Supplementary Information

Stimulus-responsive reversible thermochromism and exciplex emission of a Zn(II) complex and selective sensing of NH_3 gas

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Experimental section

Materials

The ligand *N*-(*p*-methylphenyl)iminodiacetic acid (H_2MPIDA) was prepared by the reaction of *p*-methylaniline with chloroacetic acid under basic condition according to the literature method.[1] All other reagents were commercially purchased and used without further purification.

Instruments

The elemental analysis was carried out using a Perkin Elmer 2400II Elemental Analyzer. FT-IR spectra (KBr pellets) were recorded on a Perkin Elmer Spectrum RX I spectrometer in the 4000-400 cm^{-1} region. NMR spectra were obtained with a Bruker Avance 400 MHz spectrometer. Single-crystal X-ray diffraction measurements were conducted on an Oxford Diffraction Gemini E diffractometer. The structure was solved by direct methods and refined by a full-matrix least-squares technique on F^2 using SHELXL-2014 programs.[2] Powder XRD patterns were recorded by using a D8 Focus diffractometer equipped with Cu-K_α radiation (λ =1.5406 Å). Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer Diamond TG/DTA Analyzer in an air atmosphere in the temperature range 30 - 800 ^oC (heating rate 10 $^oC \cdot min^{-1}$). Electronic absorption spectra were recorded on a Shimadzu UV-3101PC UV-VIS-NIR Spectrometer. Emission spectra were recorded on an Edinburgh FLS920 spectrometer, using a front-face solid sample configuration. The emission lifetimes were recorded using the time-correlated single-photo-counting method, and the excitation source is an ns flash lamp filled with hydrogen. The SEM picture was taken with an S-2500 machine. ESR spectra were recorded by using an X-band Bruker A300 spectrometer. The frequency of microwaves was 9.86 GHz, the magnetic field was 100 KHz, the center sweeping field was at 3500 G and the modulation amplitude was set as 5 G. The pictures of the color changes of a single crystal were taken with a Leica DM2500 microscope.

Synthesis of $[Zn_2(MPIDA)_2(4,4'\text{-bipy})(H_2O)_4]\cdot 3H_2O$ (1)

A solution of $Zn(NO_3)_2\cdot 6H_2O$ (0.146 g, 0.5 mmol) in 10 mL of water/ethanol (1:1, *V/V*) was added dropwise to a solution of H_2MPIDA (0.112 g, 0.5 mmol) in 10 mL of water/ethanol (1:1, *V/V*). After stirring for 30 min, 4,4'-bipy (0.078 g, 0.5 mmol) was added to the reaction mixture which was further stirred for 1 h at 80 ^oC. The resulting mixture was filtered to produce a yellowish filtrate. Colorless crystals (0.088 g, yield 41% based on Zn) of **1** suitable for X-ray diffraction started to grow once the filtrate was cooled to room temperature. Anal. Calcd. for $C_{32}H_{44}Zn_2N_4O_{15}$, C 44.92; H 5.18; N 6.55%. Found: C 44.85; H 5.33; N 6.51%; IR (KBr, cm^{-1}): 3401(s), 2928(w), 1610(s), 1515(m), 1397(s), 1293(m), 806(s), 633(m).

Gas sensing experiments: ca. 5 mg of **1B** powder was dispersed in 0.1 mL of CH_2Cl_2, and drop-cast onto a quartz plate or a piece of filter paper, and the quartz plate/test paper was dried at 50 ^oC before

use.

The quartz plate was put into a 100-mL Schlenk flask, which was evacuated and ca. 10 mL of gas was injected with a syringe. After ca. 5 min. the quartz plate was taken out and the emission spectrum was measured. In the case of aqueous ammonia, the quartz plate was put into a closed bottle where a few drops of aqueous ammonia were present and the color change of **1B** was observed within 1 min.

In the examination of response time of ammonia, a piece of test paper was put in a capped cuvette and ca. 1 mL of ammonia gas was injected with a syringe and the time-resolved emission spectra were measured immediately after the injection of ammonia.

References

1 a) D. K. Patel, D. Choquesillo-Lazarte, J. M. Gonzalez-Perez; A. Dominguez-Martin, A. Matilla-Hernandez, A. Castineiras and J. Niclos-Gutierrez, *Polyhedron*, 2010, **29**, 683; b) E. Bugella-Altamirano, D. Choquesillo-Lazarte, J. M. Gonzalez-Perez, M. J. Sanchez-Moreno, R. Marin-Sanchez, J. D. Martin-Ramos, B. Covelo, R. Carballo, A. Castineiras, J. Niclos-Gutierrez, *Inorg. Chim. Acta*, 2002, **339**, 160.

2 a) G. M. Sheldrick, *Acta Cryst.*, 2015, C71, 3; b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

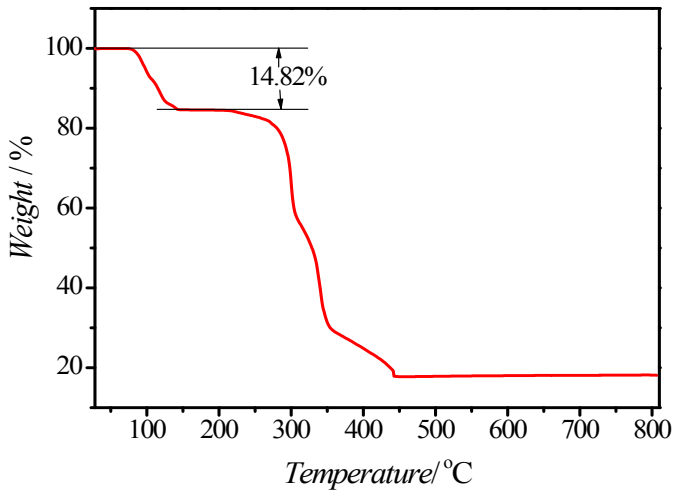

Figure S1. TG curve of **1** under an air atmosphere (temperature range 30 - 800 °C).

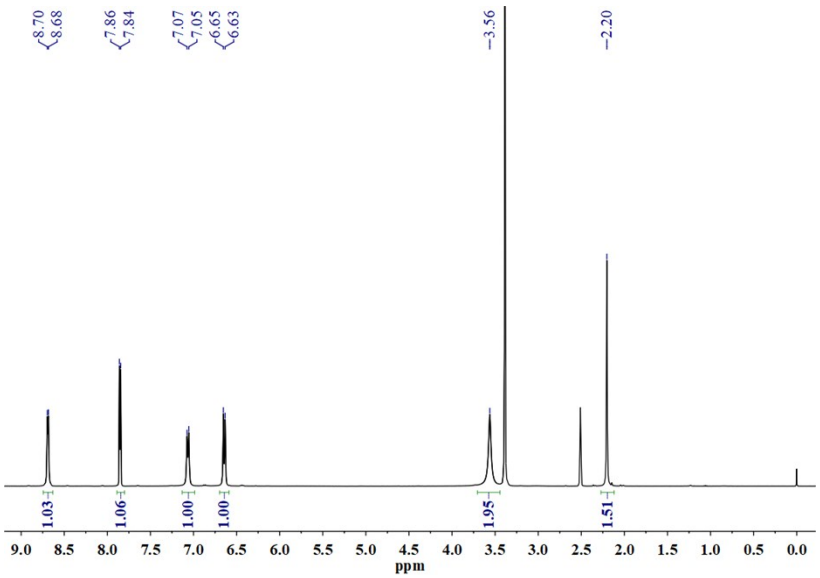

Figure S2. ^{1}H-NMR spectrum of the completely rehydrated form of **1B** in DMSO-d_6.

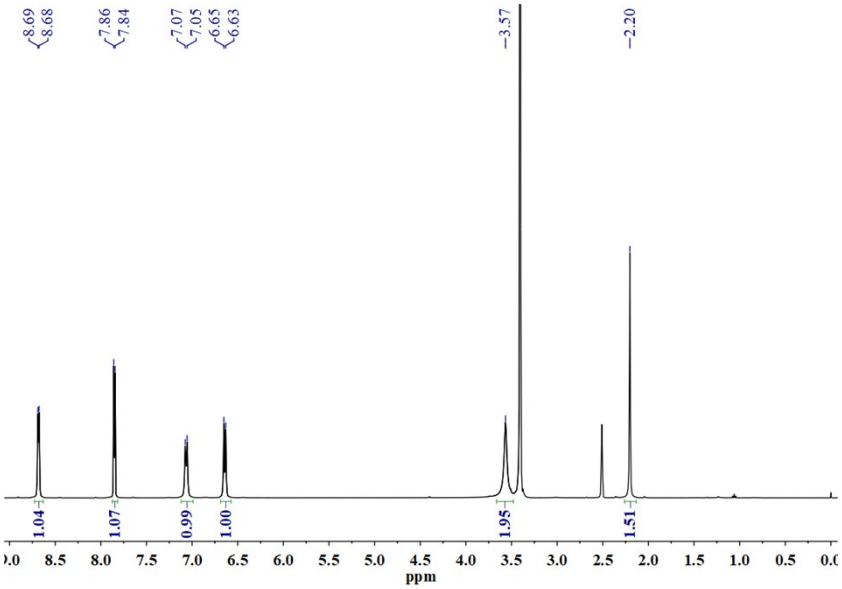

Figure S3. ^{1}H-NMR spectrum of **1A'** in DMSO-d_6.

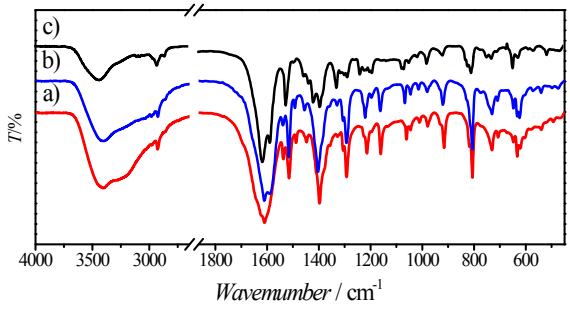

Figure S4. FT-IR spectra of **1** (a), **1A'** (b), and **1B** (c).

Table S1. The absorption peaks of the COO moieties in **1**, **1A'** and **1B**.

Compound	v_{as} (COO)/cm^{-1}	v_s(COO)/cm^{-1}	Δv(COO)/cm^{-1}
1	1610	1397	213
1A'	1611	1404	207
1B	1613	1417	196

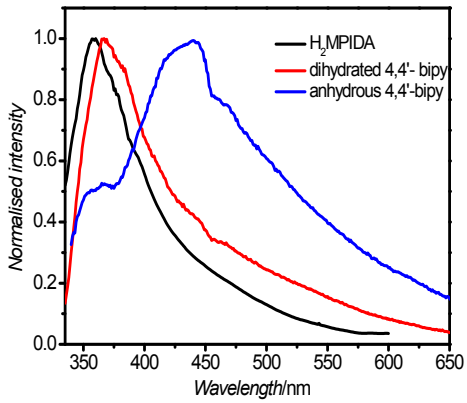

Figure S5. Emission spectra of the ligands H_2MPIDA, dihydrated 4,4′-bipy and anhydrous 4,4′-bipy upon excitation at 320 nm.

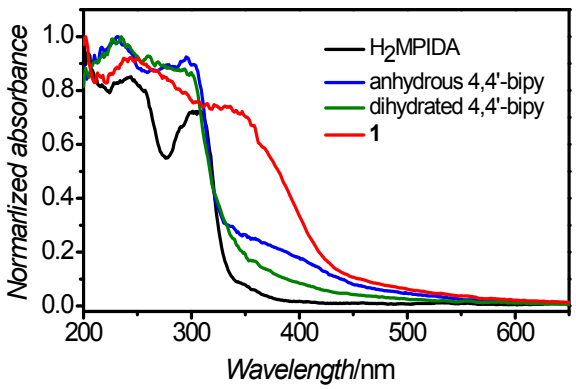

Figure S6. Solid state absorption spectra of **1** and the ligands.

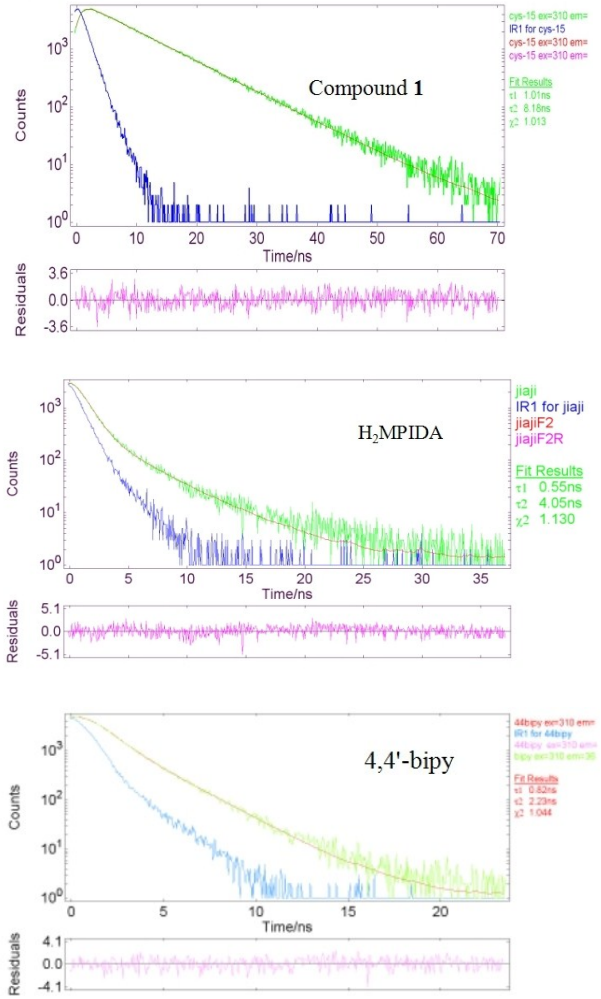

Figure S7. Fluorescence lifetime profiles of **1** and the ligands.

Table S2. Details of the average lifetime analysis of **1** and the ligands.

compound	λ_{em} (nm)	τ_i (ns)	B_i	$\tau_{average}$ (ns)	$\tau_{average} = \frac{B_1\tau_1^2 + B_2\tau_2^2}{B_1\tau_1 + B_2\tau_2}$
1	567	1.01	0.002271	7.73	
		8.18	0.04194		
H_2MPIDA	360	0.55	0.0949	1.09	
		4.05	0.002373		
4,4-bipy	366	0.82	0.054	1.32	
		2.23	0.011		

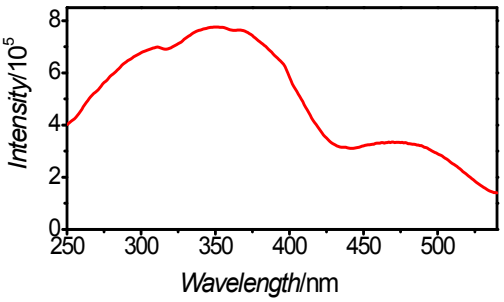

Figure S8. Solid state excitation spectrum of **1** with emission at 567 nm.

Equation S1 and S2. Formation of exciplex.

$$A + D \xrightarrow{h\nu_1} A^* + D \rightleftharpoons (A-D)^*_{EX} \qquad \text{(Equation S1)}$$

$$A + D \rightleftharpoons (A-D)_{CT} \xrightarrow{h\nu_2} (A-D)^*_{CT} \rightleftharpoons (A-D)^*_{EX} \qquad \text{(Equation S2)}$$

Where A and D are the two moieties to form exciplex, Ex: exciplex, CT: charge transfer.

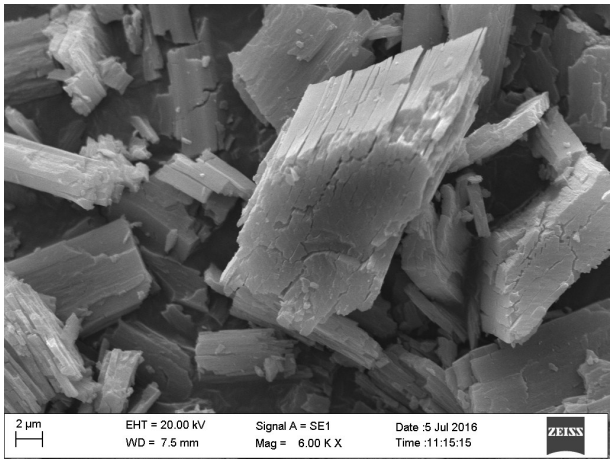

Figure S9. SEM image of **1B**.

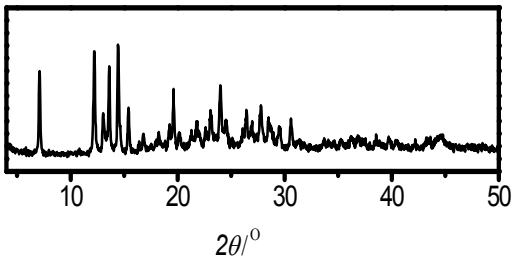

Figure S10. PXRD pattern of **1B-NH$_3$**.

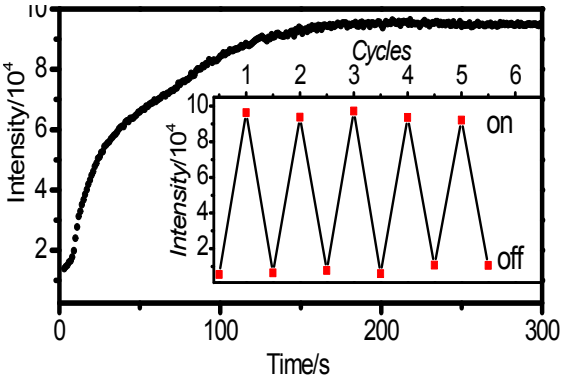

Figure S11. Emission intensity changes of **1B** when exposed to NH_3 with time and repeated cycles (inset) monitored at 570 nm.

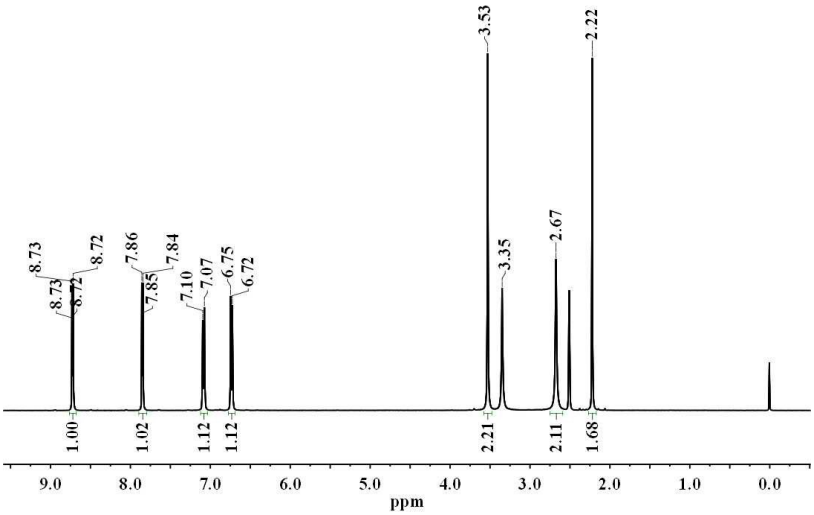

Figure S12. ^{1}H-NMR spectrum of **1B-NH$_3$** in DMSO-d_6.

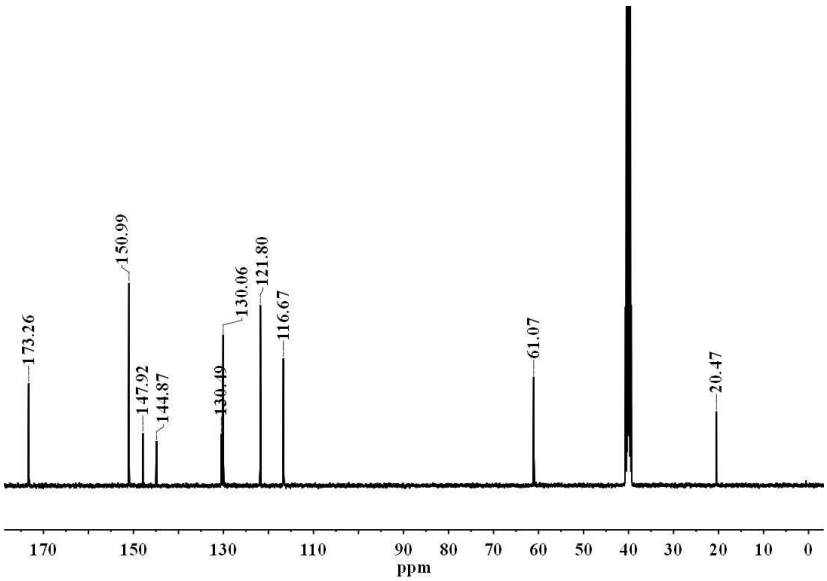

Figure S13. ^{13}C-NMR spectrum of **1B-NH$_3$** in DMSO-d_6.

Table S3. Crystal data and refinement parameters for **1**.

Empirical formula	$C_{32}H_{44}N_4O_{15}Zn_2$
Mr	855.450
crystal System	Monoclinic
space group	*C*2/c
a (Å)	26.1429(10)
b (Å)	7.5779(2)
c (Å)	18.5411(7)
α (°)	90
ß (°)	97.456(3)
γ (°)	90
V (Å^3)	3642.1(2)
Z	4
T (K)	291(2)
*D*c (g ·cm^{-3})	1.560
μ(mm^{-1})	1.393
F (000)	1776
θ_{max} (°)	26.37
λ(Mo Kα)(Å)	0.71073
tot. data	11598
unique data, R_{int}	3715, 0.0309
data [$I > 2\ \sigma(I)$]	2815
R	0.0324
R_w	0.0708
s	1.032
CCDC number	822713

Table S4. Selected bond lengths and angles of **1**.

Bond lengths (Å)		Bond angles (°)	
Zn1-O4	2.0122(15)	O4-Zn1-O6	97.13(7)
Zn1-O6	2.0200(16)	O4-Zn1-O2	151.76(6)
Zn1-O2	2.0382(14)	O6-Zn1-O2	110.39(7)
Zn1-O5	2.1373(18)	O4-Zn1-O5	90.80(7)
Zn1-N2	2.1428(18)	O6-Zn1-O5	85.71(8)
Zn1-N1	2.4384(18)	O2-Zn1-O5	85.24(7)
		O4-Zn1-N2	95.88(7)
		O6-Zn1-N2	89.27(7)
		O2-Zn1-N2	90.82(6)
		O5-Zn1-N2	172.10(7)
		O4-Zn1-N1	76.13(6)
		O6-Zn1-N1	171.82(8)
		O2-Zn1-N1	75.91(6)
		O5-Zn1-N1	89.72(7)
		N2-Zn1-N1	95.96(7)