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A five-connected 2D + 2D → 3D polycatenation network for selective and sensitive sensing of 2,4,6-trinitrophenol

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Materials and methods

Reagents and solvents were purchased from Aladdin Industrial Corporation (Shanghai, China) and used as received. Ligand mfdp was synthesized according to the literature method.[S1] Elemental analyses (EA) were performed on an Elementar Vario ELIII elemental analyzer. The infrared (IR) spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. The luminescence spectra were measured on a Hitachi F-4600 fluorescence spectrometer. UV-vis spectra were recorded with an Agilent Cary5000 spectrophotometer. Thermogravimetric analyses (TGA) were carried out on a NETZSCH STA 449F3 unit at a heating rate of 10 K min^{-1} under a nitrogen atmosphere. X-ray powder diffraction data were measured on a Rigaku SmartLab (3) diffractometer with Cu Kα radiation (λ = 1.54184 Å, 40 kV, 30 mA) and scans were run for each sample over the range $3^{o} \leq 2\theta \leq 50^{o}$.

Synthesis of complex 1

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.10 mmol), mfdp (0.05 mmol), and H_2ndc (0.05 mmol) in DMA / H_2O (2 mL / 2 mL) was added in a 15 mL Teflon-lined stainless steel reactor and heated at 95 ºC for 6 days, after which it was cooled to ambient temperature. Corlorless block crystals were obtained by filtration. Yield: 48% (based on mfdp). – *Anal. Calcd*. for $C_{86}H_{62}N_4O_{15}Zn_4$ (%): C, 62.49; H, 3.78; N, 3.39. Found (%), C, 62.33; H, 3.52; N, 3.55. IR (cm^{-1}): 3456, 3078,

3049, 2968, 2925, 2860, 2831, 2025, 1610, 1585, 1568, 1512, 1461, 1409, 1363, 1328, 1259, 1226, 1209, 1149, 1068, 1041, 1022, 1005, 977, 869, 829, 810, 787, 729, 687, 665, 629, 586, 548, 528, 453.

***Crystallographic data for* 1**

$C_{86}H_{62}N_4O_{15}Zn_4$, ($M$ = 1652.88), triclinic, space group $P\bar{1}$, at 293 K: a = 12.7476(9), b = 13.2428(8), and c = 13.3763(8) Å, α = 102.648(5)°, β = 106.069(6)°, γ = 110.198(6), V = 1908.6(2) Å^3, Z = 1, d_{calc} = 1.438 g·cm^{-3}, μ(Mo-Ka) = 1.312 mm^{-1}, F(000) = 846. Analysis was performed at 293(2) K on a Bruker Smart-1000 CCD diffractometer by standard procedure (graphite monochromated MoK$_\alpha$ radiation, φ and ω scanning). On the angles 2.49<θ<25.02° total of 13933 reflections were measured, 6716 unique reflections (R_{int} = 0.0252), 5406 reflections with $I > 2\sigma(I)$. The structure was solved and refined using the SHELXTL program package.[12] GOOF = 1.028, S = 1.044; final R values: R_1 = 0.0430, wR_2 = 0.1176 [$I > 2\sigma(I)$]; R_1 = 0.0571, wR_2 = 0.1258 (all data). Residual electronic density max/min was 0.581 / -0.292 e Å^{-3}.

CCDC 2545633 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Table S1. Selected bond lengths (Å) and bond angles (°) for complex 1

1					
Zn(1)-O(7)$^{\#2}$	1.960(2)	Zn(1)-O(1)	1.975(3)	Zn(1)-O(3)	1.908(2)
N(1A)-Zn(2)	2.07(2)	Zn(2)-O(2)	2.012(3)	Zn(2)-O(4)	1.916(3)
Zn(1)-N(2)$^{\#3}$	2.073(3)	Zn(2)-O(3)	1.899(3)		
O(3)-Zn(1)-O(7)$^{\#2}$	123.46(11)	O(3)-Zn(1)-N(2)$^{\#3}$	108.60(12)	O(3)-Zn(2)-O(4)	125.89(14)
O(3)-Zn(1)-O(1)	105.91(11)	O(7)$^{\#2}$-Zn(1)-N(2)$^{\#3}$	95.24(12)	O(3)-Zn(2)-O(2)	101.45(11)
O(7)$^{\#2}$-Zn(1)-O(1)	121.76(12)	O(1)-Zn(1)-N(2)$^{\#3}$	96.44(13)	O(4)-Zn(2)-O(2)	95.57(14)
O(3)-Zn(2)-N(1B)	106.1(4)				

Symmetry codes: #1 -x+1, -y+1, -z; #2 x, y+1, z; #3 x+1, y, z-1.

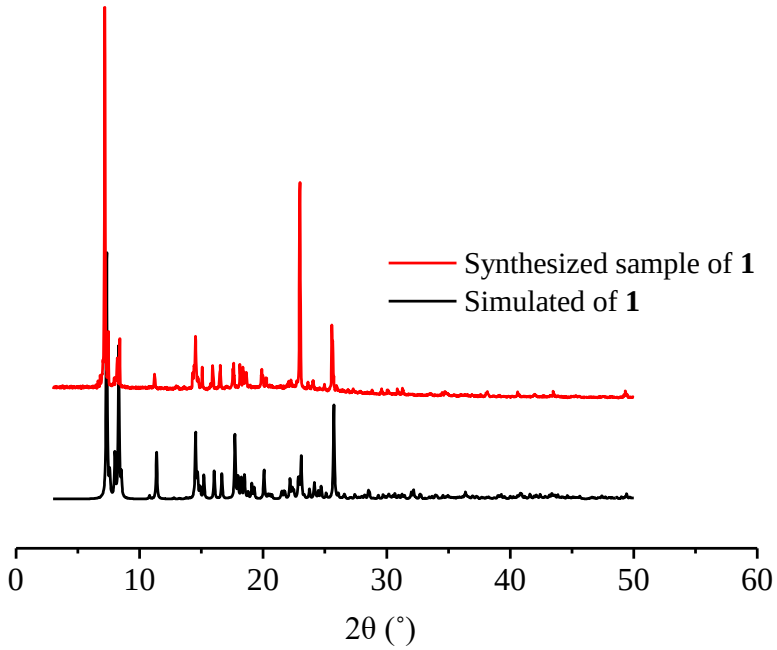


Figure S1 PXRD patterns of complex **1**

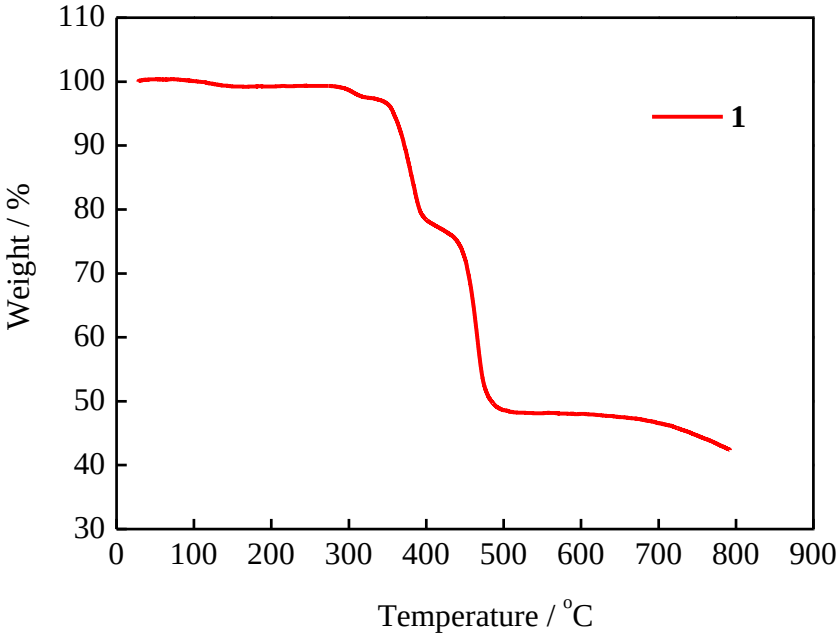
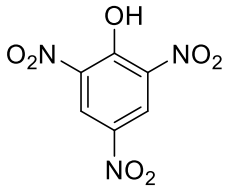
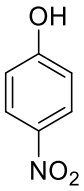
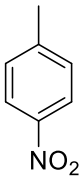
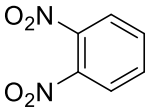
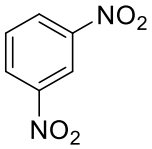
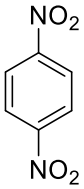


Figure S2 TGA curves of complex **1**

Table S2 Structures of nitro explosives tested

Name	Structure
2,4,6-trinitrophenol (TNP)	
4-nitrophenol (4-NP)	
4-nitrotoluene (4-NT)	
1, 2-dinitrobenzene (1,2-DNB)	
1, 3-dinitrobenzene (1,3-DNB)	
1,4-dinitrobenzene (1,4-DNB)	

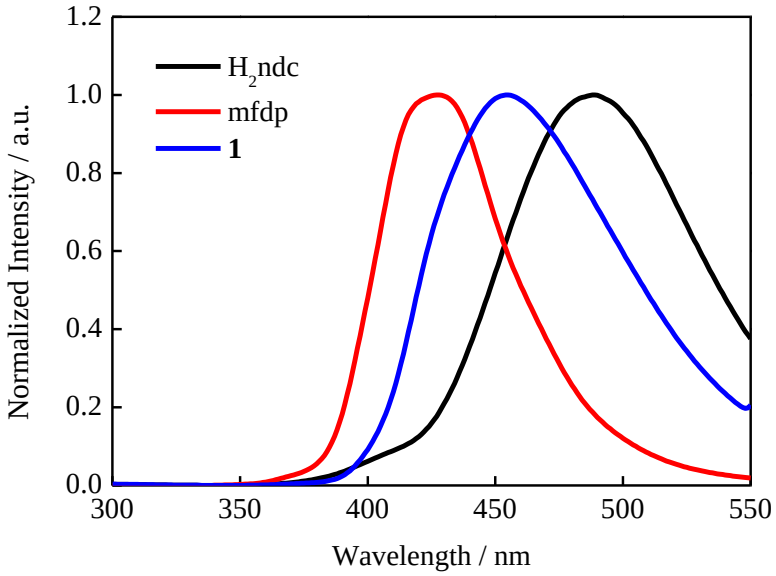


Figure S3 Normalized fluorescence emission spectra of complex **1** and the ligands

Table S3. The quenching constants of the reported CPs for detecting TNP in DMF, DMA, or H_2O suspension.

Molecular Formula	Quenching constant (K_{sv} / $dm^3 \cdot mol^{-1}$)	LOD ($\mu mol \cdot dm^{-3}$)	Solvent	Ref.
$\{[Zn_4(OH)_2(mfdp)_2(ndc)_3]H_2O\}_n$ (**1**)	5.92×10^4	0.281	DMF	This work
UiO-68@NH_2	5.8×10^4	1.7(0.4 ppm)	H_2O	S2
$\{[Zn(2,5\text{-tdc})(3\text{-abit})]\cdot H_2O\}_n$	4.71×10^4	1.46	DMF	S3
$Cd(INA)(pytpy)(OH)\cdot 2H_2O$	4.3×10^4	2.41	DMF	S4
$Cd(INA)(pytpy)(OH)\cdot 2H_2O$	3.3×10^4	9.1	H_2O	S4
$(Me_2NH_2)[Zn_2(L)(H_2O)]\cdot 0.5DMF$	1.42×10^4	2.4 (0.54 ppm)	DMF	S5
$[Pr_2(TATMA)_2\cdot 4DMF\cdot 4H_2O]$	1.6×10^4	NA	DMF	S6
$[(Zn_4O)(DCPB)_3]\cdot 11DMF\cdot 5H_2O$	3.7×10^4	NA	DMF	S7
[Zn(BDC)(L)]·xG	1.16×10^4	0.49	H_2O	S8
[Cd(BDC)(L)]·xG	1.35×10^4	0.36	H_2O	S8
$[Zn_2(H_2L)_2(Bpy)_2(H_2O)_3]\cdot H_2O$	1.36×10^4	0.15	H_2O	S9
$[Zn(L)(HCOO)\cdot H_2O]_n$	2.11×10^4	NA	H_2O	S10
$[Cd(5\text{-BrIP})(TIB)]_n$	2.68×10^4	0.27	H_2O	S11
$[Eu_3(bpydb)_3(HCOO)(\mu_3\text{-}OH)_2(H)]$	1.5×10^4	4.98	H_2O	S12
$[Zn(phen)(H_2O)_2][L]\cdot 2H_2O$	1.90×10^4	9.6	H_2O	S13

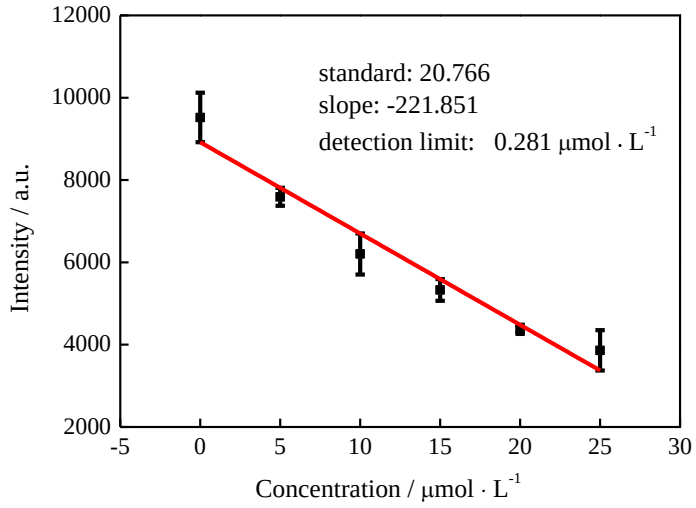


Figure S4 The detection limit for TNP of **1** in DMF suspension was calculated with 3σ/*k* (*k*: slope, σ: standard) at the low concentration (0-25 μmol dm^{-3}).

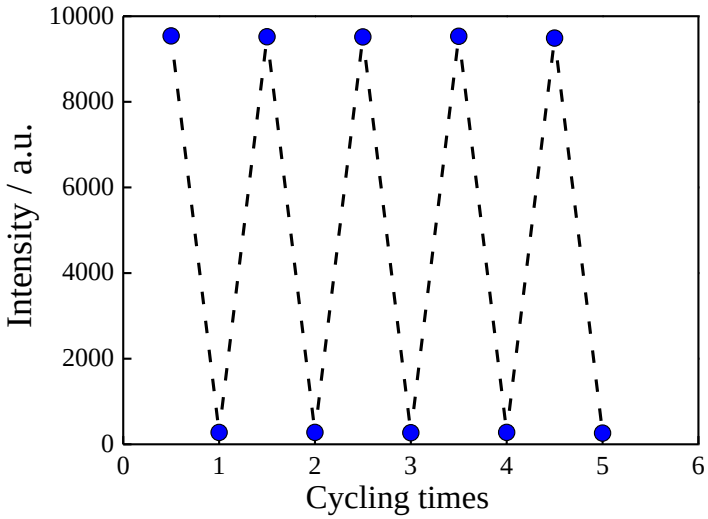


Figure S5 Cyclic stability of TNP detecting by **1**

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