao,[a,b] Chao-Ping Li,[a,b] Xiao-Ying Zhang,[a,b] Jin-Xin Hou,[a,b] Xu Jing,*[a,d] Ya-Juan Mu,[c] and Li-Jun Li[a,b]

[a]*College of Chemistry & Environmental Science, and Chemical Biology Key Laboratory of Hebei Province, Hebei University, Baoding 071002, P. R. China*

[b]*Key laboratory of Medicinal Chemistry and Molecular Diagnosis of Ministry of Education, Hebei University, Baoding 071002, P. R. China*

[c]*College of Traditional Chinese Medicine, Hebei University, Baoding 071000, P. R. China*

[d]*State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, P. R.China*



Scheme S1. Syhthesis of H_3**L**. Reagents and conditions: (a) K_2CO_3, DMSO, 140 ˚C; (b) KI, KIO_3, HOAc, 85 ˚C; (c) CuCN, DMF, N_2, 140 ˚C; (d) 6 M KOH, reflux.

Synthesis of ligand H_3**L**

M1. Carbazole (12.08 g, 72 mmol) and K_2CO_3 (32.88 g, 238 mmol) and DMSO (120 mL) was stirred at room temperature for 2 h, then 4-fluorobenzonitrile (10.44 g, 86 mmol) was added and the suspension was heated to 140 ˚C until consumed raw material completely. The reaction mixture was poured into an ice-water mixture, and the crude product was obtained, which was recrystallized with ethyl acetate to generate 16.86 g of pure product, yield 87%. M.p.: 189.8-192.5 ˚C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ 8.27 (d, J = 7.8 Hz, 2H), 8.18 (d, J = 8.4 Hz, 2H), 8.16 (s, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.52 (s, 1H), 7.46 (d, J = 5.4 Hz, 4H), 7.33-7.30 (m, 2H); IR (KBr): 3196 w, 2919 m, 2850 w, 1647 s, 1518 m, 1479 w, 1452 s, 1417 w, 1398 m, 1363 w, 1334 w, 1317 w, 1228 m, 745 s, 724 m.

M2. M1 (8.55 g, 29 mmol) and glacial acetic acid (80 mL) were heated to 85 ˚C until the solid dissolved completely. Then KI (6.45 g, 39 mmol) was added, after 20 minutes, KIO_3 (9.46 g, 44 mmol) was added four times. After the reaction was complete, 5% $NaHSO_3$ (100 mL) was added. The product (12.91 g) was obtained by filtration, yield 80%. M.p.: >230 ˚C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ 8.74 (d, J = 1.2 Hz, 2H), 8.16 (S, 1H), 8.16(S, 2H), 7.74 (dd, J = 8.4, 1.2 Hz, 2H),

7.71 (d, *J* = 8.4 Hz, 2H), 7.52 (s, 1H), 7.27 (d, *J* = 8.4 Hz, 2H); IR (KBr): 3164 w, 1668 m, 1515 m, 1465 s, 1428 w, 1401 w, 1380 w, 1361 w, 1278 m, 1227 m, 793 m.

M3. M2 (6.01 g, 11 mmol), CuCN (4.05 g, 45 mmol), DMF (100 mL) were heated to 140 ˚C in an inert atmosphere of N_2. After cooled to room temperature, Ethylenediamine (40 mL) and H_2O (100 mL) were added and stirred at 80 ˚C for 30 min. After that the crude produced was obtained, by filtration and recrystallized (DMF / H_2O = 1 / 1) to get 1.78 g of pure product, yield 48%. M.p.: >252 ˚C. ^{1}H NMR (DMSO-d6, 600 MHz): δ 8.97 (s, 2H), 8.21 (s, 1H), 8.20 (s, 2H), 7.93 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 3H); IR (KBr): 2920 w, 2224 s, 1663 s, 1598 w, 1516 m, 1481 m, 1457 w, 1416 w, 1399 w, 1364 w, 1237 m.

H_3**L**. M3 (3.38 g, 10 mmol) was suspended in EtOH (25 mL), 6 M KOH (25 mL) aqueous solution and the intermixture was refluxed for 12 hours. After that the EtOH was removed, dilute HCl was added to ajust the pH to 1. The solid was dried, H_3**L** was obtained 3.60 g, yield 96%. M.p.: >250 ˚C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ 8.98 (s, 2H), 8.26 (d, *J* = 8.4 Hz, 2H), 8.11 (dd, *J* = 9 Hz, 2H), 7.85 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H); IR (KBr): 2922 w, 2360 m, 1685 s, 1632 w, 1514 s, 1414 s, 1355 m, 1346 m, 1293 w, 1258 s, 1169 m, 768 s. Anal. calcd. for $C_{21}H_{13}NO_6$: C, 67.20; H, 3.49; N, 3.73; Found: C, 67.25; H, 3.38; N, 3.65%.

Table S1. Crystal data and structure refinement parameters for **1**

	1
Empirical Formula	$C_{42}H_{20}Cd_3N_2O_{17}$
Formula weight	1161.80
Crystal system	Orthorhombic
Space group	*P*bam
a (Å)	17.038(2)
b (Å)	20.632(3)
c (Å)	29.069(4)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	10218(2)
Z	8
*D*calc (g cm^{-3})	1.510
μ (mm^{-1})	1.302
F(000)	4528
R_1 [a] / wR_2 [b]	0.0611 / 0.1918
GOF on F^2	1.026

[a] $R_1 = \Sigma(||F_0|-|F_C||)/\Sigma|F_0|$, [b] $wR_2 = [\Sigma w(|F_0|^2-|F_C|^2)^2/\Sigma w(F_0^2)]^{1/2}$.

Table S2. Selected bond length (Å) and angles (˚) for **1**.

Cd(1)-O(1W)	2.261(8)	Cd(1)-O(10)	2.324(5)
Cd(1)-O(3)$^{\#1}$	2.354(5)	Cd(1)-O(4)	2.422(5)
Cd(2)-O(2W)	2.292(10)	Cd(2)-O(3W)	2.272(11)
Cd(2)-O(10)$^{\#1}$	2.384(5)	Cd(2)-O(9)$^{\#1}$	2.393(5)
Cd(3)-O(8W)	2.455(7)	Cd(3)-O(9W)	2.296(6)
Cd(3)-O(12)	2.326(5)	Cd(3)-O(6)#2	2.322(6)
Cd(3)-O(12)$^{\#3}$	2.365(5)	Cd(3)-O(5)#2	2.365(7)
Cd(4)-O(7)$^{\#4}$	2.490(6)	Cd(4)-O(1)#5	2.444(14)
Cd(4)-O(8)$^{\#4}$	2.228(6)	Cd(5)-O(7W)$^{\#4}$	2.394(8)
Cd(5)-O(1)	2.398(12)		
O(10)-Cd(1)-O(10)$^{\#1}$	71.5(2)	O(1W)-Cd(1)-O(3)$^{\#1}$	134.61(16)
O(10)-Cd(1)-O(3)$^{\#1}$	127.3(2)	O(10)$^{\#1}$-Cd(1)-O(3)$^{\#1}$	78.5(2)
O(10)-Cd(1)-O(4)$^{\#1}$	170.15(19)	O(10)$^{\#1}$-Cd(1)-O(4)$^{\#1}$	100.18(17)
O(3)-Cd(1)-O(4)$^{\#1}$	111.1(2)	O(2W)-Cd(2)-O(4W)	88.3(5)
O(2W)-Cd(2)-O(3W)	174.4(4)	O(2W)-Cd(2)-O(10)$^{\#1}$	83.7(3)
O(3W)-Cd(2)-O(10)$^{\#1}$	100.9(3)	O(4W)-Cd(2)-O(10)	144.02(15)
O(8W)-Cd(3)-O(9W)	78.9(3)	O(9W)-Cd(3)-O(12)	87.5(2)
O(9W)-Cd(3)-O(6)$^{\#2}$	90.1(2)	O(8W)-Cd(3)-O(12)$^{\#3}$	73.6(2)
O(9W)-Cd(3)-O(12)$^{\#3}$	148.7(2)	O(8W)-Cd(3)-O(5)$^{\#2}$	141.0(3)
O(12)-Cd(3)-O(5)$^{\#2}$	128.5(2)	O(6)$^{\#2}$-Cd(3)-O(5)$^{\#2}$	55.9(2)
O(7)-Cd(4)-O(7)$^{\#4}$	79.5(2)	O(7)$^{\#4}$-Cd(4)-O(1)$^{\#5}$	131.2(4)
O(7)$^{\#4}$-Cd(4)-O(1)$^{\#6}$	85.7(3)	O(1)$^{\#5}$-Cd(4)-O(1)$^{\#6}$	70.2(5)
O(7)-Cd(4)-O(8)$^{\#4}$	115.0(2)	O(1)$^{\#6}$-Cd(4)-O(8)$^{\#4}$	92.5(3)
O(1)-Cd(5)-O(7W)	130.3(4)	O(7W)$^{\#4}$-Cd(5)-O(7W)	89.1(5)

Symmetry codes for **1**: #1 x, y, -z+1; #2 -x+5/2, y+1/2, z; #3 -x+2, -y+1, z; #4 x, y, -z; #5 x-1/2, -y+1/2, z; #6 x-1/2, -y+1/2, -z; #7 x+1/2, -y+1/2, z; #8 –x+5/2, y-1/2, z.

Table S3. HUMO and LUMO for calculated H_3**L** ligand and NACs at B3LYP/6-31G* level of theory [1].

	H_3**L**	***p*-NP**	**4-NT**	***m*-NP**	**NB**	**2,4-DNT**	**TNP**
LUMO / eV	-2.162	-2.222	-2.318	-2.397	-2.428	-2.987	-3.899
HUMO / eV	-6.416	-6.920	-7.362	-6.778	-7.591	-8.166	-8.237
Bond gap	4.254	4.698	5.044	4.381	5.163	5.179	4.338

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford CT, **2009**.

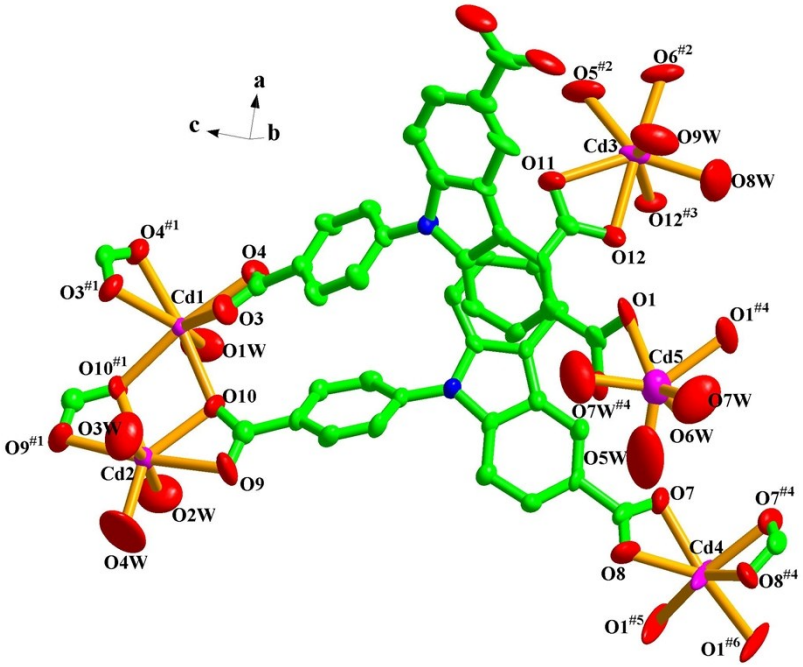


Fig. S1 ORTEP-style structure of **1**

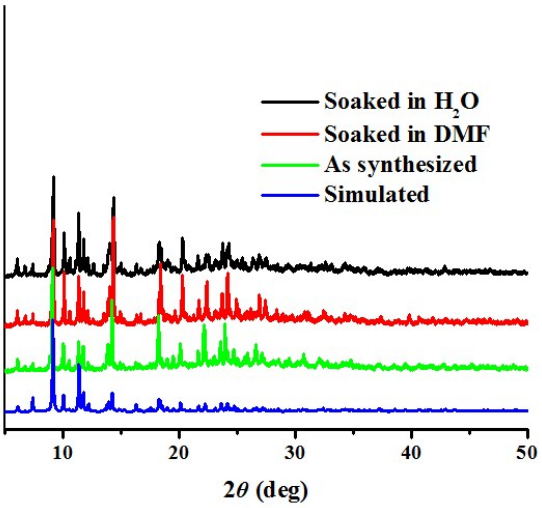


Fig. S2 PXRD of **1**

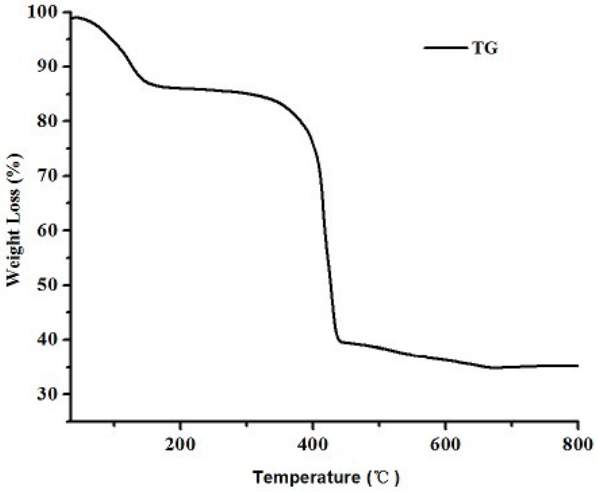


Fig. S3 TGA curves of **1**

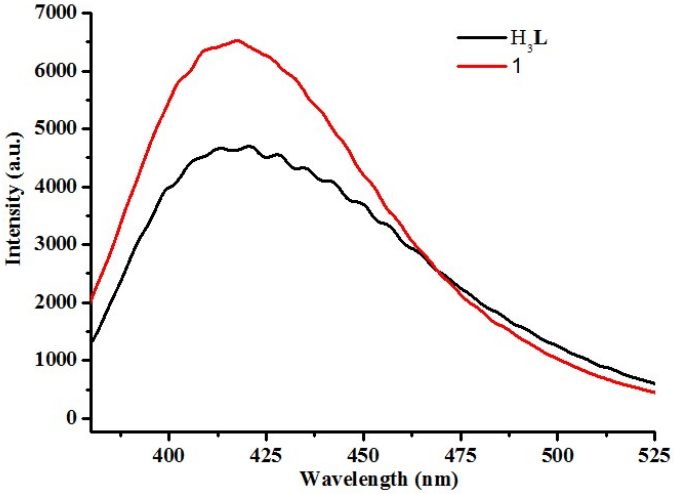
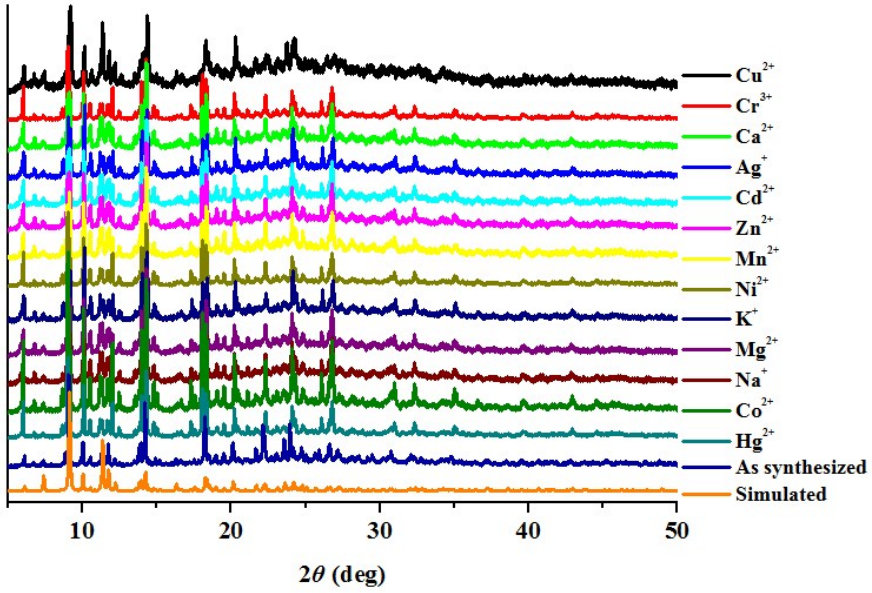
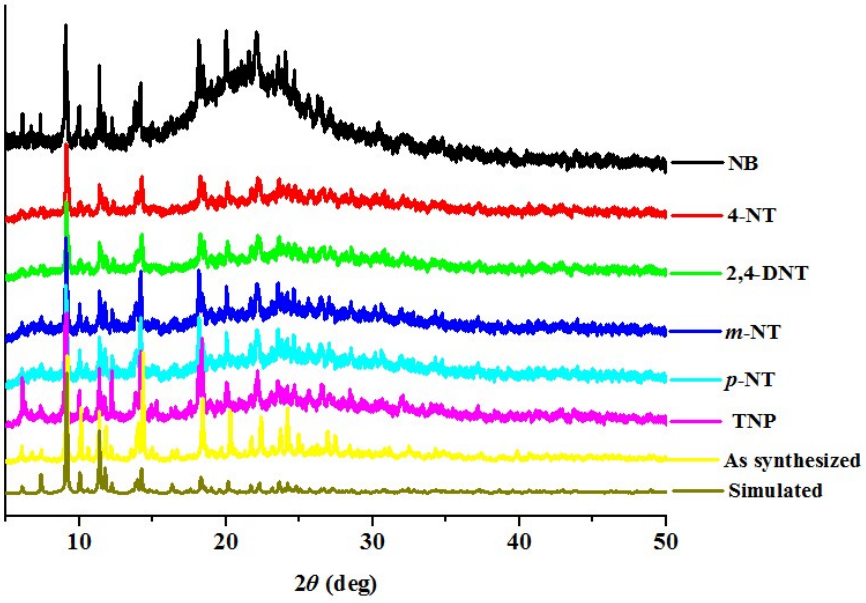


Fig. S4 Emission spectra of H_3**L** and compound **1** in solid state at room temperature.



(a)



(b)

Fig. S5 The PXRD patterns of **1** (a) after immersed in different 10^{-3} M $M(NO_3)_x$ aqueous solutions; (b) and nitroaromatic compounds.

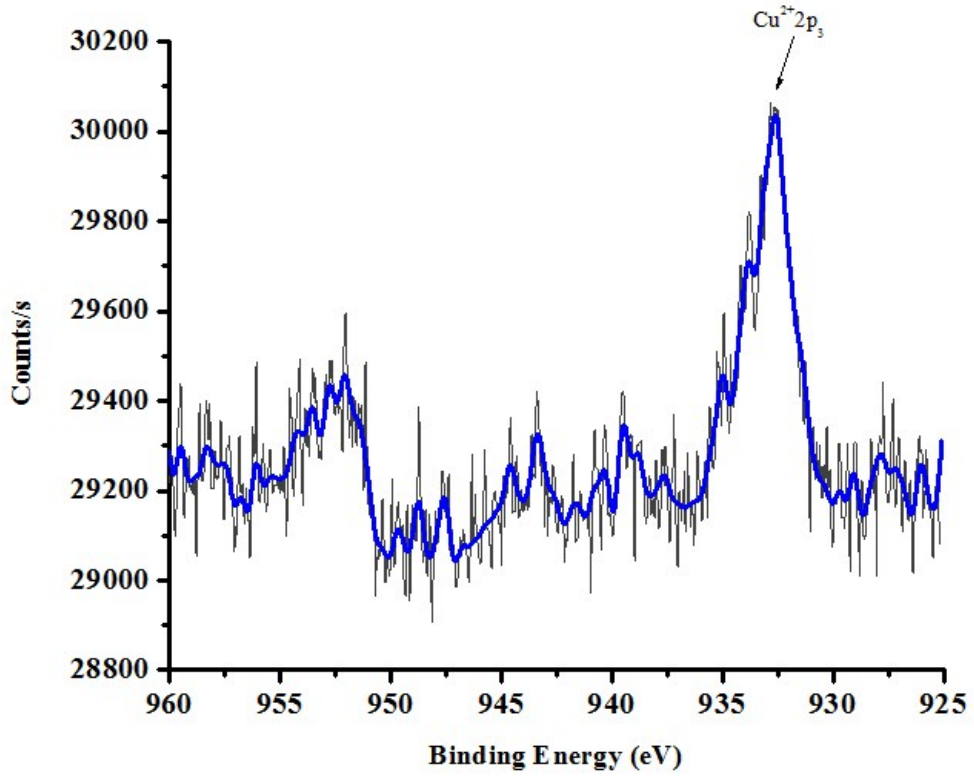


Fig. S6 X-ray photo-electron spectroscopy (XPS) of Cu^{2+}@**1**.

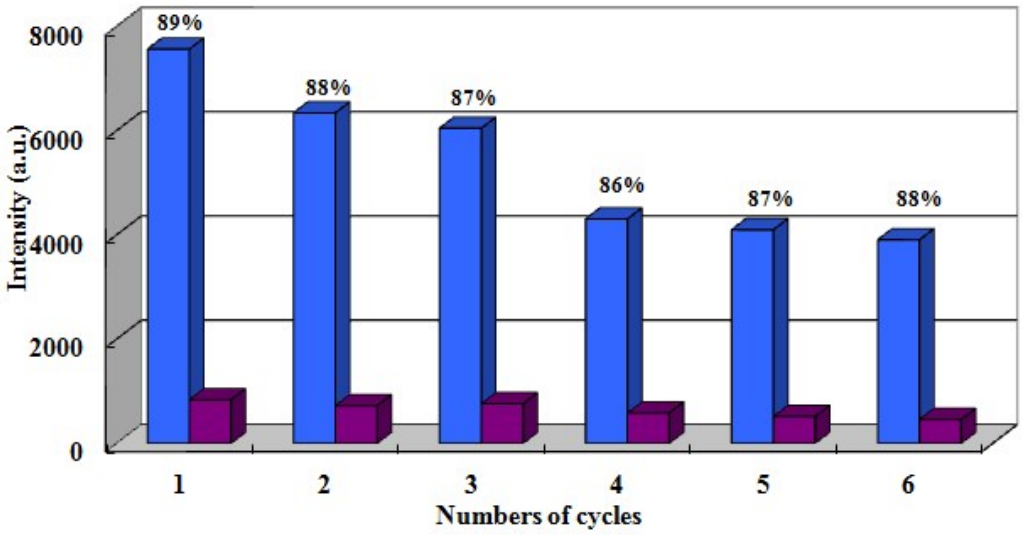


Fig. S7 The luminescence intensity of **1** in Cu^{2+} aqueous solution after every run of recycling.

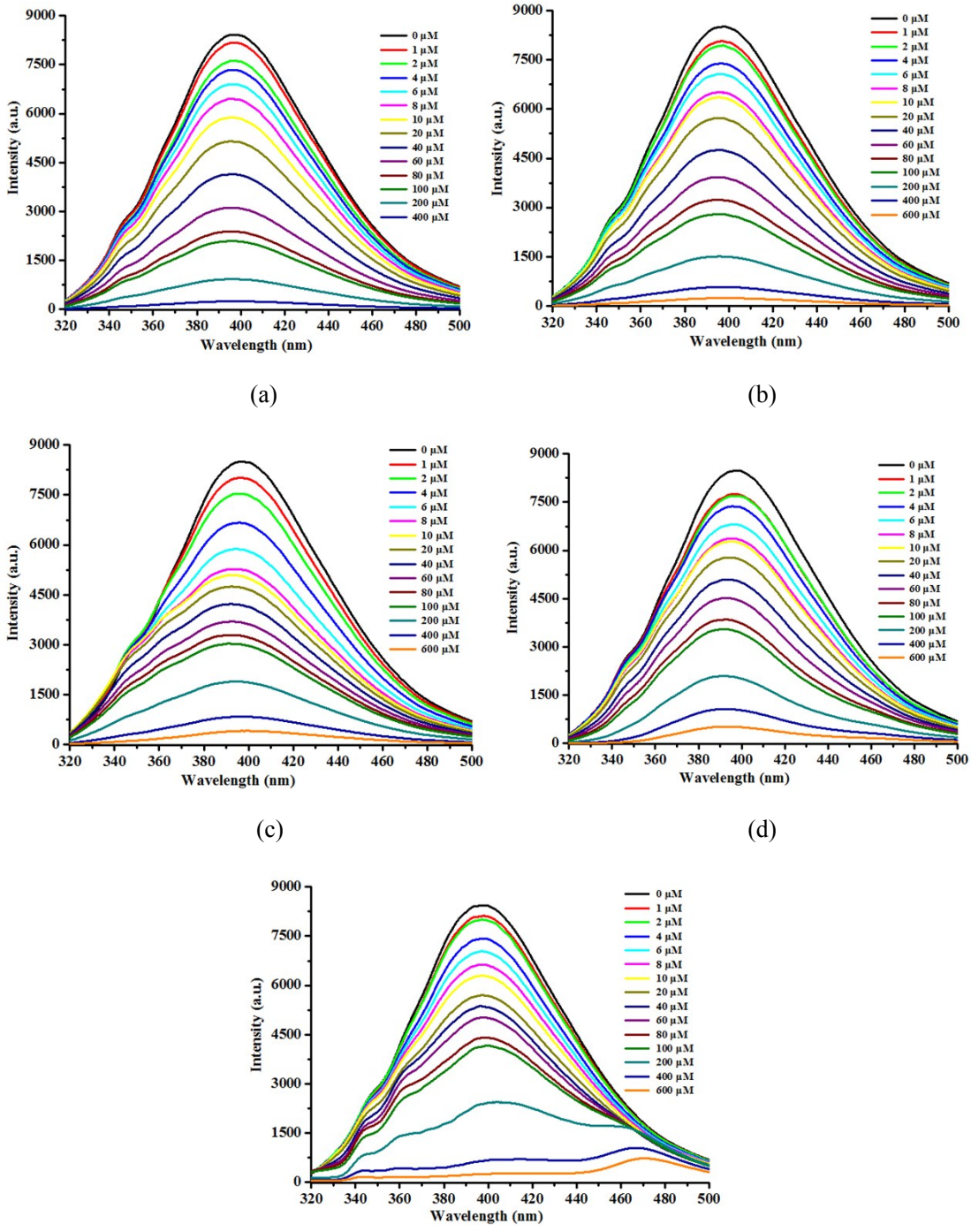


Fig. S8 The fluorescence emission spectra of the **1** upon gradual addition of (a) for 4-NT, (b) for 2,4-DNT, (c) for *m*-NP, (d) for *p*-NP, (e) for TNP (λ_{ex} = 366 nm).

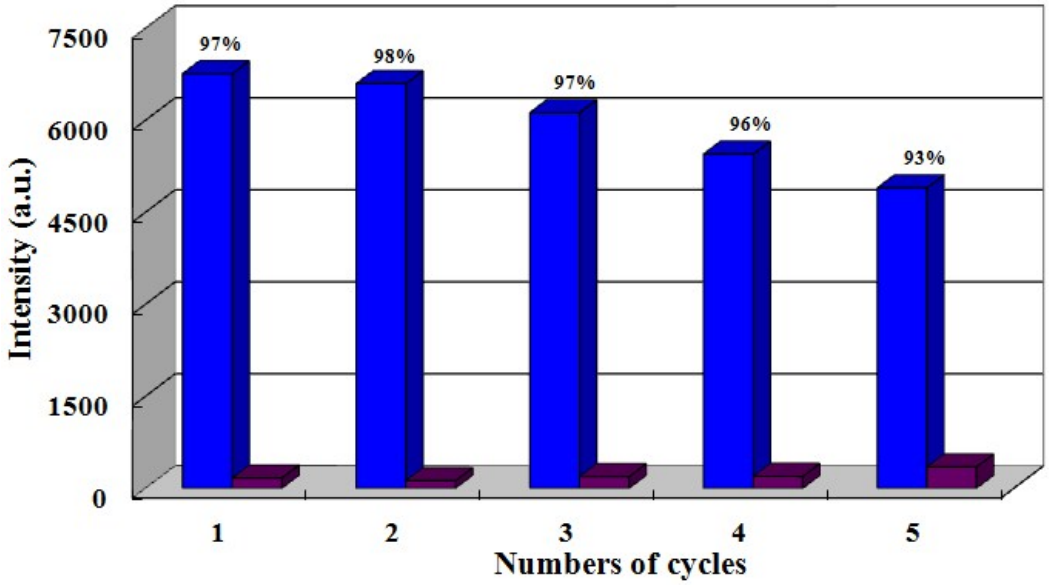


Fig. S9 The luminescence intensity of **1** in TNP DMF solution after every run of recycling.

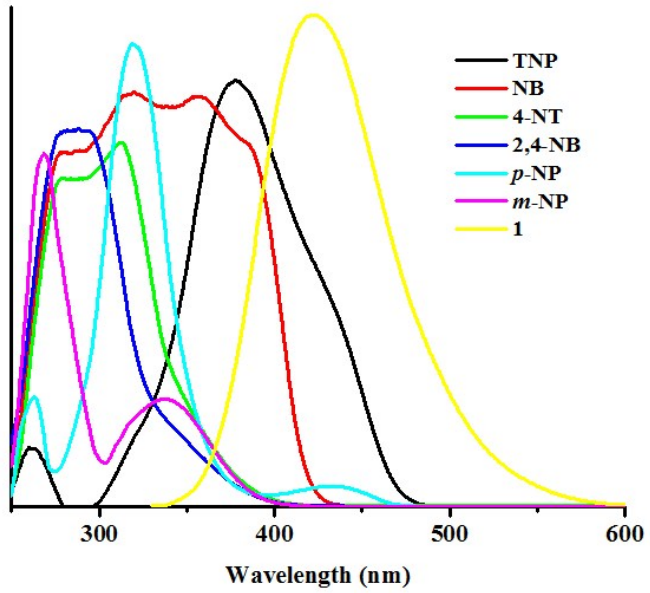


Fig. S10 Spectra overlap between the UV-Vis adsorption spectrum of NACs and the emission spectra of **1.**