

Supporting information

Three-dimensional cage Zinc triazine framework compound: Fluorescence sensing of aromatic compounds containing NO₂/OH groups

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Materials and methods

All starting materials were of reagent grade quality and were obtained from commercial sources without further purification. The powder X-ray diffraction pattern (PXRD) was obtained on an Advance-D8 equipped with Cu-K α radiation in the range $5^\circ < 2\theta < 50^\circ$, with a step size of 0.02° (2θ) and a count time of 2 s/step at room temperature. All IR measurements were obtained using a Bruker AXS TENSOR-27 FT-IR spectrometer with pressed KBr pellets in the range of 400–4000 cm^{-1} at room temperature. Elemental analyses for C, H and N were measured on a Model 240C automatic Perkin-Elmer elemental analyzer. UV-vis absorption spectra of solid samples were collected on a JASCO V-570 spectrophotometer and Lambda 35 spectrometer was applied to record the UV-vis absorption spectra of suspension sample and detectors solutions in 200-800 nm. Thermogravimetric analysis (TG) was performed on a PerkinElmer Diamond TG/DTA under atmosphere from room temperature to 1000 $^\circ\text{C}$ with a heating rate of 10 $^\circ\text{C}/\text{min}$. Fluorescence spectra were measured on a JASCO FP-4600 and HORIBA Fluoromax-4-TCSPC fluorimeter.

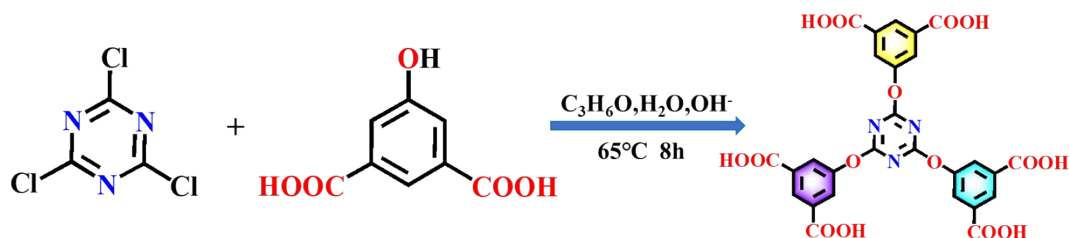
X-ray Crystallography Determination:

Single crystal of the compound **1** was mounted on glass fibers for X-ray measurement. Reflection data was collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). All the measured independent reflections ($I > 2\sigma(I)$) were used in the structural analyses, and semi-empirical absorption corrections were applied using the SADABS program^[1]. All calculations were performed in OLEX2 platform^[2,3]. The crystal was kept at 296 K during data collection. In the process of crystal analysis, we used DFIX, DANG, SIMU and AFIX instructions to limit the C and N of the ligand. SQUEEZE the diffraction peaks of the disordered guest molecules of the compound **1** using PLATON software. The results show that there are 289 electrons in each structural unit of the compound **1**. According to the calculation result of SQUEEZE, including three free H₂O, two free OH⁻ and five free DMA was directly added to the final molecular formula of the compound, and it was verified by elemental analysis and thermogravimetric analysis. The crystal was measured using a single

axis diffractometer, we made various attempt to grow crystals of the better quality without success. Making many attempts to synthesize a good quality crystal, however, present result is the best data. We tried to resolve the alert B of Checkcif, unfortunately, all the efforts failed. (I) PLAT026_ALERT_3_B, PLAT084_ALERT_3_B, PLAT341_ALERT_3_B and PLAT369_ALERT_2_B: These issues of alert level B possibly result from the poor diffraction data with reflections of moderate intensity as showed the R_{int} . (II) PLAT242_ALERT_2_B: This alert B may be because O1, O2 and O3 are water molecules bound to the heavier Zn leading to a significant discrepancy in Ueqs. Some refined commands such as ISOR, DELU and SIMU were used to address such abnormal Ueq value of some Zn atoms, but did not achieve the result we expected. (III) PLAT420_ALERT_2_B: These issues of alert level B possibly result from the solvent molecules are highly disordered, which supposed to form hydrogen bond between water molecules had been removed by the SQUEEZE routine in the PLATON software package. (IV) PLAT910_ALERT_3_B: The missing FCF reflections below theta(min) were caused by the high beam stop theta(min) limit set and large unit cell, and so on. (V) PLAT973_ALERT_2_B: This alert B were caused by difficulties in absorption correction. The crystallographic data for compound **1** was listed in **Table S1**. The major bond lengths of the compound **1** was listed in **Table S2.1**. The selected bond angles of compound **1** was listed in **Table S2.2**.

Synthesis of the ligand H₆DPOT and compound 1

Synthesis of 5, 5', 5''-(1, 3, 5-triazine-2, 4, 6-triyl) tris(oxy)) tri-isophthalic acid (H₆DPOT). The synthetic route was shown in the **Scheme S1** below. The specific synthetic method is as follows: Weigh 4.097 g of 5-hydroxyisophthalic acid into a 500 mL three-necked flask, and then add 20 mL of acetone; weigh 2.7 g of NaOH, add 20 mL of distilled water to it, add it to a three-necked flask, and stir continuously under ice-water bath conditions. Dissolve 1.383 g of cyanuric chloride in 100 mL of acetone, stir until it is completely dissolved, and transfer to a constant pressure dropping funnel. Add the acetone solution of cyanuric chloride dropwise to the three-necked flask. After dropping, it was stirred the mixture at room temperature for another 10 minutes. Then transfer the three-necked flask to an oil bath, and heat to 65 °C to reflux for 8 h. After cooling to room temperature, the solution in the flask was transferred to a beaker and acidified with dilute hydrochloric acid to pH = 1, and then filtered with suction. The obtained precipitate was washed 3-4 times with water to pH=7, and dried under vacuum to obtain a white powder of H₆DPOT.



Scheme S1. The synthesis route of the ligand H₆DPOT.

Preparation of compound 1: The compound **1** was prepared by the solvothermal reaction. Zn(NO₃)₂·6H₂O (53.5 mg, 0.18 mmol) and H₆DPOT (12.4 mg, 0.02 mmol) were added in H₂O and DMA (1:5) mixed solvent (1 mL) in a Pyrex vial, and ultrasonically dissolved at room temperature to obtain a colorless transparent solution. The mixed solution was kept in an 85 °C oven for a day. Colorless block-like crystal of compound **1** was obtained.

{[Zn₇(DPOT)₂(H₂O)₁₁]}·2OH·3H₂O·5DMA} (**1**) Yield: 36 mg, 76% (based on Zn (II)), Elemental analysis C₇₄H₈₃N₁₁O₅₁Zn₇ measured value (%): C, 37.03; H, 3.47; N, 6.43; theoretical value (%): C, 37.01; H, 3.45; N, 6.41. Infrared spectrum (KBr, cm⁻¹): 3442, 3070, 1618, 1561, 1456, 1244, 1193, 1082, 786, 722.

Table S1. Crystal data and structure refinement for the compound **1**

Compound 1	
Chemical formula	C ₅₄ H ₃₀ N ₆ O ₄₁ Zn ₇
M (g·mol ⁻¹)	1876.43
Crystal system	trigonal
Space group	<i>R</i> 32
<i>a</i> (Å)	27.7201(4)
<i>b</i> (Å)	27.7201(4)
<i>c</i> (Å)	67.9002(17)
<i>α</i> (deg)	90
<i>β</i> (deg)	90
<i>γ</i> (deg)	120
<i>V</i> (Å ³)	45184.7(17)
<i>Z</i>	12
ρ_{calc} (g·cm ⁻³)	0.828
<i>F</i> (000)	11208.0
μ (Mo–K α) (mm ⁻¹)	10.228
θ (deg)	4.53 to 50.03
Reflections collected	32990
Independent reflections (<i>I</i> >2 σ (<i>I</i>))	17229
Parameters	593
$\Delta(\rho)$ (e Å ⁻³)	2.61 and -1.03
Goodness of fit on F ²	0.952
<i>R</i> ^a	0.1143 (0.2590) ^b
<i>wR</i> ₂ ^a	0.2833 (0.3870) ^b

^a $R = \sum |F_o - F_c| / \sum F_o$, $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$; $[F_o > 4\sigma(F_o)]$. ^bBased on all data.

Table S2.1 Selected Bond Lengths (Å) for the compound **1**

Compound 1			
Zn(1)-O(20) ^{#1}	1.927(17)	Zn(4)-O(11)	2.000(14)
Zn(1)-O(20) ^{#2}	1.927(17)	Zn(4)-O(12)	1.986(13)
Zn(1)-O(20)	1.927(17)	Zn(4)-O(13)	2.01(2)
Zn(1)-O(22)	2.06(3)	Zn(4)-O(18) ^{#5}	2.046(14)
Zn(2)-O(19) ^{#2}	2.00(2)	Zn(4)-O(26) ^{#6}	2.068(18)
Zn(2)-O(19) ^{#1}	2.00(2)	Zn(5)-O(5)	1.92(2)
Zn(2)-O(19)	2.00(2)	Zn(5)-O(6)	2.022(16)
Zn(2)-O(21)	1.892(18)	Zn(5)-O(7)	1.914(16)
Zn(2)-O(21) ^{#1}	1.892(18)	Zn(5)-O(25)	1.88(2)
C(1)-C(16) ^{#7}	1.59(12)	Zn(6)-O(1)	1.93(2)
C(22)-C(26) ^{#8}	1.46(3)	Zn(6)-O(2)	1.94(2)
Zn(3)-O(14) ^{#3}	1.95(2)	Zn(6)-O(3)	2.01(3)
Zn(3)-O(17) ^{#4}	1.975(18)	Zn(6)-O(4)	1.99(3)
Zn(3)-O(27)	2.006(18)	Zn(6)-O(8)	1.99(2)
Zn(3)-O(28)	1.915(15)	Zn(6)-O(24)	1.94(2)

*Symmetry codes: Compound 1: #1: -x+y+1, -x+2, z; #2: -y+2, x-y+1, z, #3: y, x, -z+1; #4: -x+2, -x+y+1, -z+1; #5: -y+1, x-y, z; #6: -x+y+1, -x+1, z; #7: x-y+2/3, -y+4/3, -z+4/3; #8: y+2/3, x+1/3, -z+4/3; #9: y-1/3, x-2/3, -z+4/3

Table S2.2. Selected Bond Angles (°) for the Compound 1

Compound 1			
O(20) ^{#1} -Zn(1)-O(20)	115.7(4)	O(17) ^{#4} -Zn(3)-O(27)	88.7(8)
O(20) ^{#1} -Zn(1)-O(20) ^{#2}	115.7(4)	O(11)-Zn(4)-O(18) ^{#6}	88.0(10)
O(21) ^{#1} -Zn(2)-O(19) ^{#2}	78.1(9)	O(4)-C(1)-C(16) ^{#7}	155.9(6)
O(21) ^{#1} -Zn(2)-O(21)	95.3(8)	C(23)-C(22)-C(26) ^{#8}	106(5)
O(10) ^{#3} -Zn(3)-O(14) ^{#3}	85.3(9)	O(24)-C(26)-C(22) ^{#9}	116.2(18)
O(7)-Zn(5)-O(5)	113.5(12)	O(24)-Zn(6)-O(1)	86.6(12)

*Symmetry codes: Compound 1: #1: -x+y+1, -x+2, z; #2: -y+2, x-y+1, z, #3: y, x, -z+1; #4: -x+2, -x+y+1, -z+1; #5: -y+1, x-y, z; #6: -x+y+1, -x+1, z; #7: x-y+2/3, -y+4/3, -z+4/3; #8: y+2/3, x+1/3, -z+4/3; #9: y-1/3, x-2/3, -z+4/3

IR spectra:

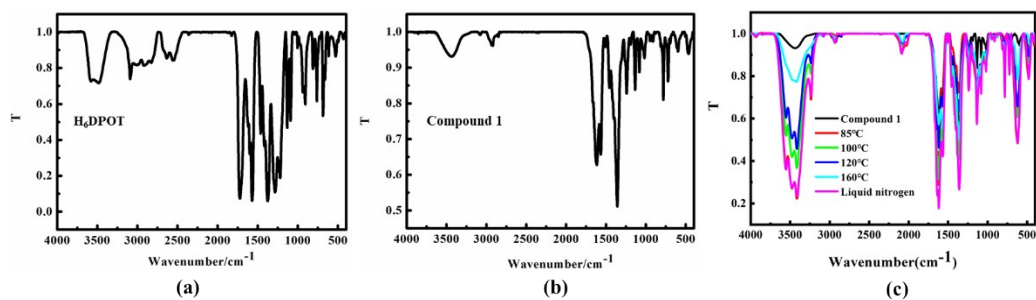


Figure S1 IR spectrum: (a) H₆DPOT; (b) Compound **1**; (c) IR spectra of compound **1** at different temperatures

Table S3 IR spectra (cm⁻¹) of H₆DPOT and compound **1**

	H ₆ DPOT	1
$\nu_{\text{O-H}}$	3577	3442
$\nu_{\text{Ar-H}}$	3084	3070
$\nu_{\text{asCOO-}}$	1723	1618
$\nu_{\text{sCOO-}}$	1575	1561
$\nu_{\text{C=C}}/\nu_{\text{C=N}}$	1467	1456
$\nu_{\text{C-N}}/\nu_{\text{C-C}}$	1288, 1219	1244, 1193
$\nu_{\text{C-O}}$	1090	1082
$\delta_{\text{Ar-H}}$	764, 689	786, 722

UV-vis spectra

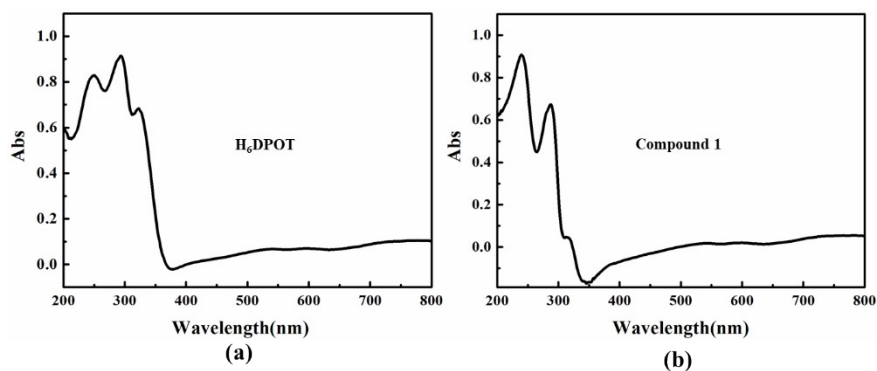


Figure S2 UV spectrum: (a) H₆DPOT; (b) Compound **1**

Table S4 UV spectrum (nm) of H₆DPOT and compound **1**

	Wavelength(nm)	Transition	Types
H ₆ DPOT	249	π - π^*	LLCT
	292	π - π^*	LLCT
	324	n- π^*	LLCT
1	239	π - π^*	LLCT
	289	π - π^*	LLCT
	318	n- π^*	LLCT

PXRD pattern

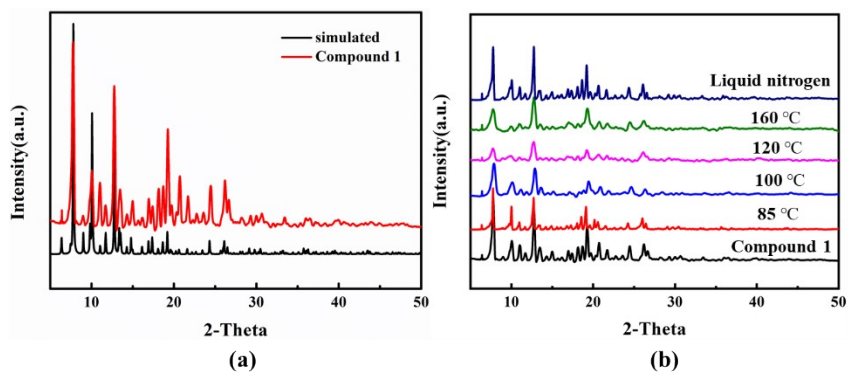


Figure S3 PXRD: (a) compound 1; (b) different temperature of compound 1

TG curve

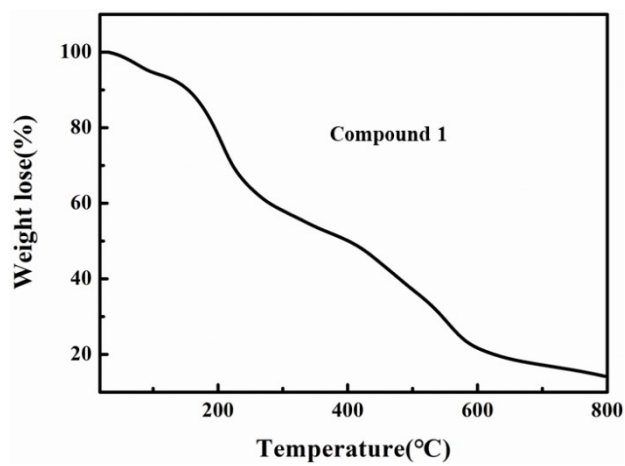
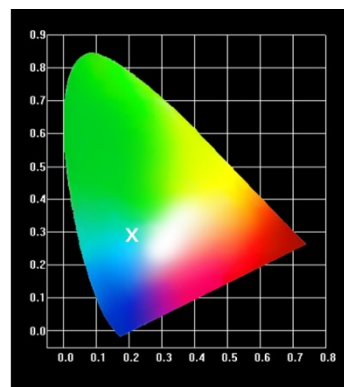
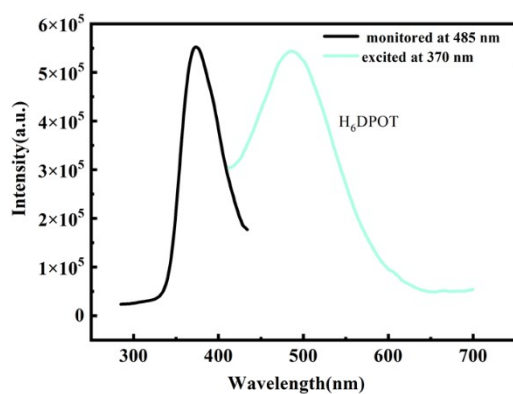
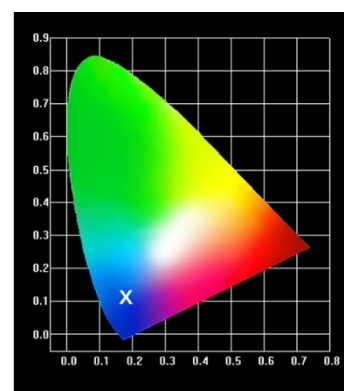
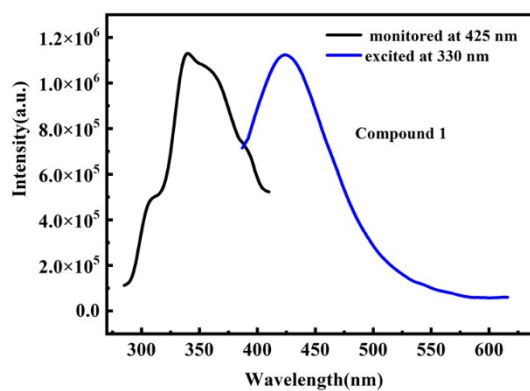


Figure S4 Thermal curve of compound 1

Solid fluorescent



(a)



(b)

Figure S5 Solid fluorescent excitation, emission spectra and CIE: (a) H₆DPOT; (b) Compound 1

Recyclability experiment

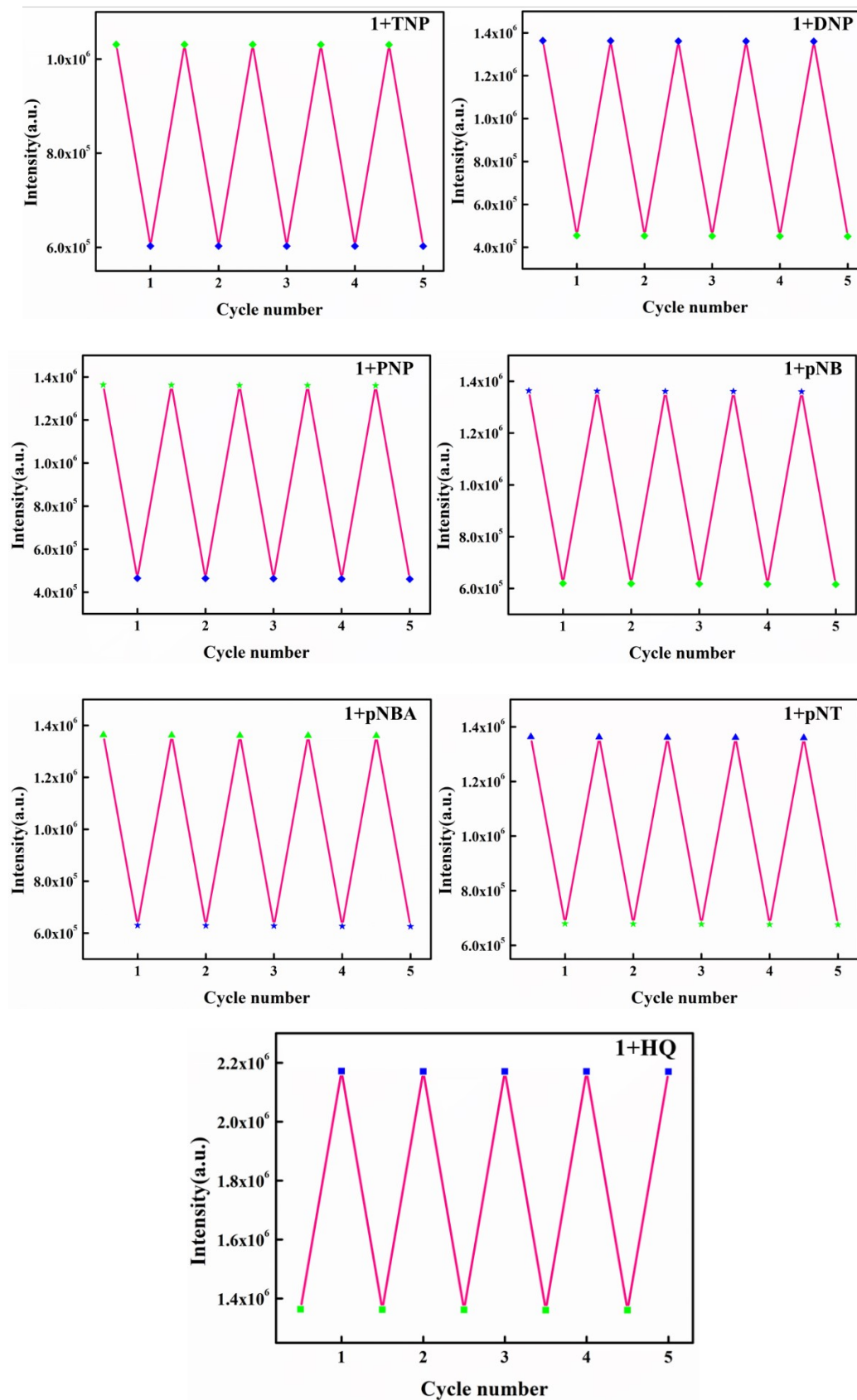


Figure S6 Recyclability tests of detecting of analytes

PXRD and UV-vis spectra

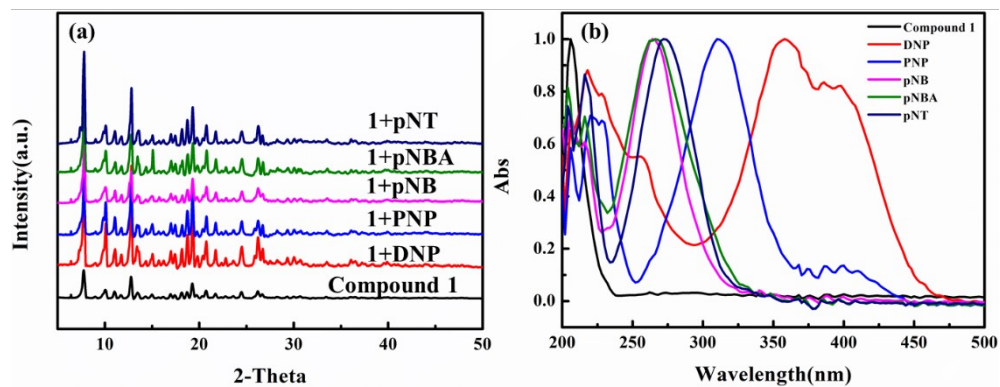


Figure S7 (a) PXRD patterns of compound 1 after the detection of NACs; (b) the overlap of the absorption spectra of compound 1 and NACs

AFM

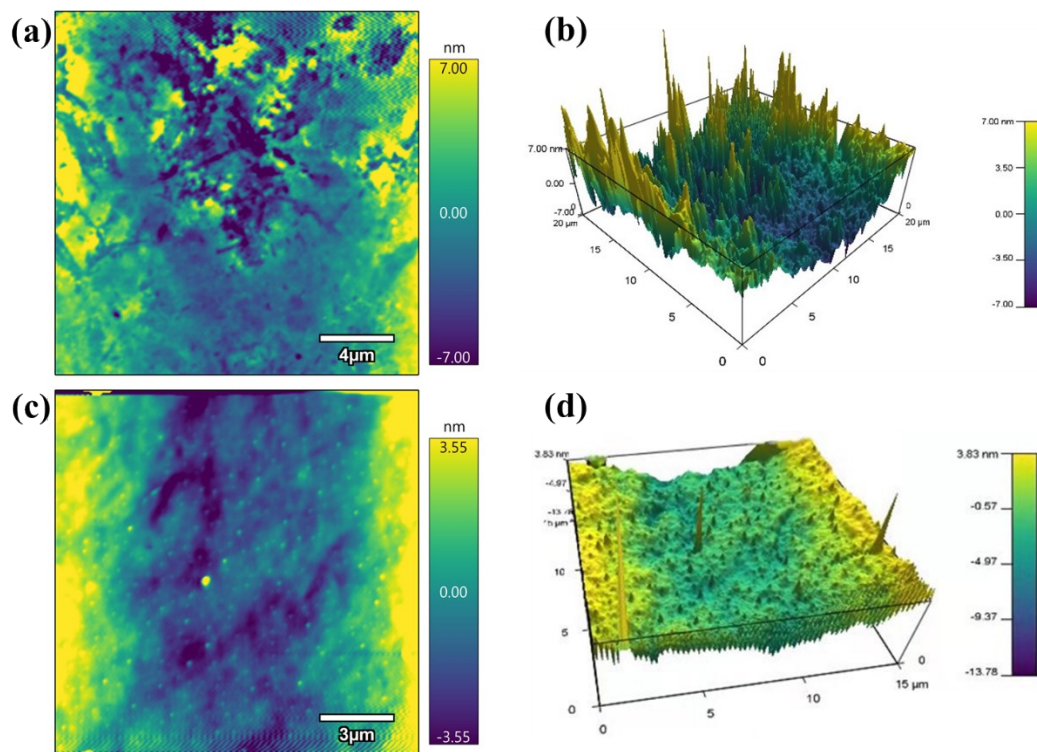


Figure S8. (a) 2D image of compound 1; (b) 3D image of compound 1; (c) 2D image of after adding TNP of compound 1; (d) 3D image of after adding TNP of compound 1

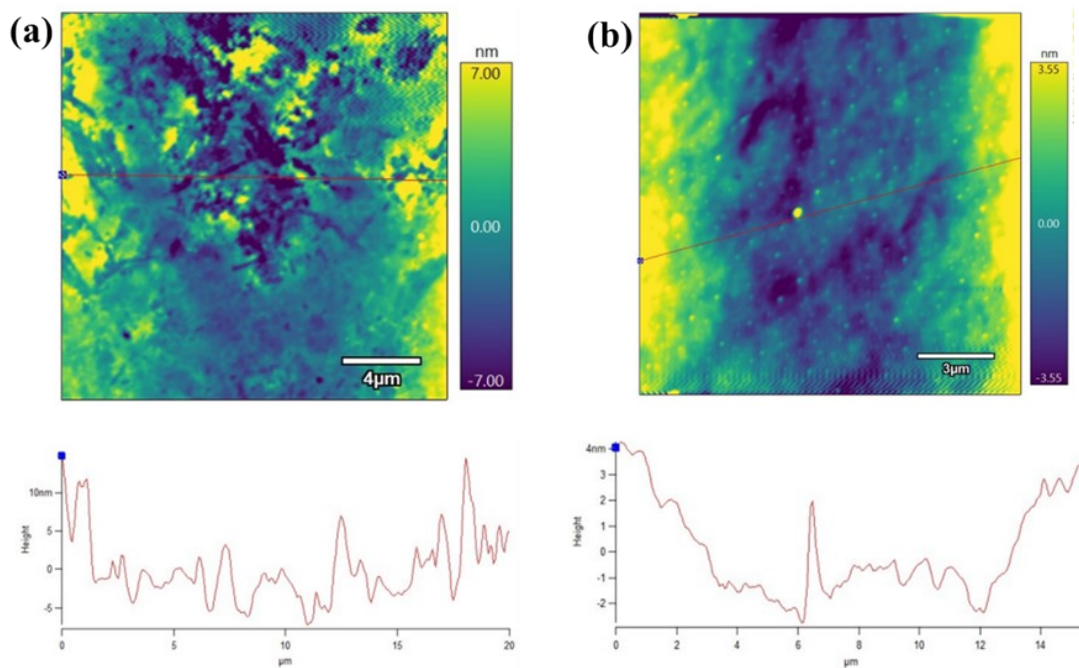


Figure S9 Selected AFM height profile charts (a) compound 1; (b) after adding TNP of compound 1

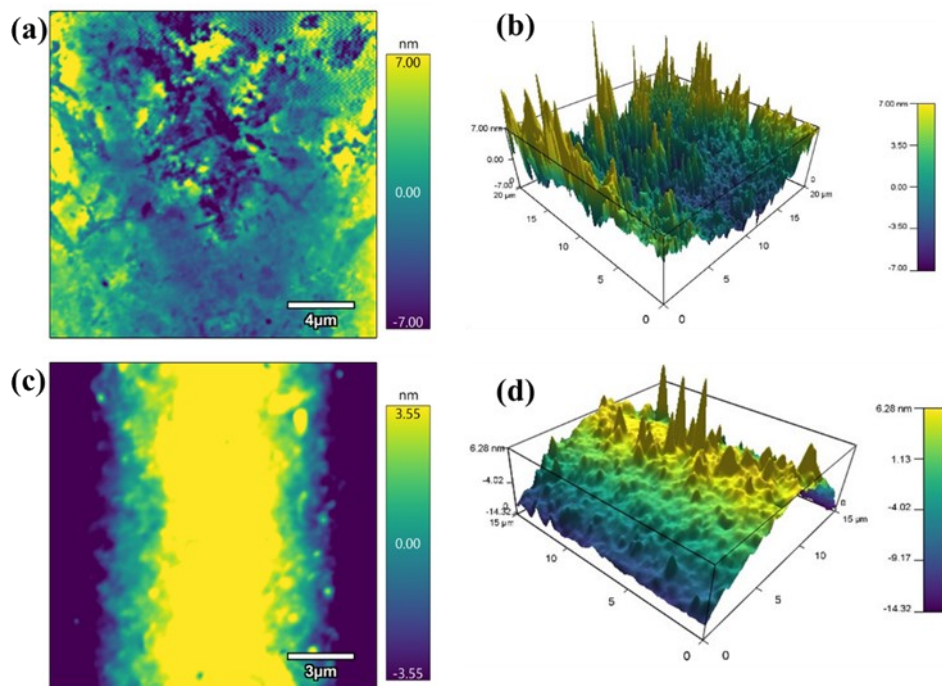


Figure S10 (a) 2D image of compound **1**; (b) 3D image of compound **1**; (c) 2D image of after adding HQ of compound **1**; (d) 3D image of after adding HQ of compound **1**

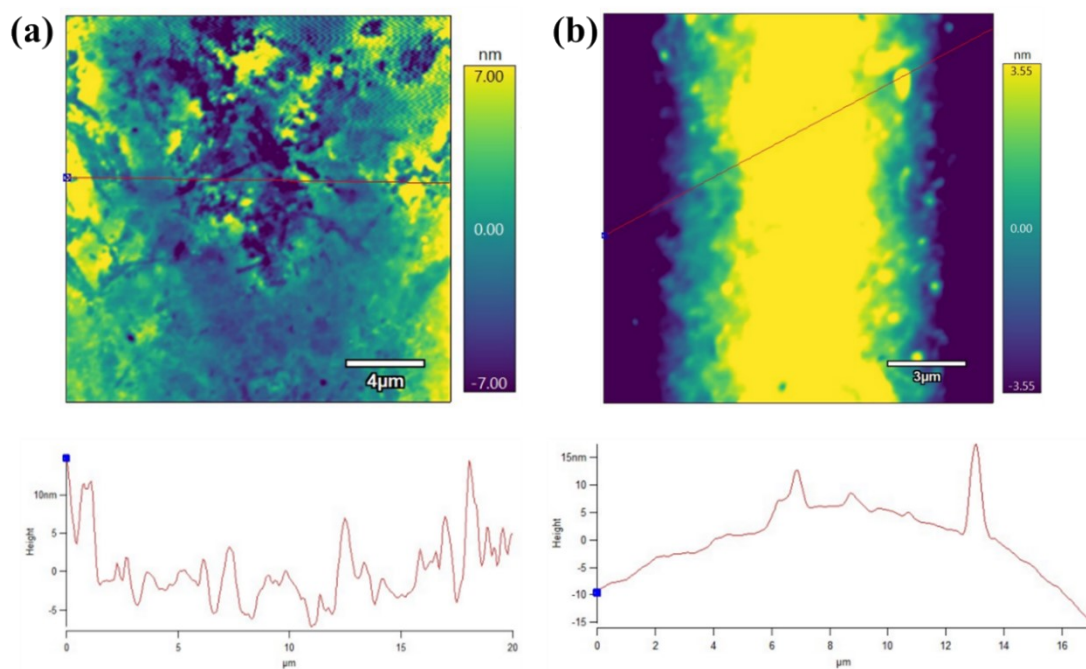


Figure S11 Selected AFM height profile charts (a) compound **1**; (b) after adding HQ of compound **1**

The changes of lifetime curves before and after

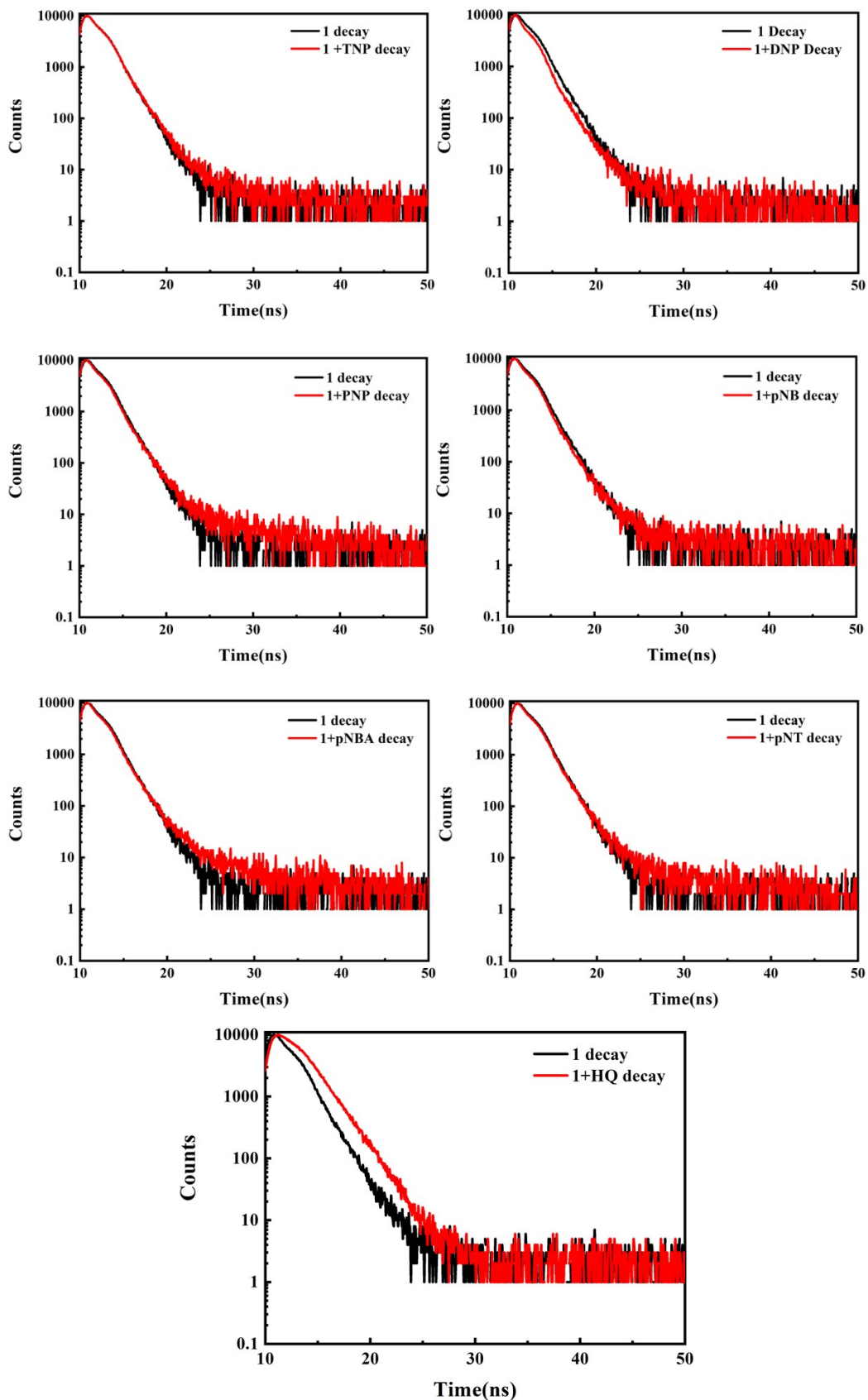


Figure S12 The changes of lifetime curves

References

- [1]. SMART and SAINT (software packages); Siemens Analytical X-ray Instruments, Inc.: Madison, WI, **1996**.
- [2]. O. V. Dolomanov, L.J. Bourhis, R.J. Gildea, J. Howard, H. Puschmann, *Journal of Applied Crystallography*, **2009**, 42, 339-341.
- [3]. G. M. Sheldrick, *Acta Crystallographica*, **2015**, 71, 3-8.