Electronic Supplementary Information

A tetraphenylethene-based zinc complex as a sensitive DNA probe by coordination interaction

Zece Zhu, Li Xu, Hao Li, Xiang Zhou, Jingui Qin and Chuluo Yang*[a]

[a] *Department of Chemistry, Wuhan University, Wuhan 430072, P.R. China. Fax: (+)86-27-68756757; E-mail: clyang@whu.edu.cn*

Experimental Details

Instrumentation. ^{1}H NMR and ^{13}C NMR spectra of **1**, **2**, TPEZn and TTAPE were measured on a MECUYRVX300 spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL III microanalyzer. Mass spectra were measured on a Micromass-ZQ mass spectrophotometer. UV–vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer.

Fluorescence Measurements. Subsequent fluorescence titration experiments were carried out at room temperature by addition of DNA or sodium salts of oxyacid dissolved in distilled water into the solutions of TPE probes. The solution of sodium pyrophosphate and DNA were prepared before measuring. All the solutions were mixed fully and then stood for 1-2 minutes before the fluorescence intensity were measured. All the titration experiments were done at least three times for calculating error bars.

Materials.

ssDNA was purchased from Sangon Biotech (Shanghai) Co., Ltd. The sequence of DNA was shown in Table S1.

Table S1. Synthetic ssDNA used in this study

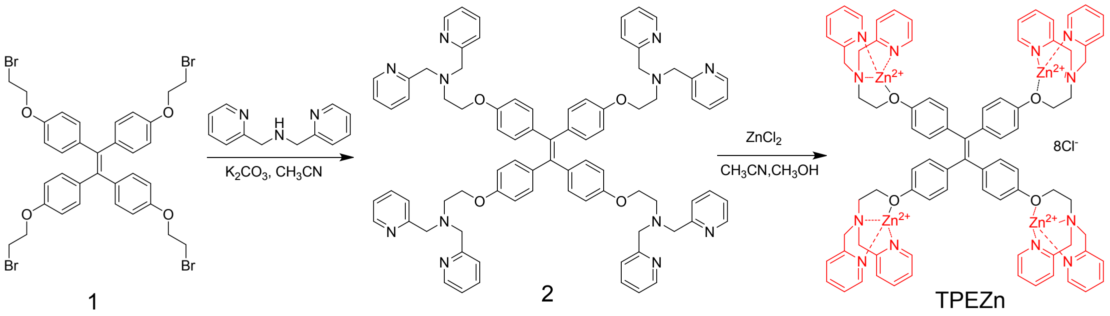
ID	sequence
X30	5'-GGTGCTAACT GGTGCTAACT GGTGCTAACT -3'
X20	5'-GGTGCTAACT GGTGCTAACT -3'
X10	5'-GGTGCTAACT-3'
Y10	5'-TGAGATCGGA-3'

1[1], TTAPE[1] and bis(pyridin-2-ylmethyl)amine (DPA)[2] were synthesized according to the reported literatures. All the other reagents were commercially available and used without further purification.

1,1,2,2-tetrakis(4-(2-bromoethoxy)phenyl)ethane (1) ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 6.92 (d, J = 8.1 Hz, 8H); 6.65 (d, J = 8.7 Hz, 8H); 4.23 (t, J = 6.3 Hz, 8H,); 3.62 (t, J = 6.3 Hz, 8H).

2,2'-dipicolylamine (DPA) ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.57(d, J = 4.2Hz, 2H); 7.65 (t, J = 7.5 Hz, 2H); 7.36 (d, J = 8.1 Hz, 2H); 7.17 (t, J = 6 Hz, 2H); 3.99 (s, 4H) ; 2.25 (br, 1H).

TTAPE ^{1}H NMR (300 MHz, CD_3OD), δ (ppm): 7.00-6.85 (m, 8H), 6.80-6.65 (m, 8H), 4.38 (br, 8H), 3.74 (br, 8H), 3.47 (q, J = 6.6 Hz, 24H), 1.36 (t, J = 6.6 Hz, 36H). ^{13}C NMR (75 MHz, CD_3OD), δ (ppm): 157.29, 140.12, 138.86, 133.65, 114.95, 62.53, 57.02, 54.92, 8.00. ESI-MS *m/z* $[M-2Br]^{2+}$: 535.



Scheme S1. The synthetic route of TPEZn.

Synthesis of 2. To a mixture of **1** (0.83 g, 1 mmol) and DPA (2.96 g, 14.8 mmol) in acetonitrile (100 ml) was added potassium carbonate (2.1 g, 15.2 mmol). The mixture was refluxed under stirring for 48 h. After filtration and solvent evaporation, the crude product was purified by a silica gel column using chloroform/methanol/triethylamine (40:1:0.1, v/v/v) as eluent to give **2** as yellow viscous liquid (0.7 g , yield: 53%) . ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.51 (d, J = 4.2 Hz, 8H), 7.62 (t, J = 7.5 Hz, 8H); 7.55 (d, J = 7.8 Hz, 8H); 7.13 (t, J = 6.0 Hz, 8H); 6.87 (d, J = 8.4 Hz, 4H); 6.57 (d, J = 8.7 Hz, 8H); 4.02 (t, J = 5.4 Hz, 8H); 3.95 (s, 16H); 3.00 (t, J = 5.4 Hz, 8H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 159.34, 156.75, 148.80, 138.06, 136.72, 136.35 , 132.33, 122.85, 121.88, 113.33, 65.69, 60.71, 52.93. ESI-MS *m/z* $[M+2H]^{2+}$: 650.

Synthesis of TPEZn. To a solution of $ZnCl_2$ (83 mg, 0.6 mmol) in 9 ml of methanol/acetonitrile (2:1, v/v) was added dropwise methanol solution (10 ml) of **2** (155 mg, 0.12 mmol). The precipitate was collected by filtration, then washed with methanol and dried overnight in vacuo to give of TPEZn as pale yellow powder (136 mg, yield: 61%). ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 8.84 (br, 8H), 8.01 (t, J = 7.5 Hz, 8H), 7.58 (m, 16H), 6.70 (d, J = 8.1 Hz, 8H), 6.56 (d, J = 8.1 Hz, 8H), 4.27 (br, 16H), 3.96 (br, 8H), 2.90 (br, 8H). ^{13}C NMR (75 MHz, DMSO-d_6), δ (ppm): 156.56, 156.51, 156.35, 155.14, 148.61, 141.10, 137.06, 132.39, 124.87, 114.11, 64.11, 57.61, 52.85. Anal. Calcd for $C_{82}H_{80}Cl_8N_{12}O_4Zn_4\cdot$ $0.5ZnCl_2$: C, 51.54; H, 4.22; N, 8.80; Found: C, 51.28; H, 4.25; N, 8.81.

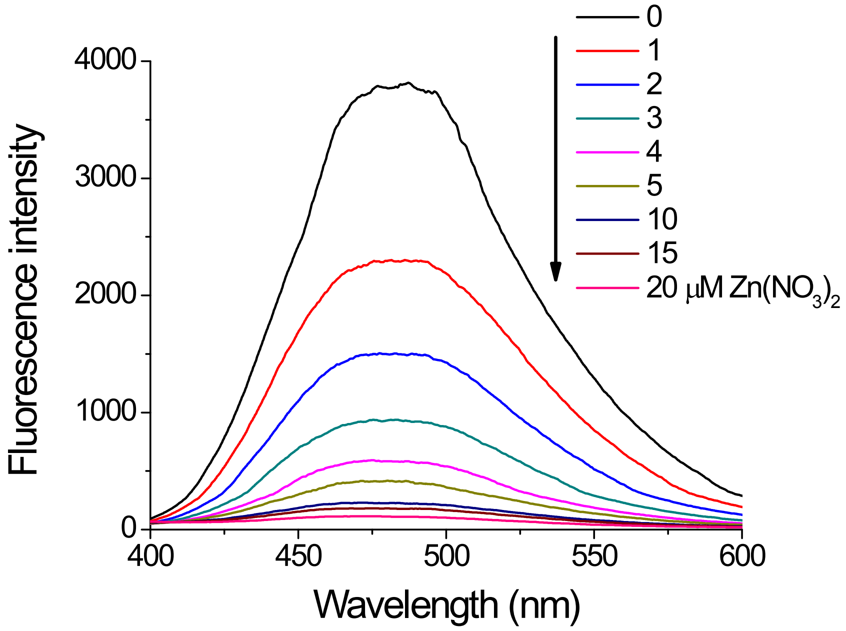


Figure S1. Fluorescence spectra of **2** (5 μM) upon the addition of $Zn(NO_3)_2$ in H_2O/DMSO (99:1, v/v) solutions. λ_{ex} = 330 nm.

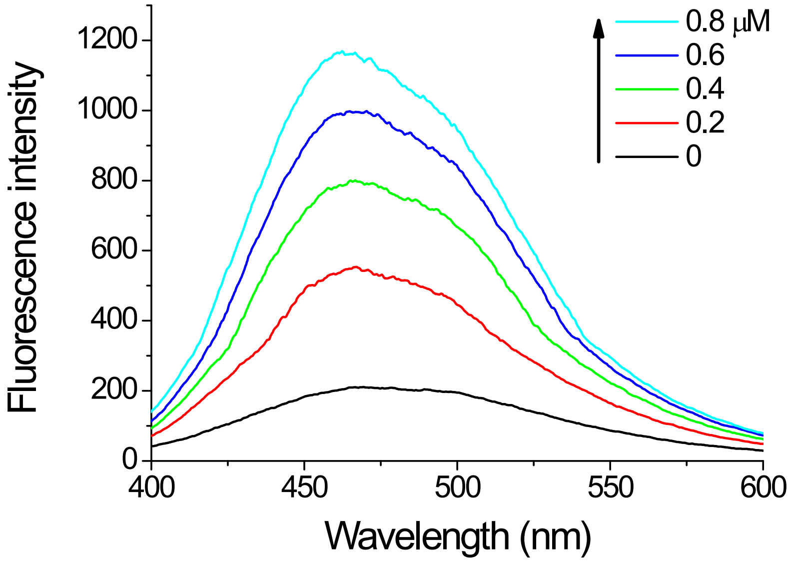


Figure S2. Fluorescence spectra of TPEZn (5 μM) upon the addition of DNA in H_2O/DMSO (99:1, v/v) solutions. $[Zn(NO_3)_2]$ = 0.1 mM. λ_{ex} = 330 nm. ssDNA was Y10.

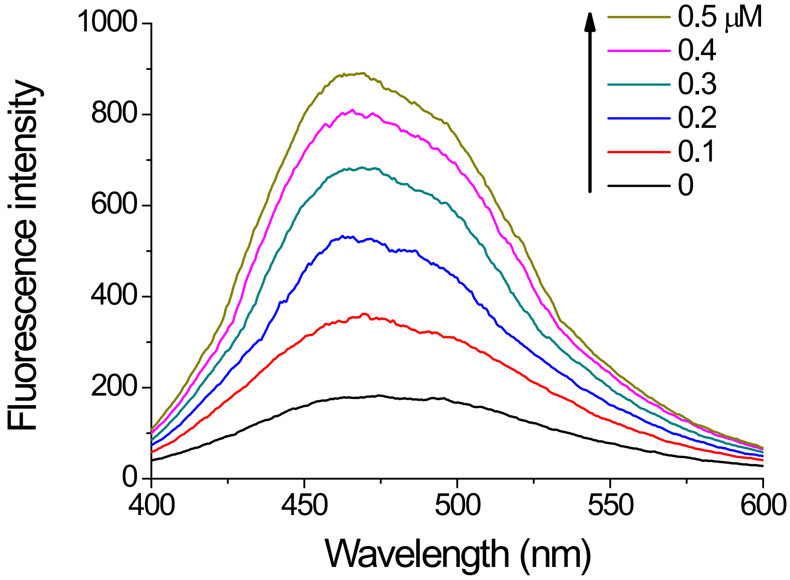


Figure S3. Fluorescence spectra of TPEZn (5 μM) upon the addition of DNA in H_2O/DMSO (99:1, v/v) solutions. $[Zn(NO_3)_2]$ = 0.1 mM. λ_{ex} = 330 nm. DNA was hybridized dsDNA of X10 and Y10.

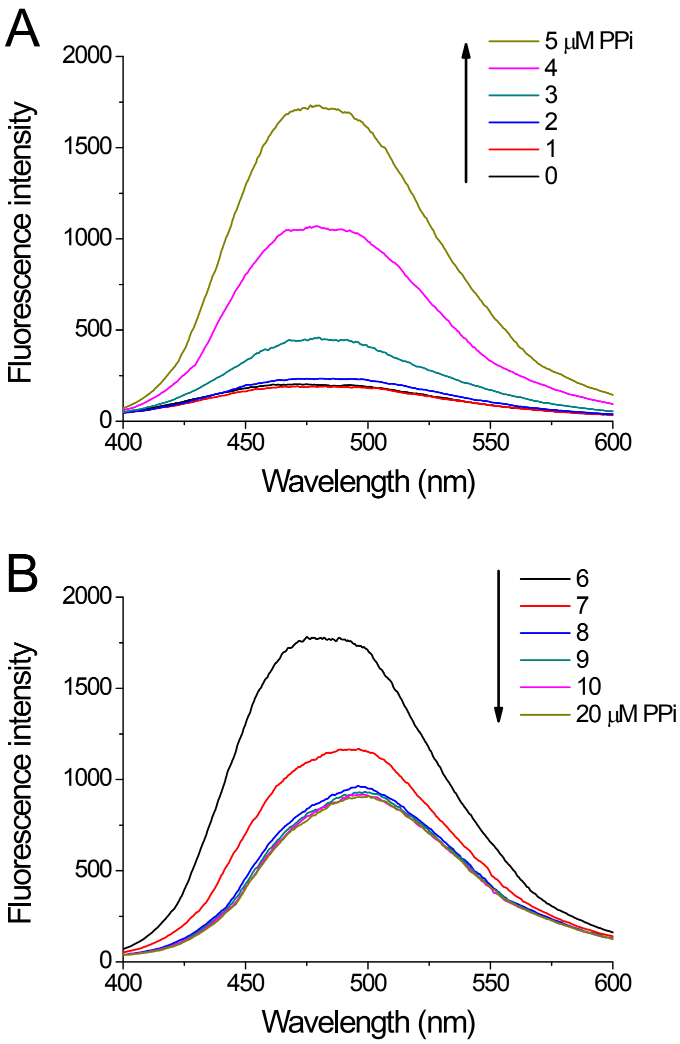


Figure S4. Fluorescence spectra of TPEZn (5 μM) upon the addition of PPi in H_2O/DMSO (99:1, v/v) solutions. $[Zn(NO_3)_2]$ = 0.1 mM. λ_{ex} = 330 nm.

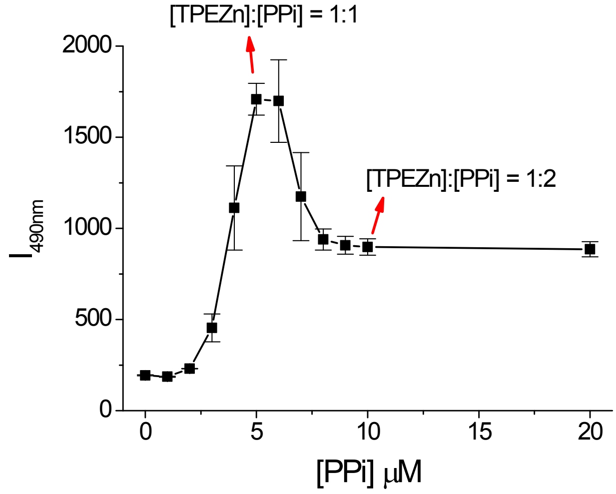


Figure S5. Fluorescence intensity of TPEZn (5 μM) vs. [PPi] in H_2O/DMSO (99:1, v/v) solutions. $[Zn(NO_3)_2]$ = 0.1 mM. λ_{ex} = 330 nm. λ_{em} = 490 nm.

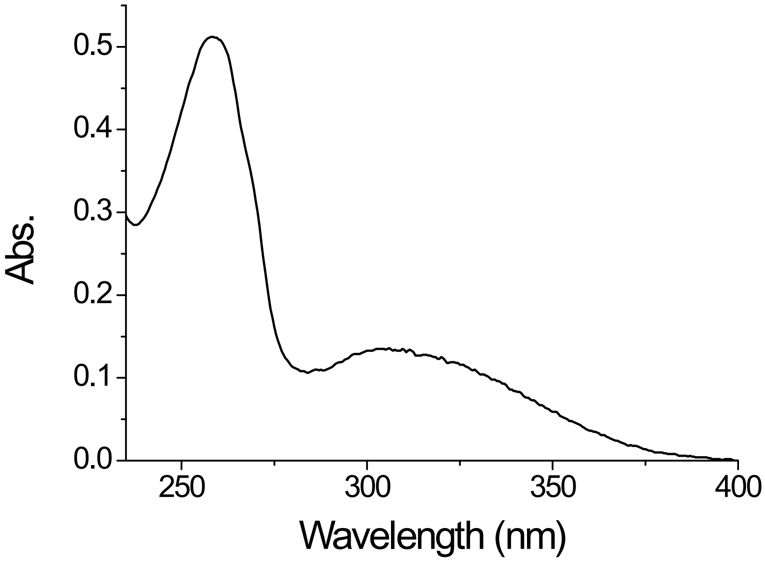


Figure S6. Absorption spectrum of TPEZn (10 μM) in water at room temperature.

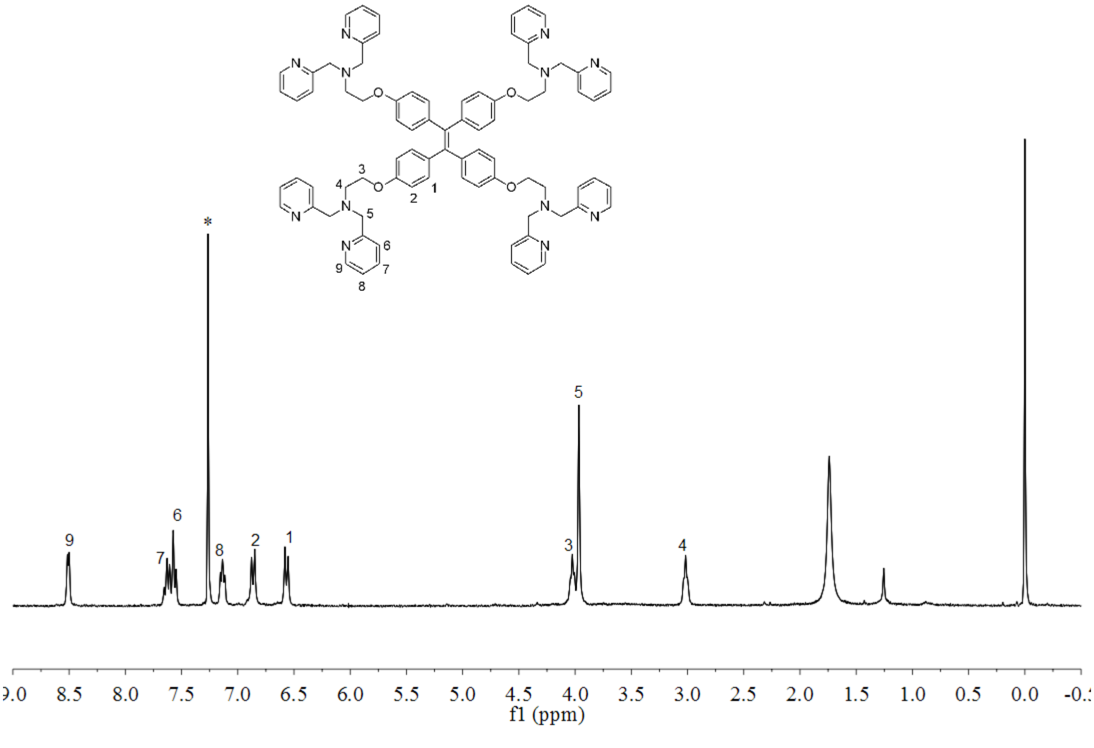


Figure S7. ^{1}H-NMR spectrum of 2 in $CDCl_3$

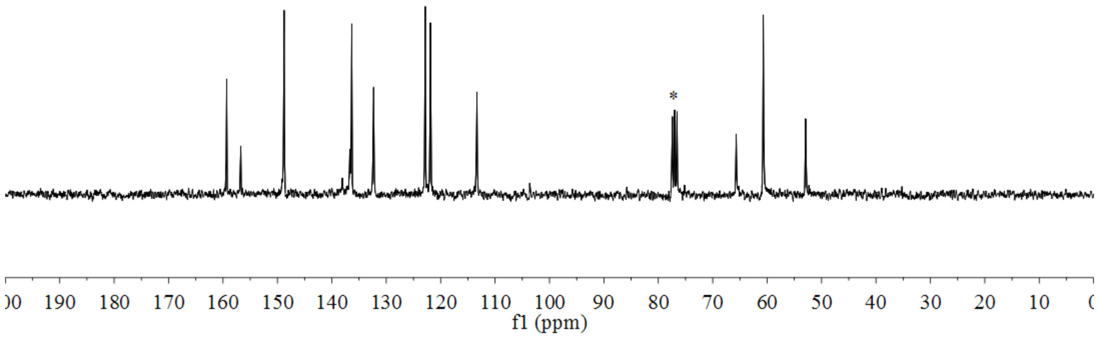


Figure S8. ^{13}C-NMR spectrum of 2 in $CDCl_3$

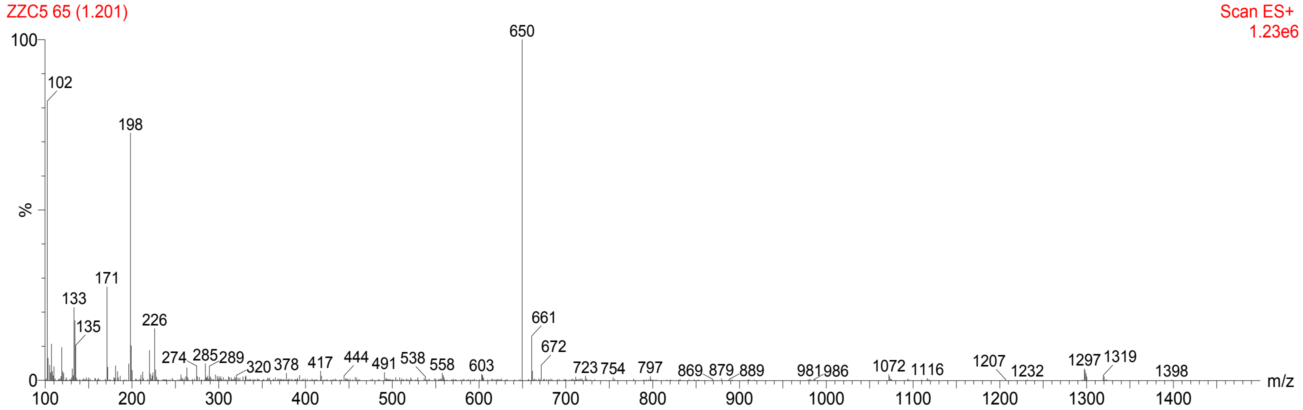


Figure S9. ESI-MS of 2. $[M+2H]^{2+}$: 650; $[M+H+Na]^{2+}$: 661; $[M+2Na]^{2+}$: 672.

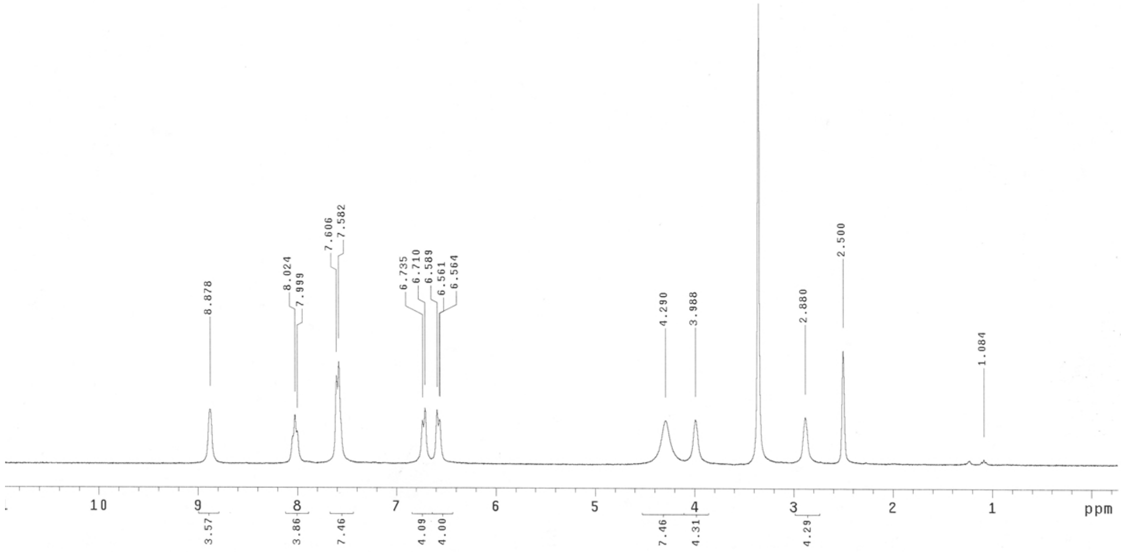


Figure S10. ^{1}H-NMR spectrum of TPEZn in DMSO-d_6

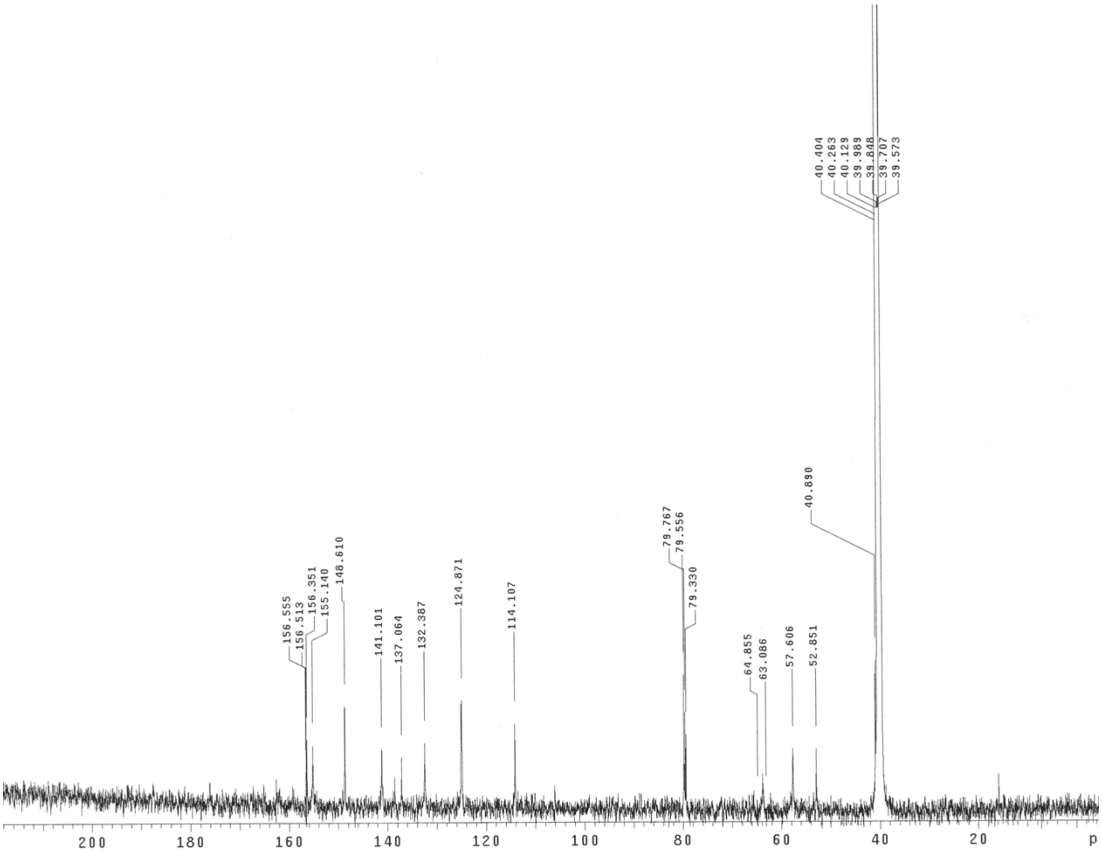


Figure S11. ^{13}C-NMR spectrum of TPEZn in DMSO-d_6

References

1, Y. Hong, M. Häuβler, J. W. Y. Lam, Z. Li, K. K. Sin, Y. Dong, H. Tong, J. Liu, A. Qin, R. Renneberg, B. Z. Tang, *Chem. Eur. J.* 2008, 14, 6428-6437.

2, W. A. Chomitz，S. G. Minasian, A. D. Sutton, J. Arnold, *Inorg. Chem*. 2007, 46, 7199-7209.