Electronic Supplementary Information (ESI)

A stable nanoscaled Zr-MOF through pH-modulated ratiometric luminescent switch for rapid detection of toxic mycotoxin

Xiaolei Guo[a], Nansong Zhu[a], Yue Lou[a], Siyuan Ren[a], Shirui Pang[a], Yiqiang He[a], Xiao-Bo Chen[b], Zhan Shi[a,*] and Shouhua Feng[a]

[a.] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China.

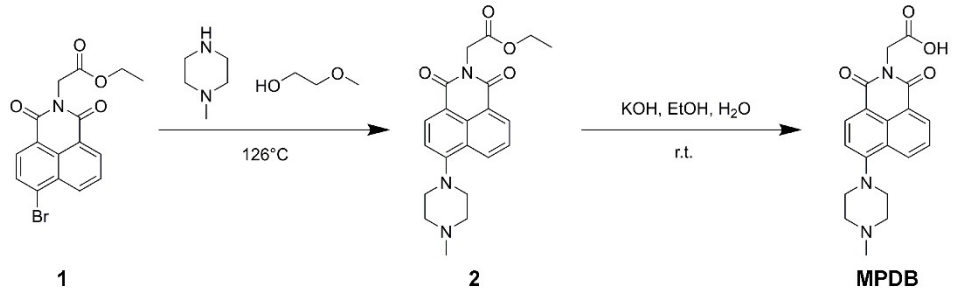
[b.] School of Engineering, RMIT University, Melbourne 3000, Australia.

Experimental section

Materials and methods

All reagents used in this work were commercially purchased and used without further purification. Powder X-ray diffraction (PXRD) was performed on a Rigaku D/MAX2550 diffractometer with Cu Ka radiation (l = 0.15406 nm) at 200 mA and 40 kV. Transmission electron microscopy (TEM) was conducted using FEI Tecnai G2 STwin with a field emission gun operated at 200 kV. Scanning electron microscopy (SEM) micrographs were collected using a JEOL JSM-6700F at 5 kV. Thermogravimetric analysis (TGA) was carried out by a TGA Q500 V20.10 Build 36 from room temperature to 800 °C at a heating rate of 10 °C min^{-1}. Element analyses were measured on a Perkin-Elmer 2400 elemental analyzer. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Bruker IFS 66v/S FT-IR spectrometer. Luminescence spectra were collected on a FluoroMax-4 fluorescence spectrometer at room temperature. ^{1}H NMR, ^{13}C NMR spectroscopy were carried out on a Bruker Avance III spectrometer at 300 MHz. Mass spectrum (MS) was measured on a high-resolution liquid chromatography-mass spectrometer Agilent1290-micrOTOF Q II.

Synthesis details



Scheme S1 Synthetic route of MPDB

Synthesis of compound 1 was prepared as previously described.[1]

Synthesis of compound 2

Compound 1 (4 mmol, 1.448 g) and 1-methylpiperazine (20 mmol, 2.25 mL) were dissolved in 30 mL 2-methoxyethanol under an Ar atmosphere. The reaction mixture was stirred and heated at reflux for 18 h in a pressure-resistant reaction bottle before being allowed to cool to room temperature. The product was precipitated by adding in 50 mL water and still standing for 2 h, isolated by vacuum filtration, washed extensively with water (200 mL), and dried under vacuum. This yielded 2 as a yellow solid without further purification (830 mg, 54%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.59 (d, J = 7.2 Hz, 1H), 8.52 (d, J = 8.1 Hz, 1H), 8.43 (d, J = 8.1 Hz, 1H), 7.74–7.64 (m, 1H), 7.22 (d, J = 8.1 Hz, 1H), 4.92 (s, 2H), 4.23 (q, J = 7.1 Hz, 2H), 3.32 (s, 4H), 2.75 (s, 4H), 2.44 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.57, 163.70, 163.08, 156.63, 133.11, 131.60, 131.50, 129.69, 126.53, 125.74, 122.35, 115.59, 115.04, 61.52, 55.06, 52.97, 46.18, 41.47, 14.51. LC-HRMS m/z ($M+H^+$) calc 382.17, obs 382.5.

Synthesis of MPDB (2-(6-(4-methylpiperazin-1-yl)-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl) acetic acid)

Compound 2 (2 mmol, 763 mg) and KOH (43 mmol, 2.4 g) were dissolved in a solution of H_2O/EtOH (v/v, 3:1). After 10 h of stirring at room temperature, 3.6 mL of concentrated HCl was added to precipitate the product. The resulting product was collected as yellow solid by vacuum filtration, washed with water (200 mL), and dried under vacuum. Yield (670 mg, 95%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.52 (s, 1H), 8.50 (s, 1H), 8.43 (d, J = 8.1 Hz, 1H), 7.89–7.83 (m, 1H), 7.45 (d, J = 8.1 Hz, 1H), 4.71 (s, 2H), 3.52 (s, 8H), 2.88 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.82, 163.65, 163.09, 154.84, 132.85, 131.57, 131.27, 129.49, 127.00, 125.84, 122.54, 116.48, 116.35, 52.88, 49.83, 42.61, 41.54. LC-HRMS m/z ($M-H^+$) calc 352.14, obs 352.1.

Preparation of PCN-224

PCN-224 nanoparticles were synthesized on the basis of previous reports with slight modifications.[2] 150 mg of $ZrOCl_2 \cdot 8H_2O$, 50 mg of H_2TCPP, and 1.4 g of benzoic acid were dissolved in 50 mL of DMF in a round-bottom flask and sonicated for 15 min. Then the mixture was stirred at 90 °C for 5 h. After the reaction is done, the obtained nanoPCN-224 was centrifuged (11000 rpm, 20 min) and washed three times with fresh DMF. Yield (70 mg, 54%). Elemental analysis: Anal. (%) (Found: C, 41.95; H, 1.58; N, 3.98. Calc. for $C_{144}H_{74}N_{12}O_{64}Zr_{12}$: C, 42.24; H, 1.81; N, 4.11).

Preparation of MPDB-PCN

As-synthesized PCN-224 (25 mg) was dispersed in 1 M HCl in DMF and stirred at 80 °C for 18 h to remove dangling ligands from Zr_6 clusters. After naturally cooling down to room temperature, the mixture was washed with 10% TEA solution to remove residual

acid and washed three times sequentially with fresh DMF. The activated PCN-224 was collected after centrifugation (11000 rpm, 20 min) and dried under vacuum. Then different amounts (0.1 mL, 0.2 mL, 0.5 mL, 1 mL) of an anhydrous DMF solution of MPDB (6 mg mL^{-1}) were added to the above activated PCN-224 nanoparticle dispersion solution (5 mL, 1 mg mL^{-1}). Afterwards, the mixture was stirred at 80 °C in dark for 24 h to yield MPDB-PCN. Final products were washed with fresh DMF three times, collected after centrifugation at 11000 rpm and dried under vacuum. Yield for MPDB-PCN (5.2 mg, 88%). Elemental analysis: Anal. (%) (Found: C, 45.49; H, 1.98; N, 5.18. Calc. for MPDB-PCN [($C_{144}H_{74}N_{12}O_{64}Zr_{12}$) ·2.3($C_{19}H_{19}N_3O_4$)]: C, 45.95; H, 2.40; N, 5.40).

Loading amount of MPDB in MPDB-PCN

The mass of nanoparticles before and after loading MPDB was measured three times. Then the average values were calculated to confirm the loading amount of MPDB. Final values were 8.92%, 14.9%, 18.4% and 30.08%, which respectively corresponds to adding different amounts of MPDB (0.1 mL, 0.2 mL, 0.5 mL, 1 mL). If not specified, all MPDB-PCN mentioned in the article is the one with 14.9% MPDB loading.

pKa of MPDB and MPDB-PCN

The pKa values of MPDB and MPDB-PCN were calculated from the Henderson-Hasselbalch equation (Equation 1).

$$y = A_{min} + (A_{max} - A_{min})\frac{1}{1 + 10^{(pKa - pH)}} \quad \textbf{(Equation 1)}$$

y: the fluorescence intensity value of MPDB/ relative intensity of fluorescence (I_{538}/I_{650} and I_{650}/I_{538}) of MPDB-PCN;

A_{min}: the minimum fluorescence intensity;

A_{max}: the maximum fluorescence intensity.

After the fluorescence titration curve was fitted to the above equation, the pKa value for MPDB is about 7.2. The pKa value for MPDB-PCN with 15% MPDB loading is about 4.16 ($y = I_{538}/I_{650}$) and 7.29 ($y = I_{650}/I_{538}$).

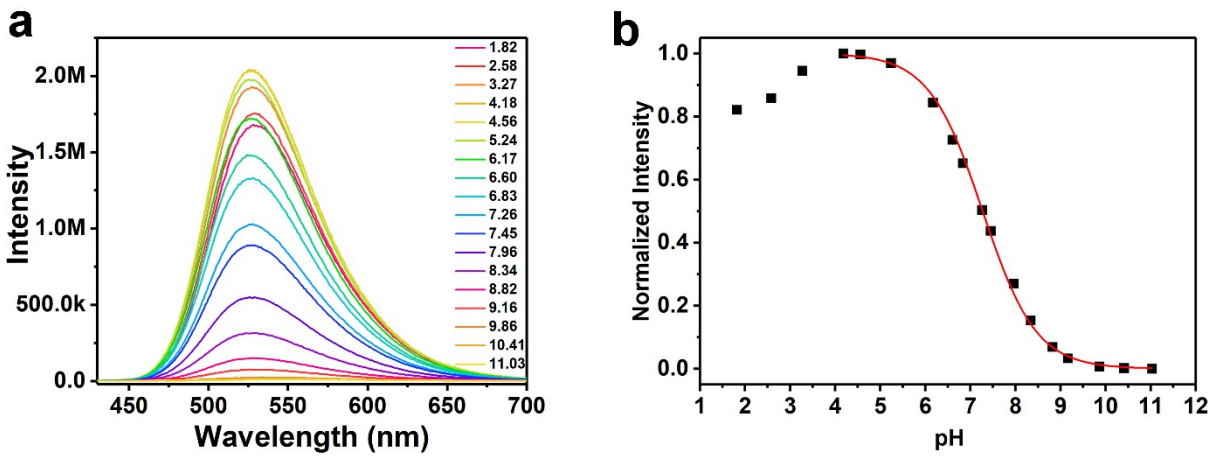


Fig. S1 (a) pH-Dependent emission spectra (λ_{ex} = 405 nm) of MPDB (20 mg L^{-1}) in the pH value from 1.82 to 11.03 in the buffer solution; (b) Normalized intensity versus pH values in the pH value from 1.82 to 11.03.

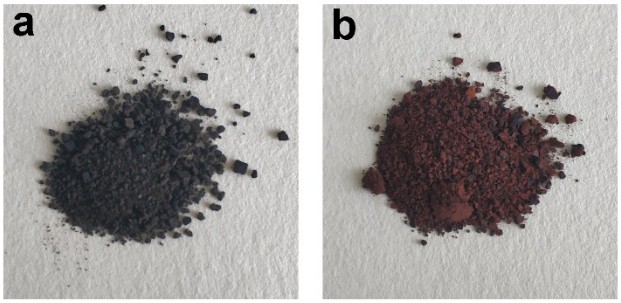


Fig. S2 (a), (b) Photographs of as-synthesized PCN-224 and MPDB-PCN, respectively.

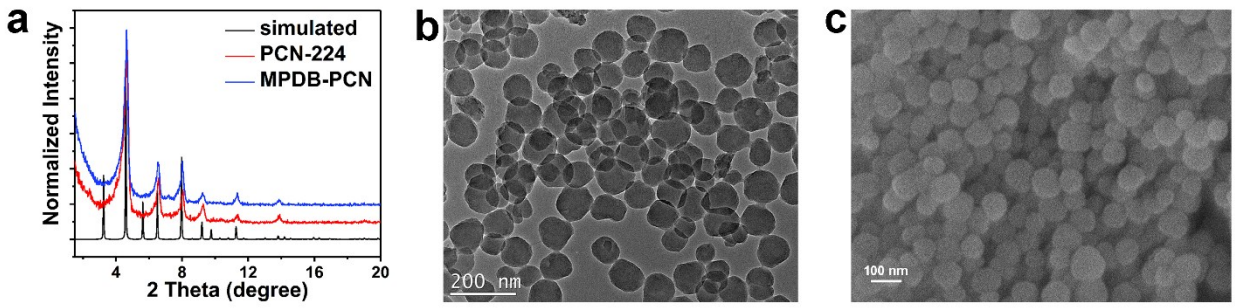


Fig. S3 (a) The PXRD patterns of simulated PCN-224, as-synthesized PCN-224, and MPDB-PCN; (b) TEM and (c) SEM of images of as-synthesized PCN-224.

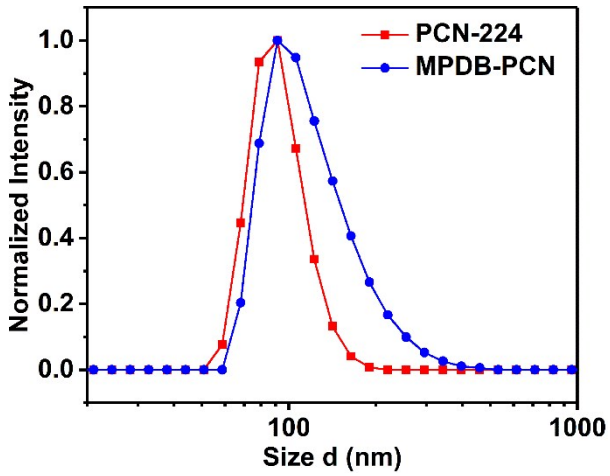


Fig. S4 Dynamic light scattering (DLS) measurement of PCN-224 and MPDB-PCN.

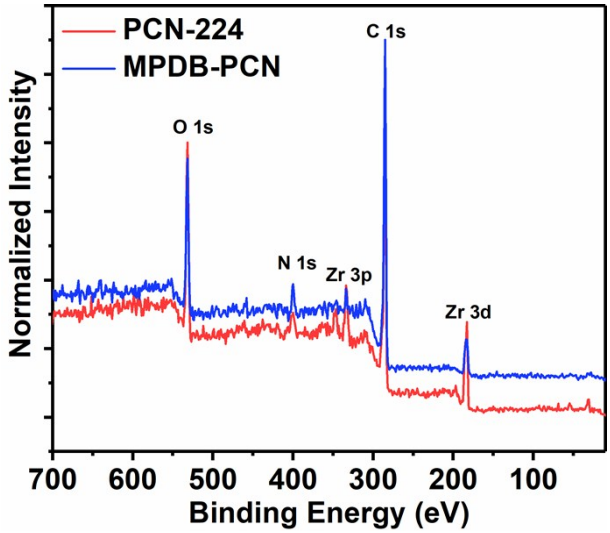


Fig. S5 XPS spectra of PCN-224 and MPDB-PCN.

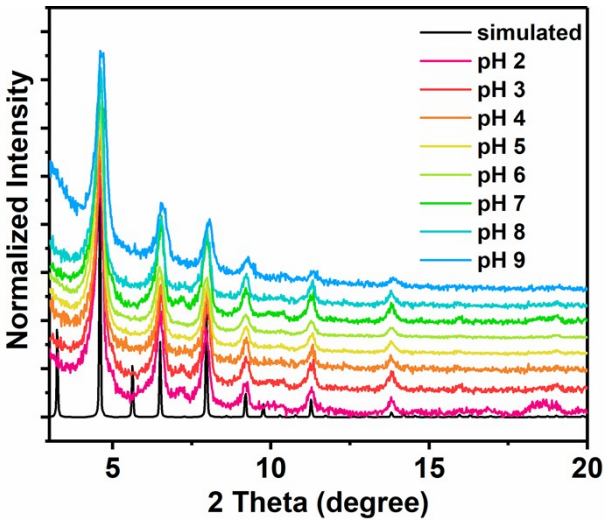


Fig. S6 PXRD patterns of simulated PCN-224, MPDB-PCN samples soaked in aqueous solutions with pH values of 2, 3, 4, 5, 6, 7, 8 and 9 for 24 h.

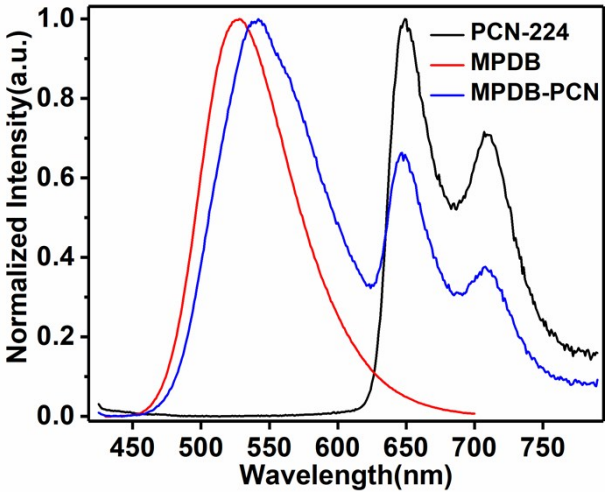


Fig. S7 Respective fluorescence emission spectrum (λ_{ex} = 405 nm) of PCN-224, MPDB, MPDB-PCN in solution.

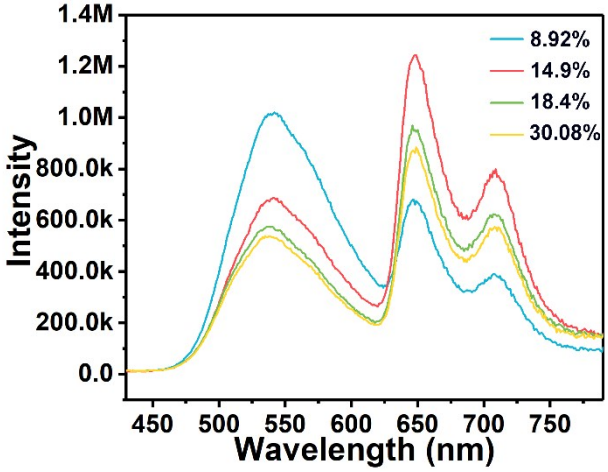


Fig. S8 Fluorescence emission spectrum (λ_{ex} = 405 nm) of MPDB-PCN (20 mg L^{-1}) with different MPDB load amounts at pH = 5.

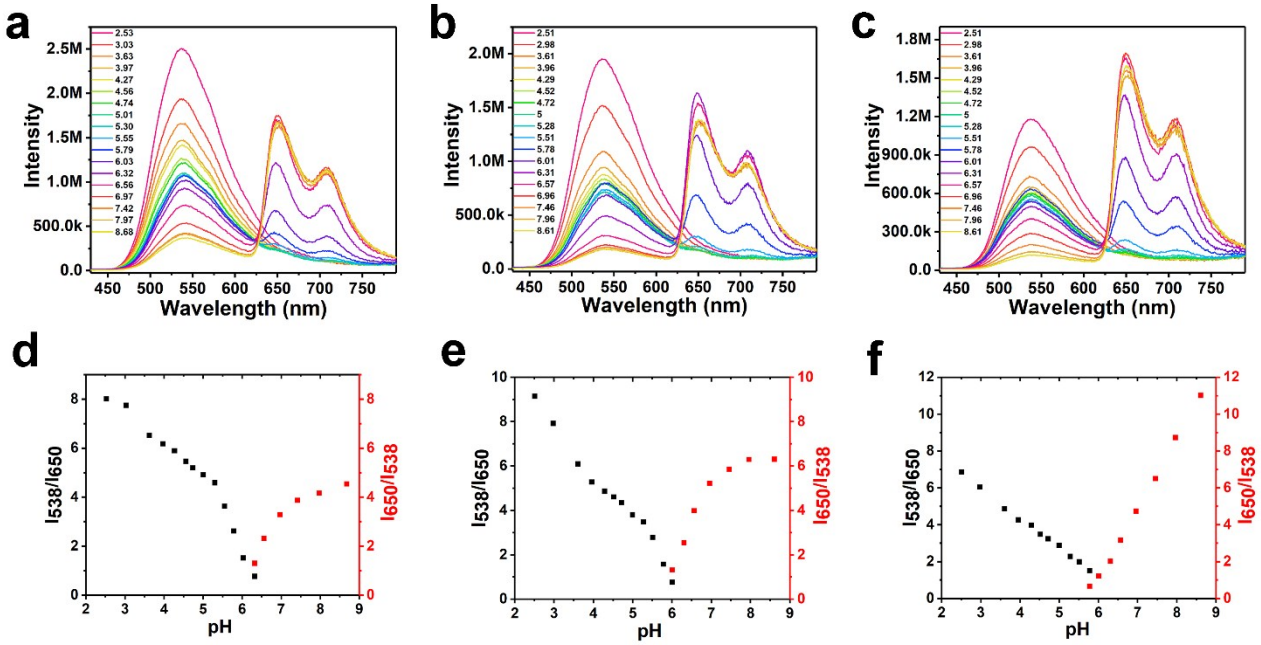


Fig. S9 pH-dependent emission spectra (λ_{ex} = 405 nm) of MPDB-PCN (20 mg L^{-1}) in the pH value from 2.51 to 8.61 in the HEPES buffer solution with MPDB (a) 30.08%, (b)18.4%, (c) 8.92% loading; relative fluorescence intensity (I_{538}/I_{650} and I_{650}/I_{538}) versus pH values with MPDB (d) 30.08%, (e)18.4%, (f) 8.92% loading.

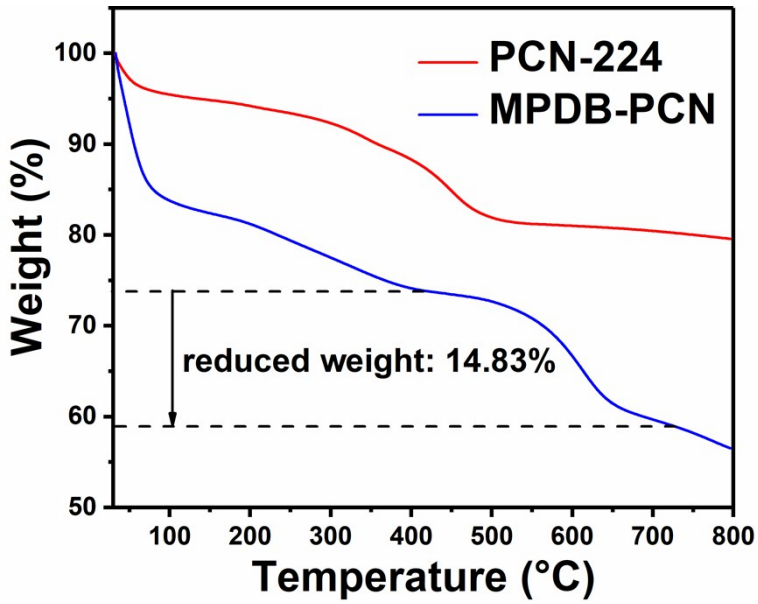


Fig. S10 Thermogravimetric analysis (TGA) curves of PCN-224 and MPDB-PCN.

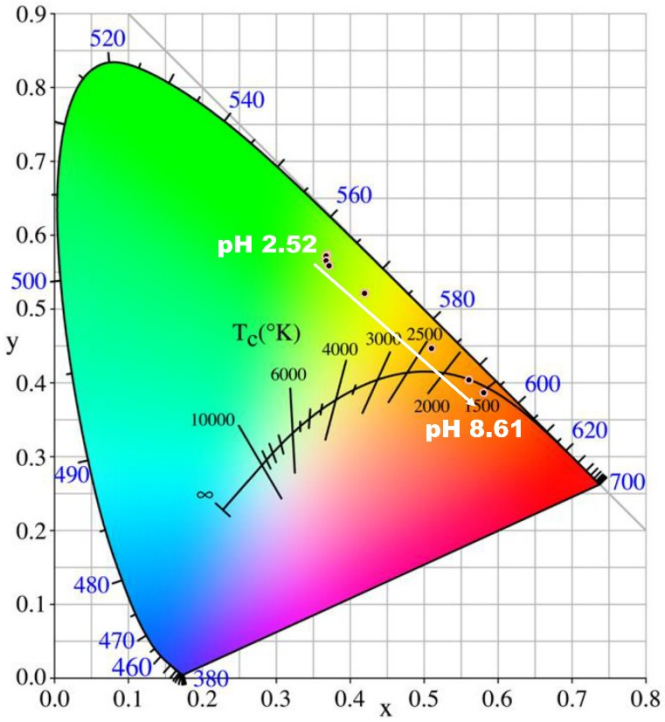


Fig. S11 CIE chromaticity coordinates diagram showing fluorescent color change of MPDB-PCN (20 mg L^{-1}) in pH = 2.52 to pH = 8.61.

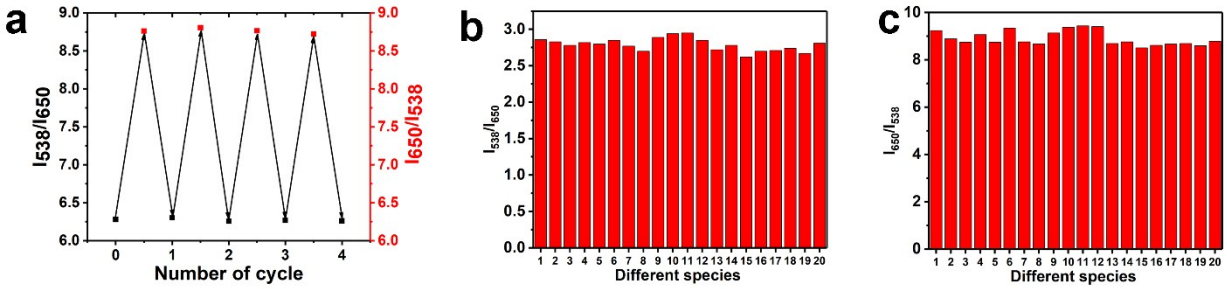


Fig. S12 (a) The response reversibility of MPDB-PCN between pH 3.0 and 8.0; Relative fluorescence intensity (I_{538}/I_{650}) of MPDB-PCN in pH= 5.0 (b) and in pH = 8.0 aqueous solutions in the presence different species (1-K^+, 2-Na^+, 3-Ca^{2+}, 4-Mg^{2+}, 5-Ba^{2+}, 6-Zn^{2+}, 7-Al^{3+}, 8-Ni^{2+}, 9-Fe^{2+}, 10-Fe^{3+}, 11-Cu^{2+}, 12-Cd^{2+}, 13-SO_4^{2-}, 14-NO_3^-, 15-SO_3^{2-}, 16-CO_3^{2-}, 17-Ac^-, 18-HCO_3^-, 19-glucose, 20-blank).

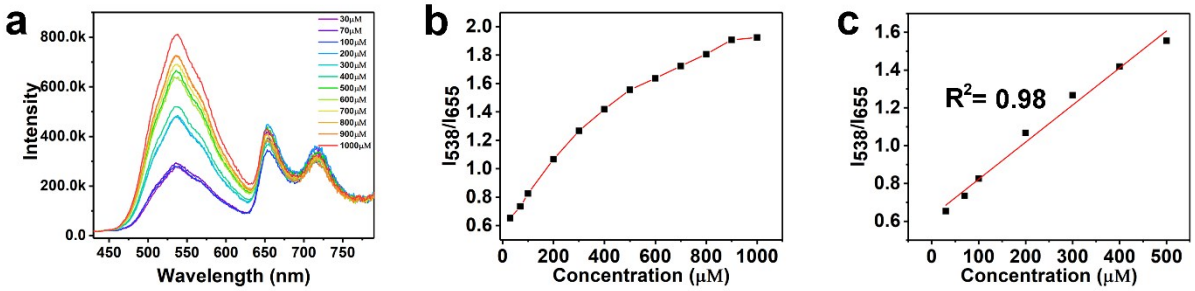


Fig. S13 (a) Fluorescence emission spectra (λ_{ex} = 405 nm) of MPDB-PCN (20 mg L^{-1}) with the addition of different concentrations of aqueous solutions of 3-NPA; (b) I_{538}/I_{650} versus concentrations of 3-NPA curve in aqueous solutions (30-1000 μM); (c) the linear variation of I_{538}/I_{650} versus concentrations of 3-NPA in low concentrations aqueous solutions (30-500 μM).

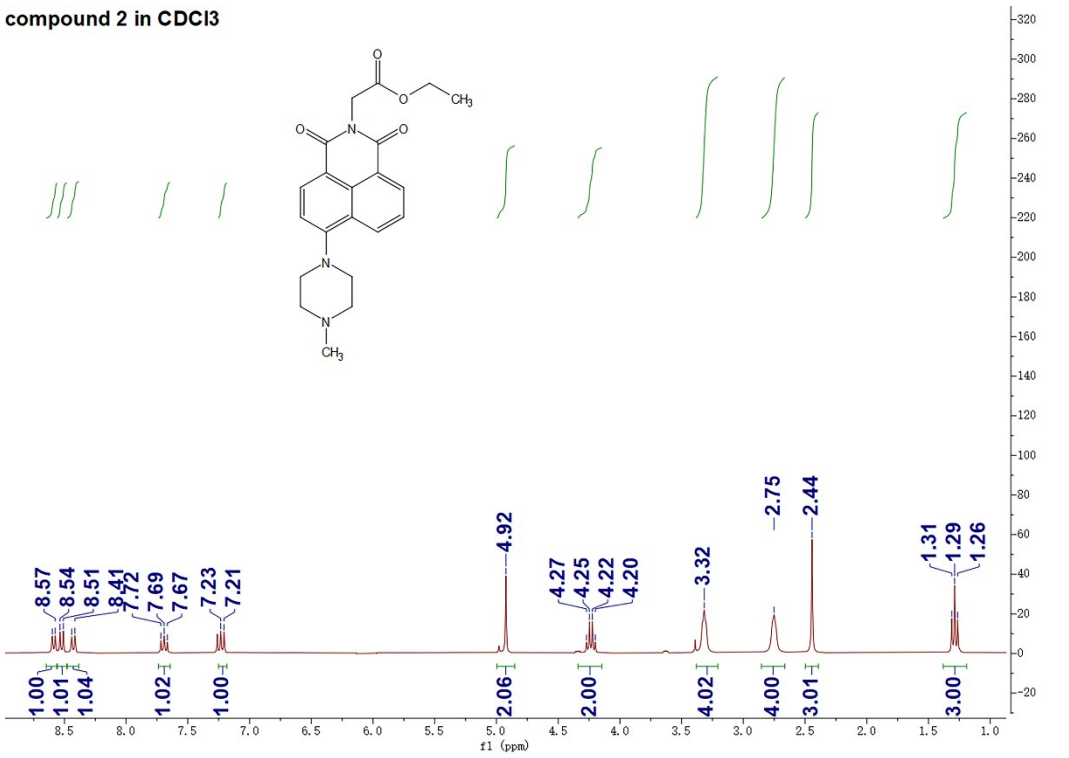


Fig. S14 ^{1}H NMR spectrum of compound 2 in $CDCl_3$ solution.

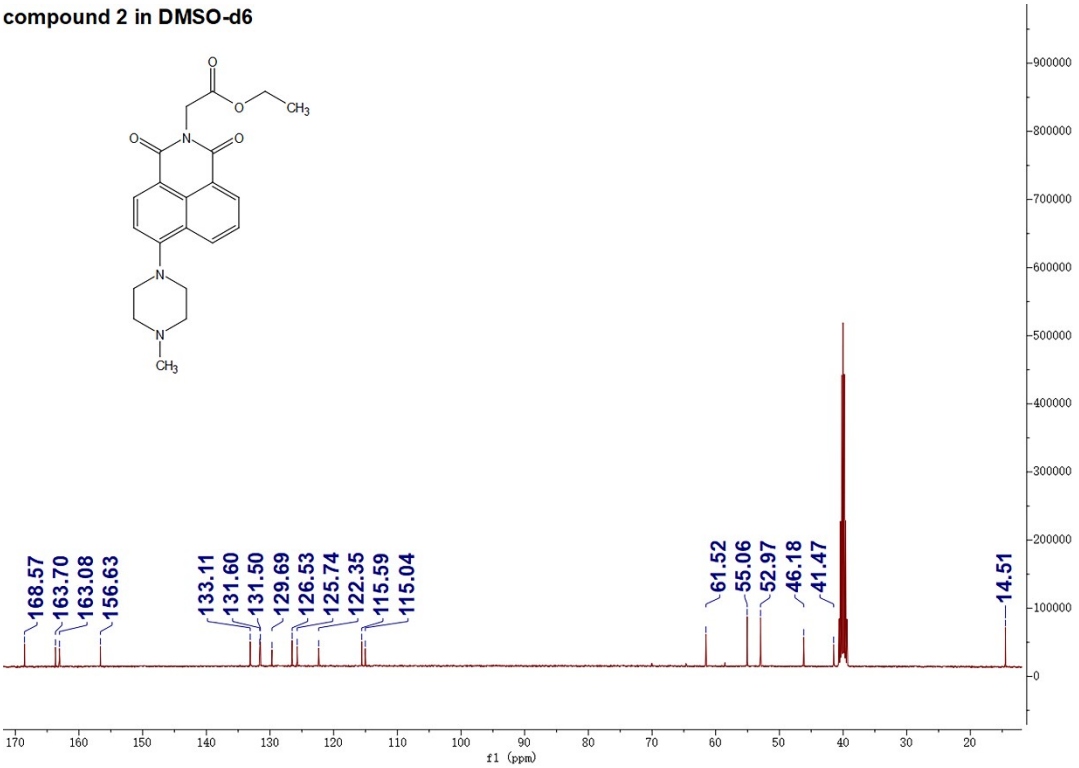


Fig. S15 ^{13}C NMR spectrum of compound 2 in DMSO-d_6 solution.

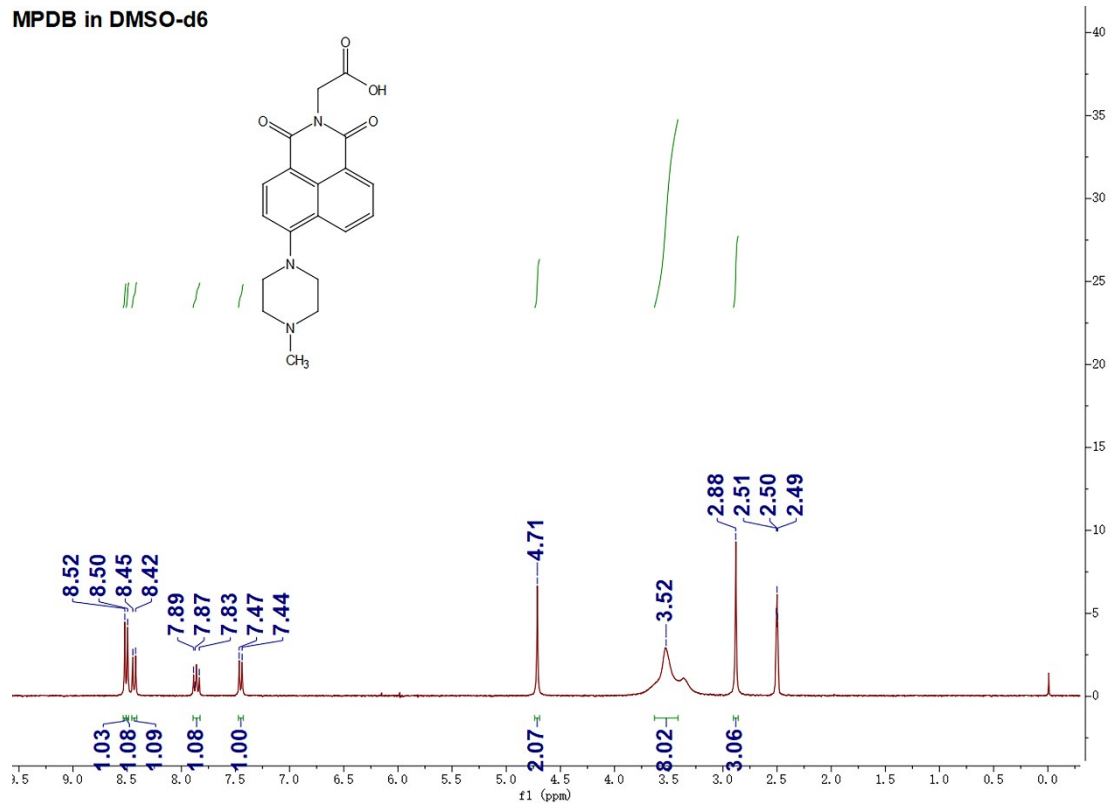


Fig. S16 ^{1}H NMR spectrum of compound MPDB in DMSO-d_6 solution.

Fig. S17 ^{13}C NMR spectrum of compound MPDB in DMSO-d_6 solution.

References

1. X. Liu, Q. Qiao, W. Tian, W. Liu, J. Chen, M. J. Lang and Z. Xu, *J. Am. Chem. Soc.*, 2016, **138**, 6960-6963.
2. J. Park, Q. Jiang, D. Feng, L. Mao and H.-C. Zhou, *J. Am. Chem. Soc.*, 2016, **138**, 3518-3525.