

## Supporting information

### A Pyrene-Functionalized Zinc(II)-BPEA Complex: Sensing and Discrimination of ATP, ADP and AMP†

Qin-chao Xu,<sup>a</sup> Hai-juan Lv,<sup>a</sup> Zi-qi Lv,<sup>a</sup> Min Liu,<sup>a</sup> Yang-jie Li,<sup>a</sup> Xiang-feng Wang,<sup>b</sup> Yuan Zhang<sup>a,c</sup> and Guo-wen Xing<sup>a\*</sup>

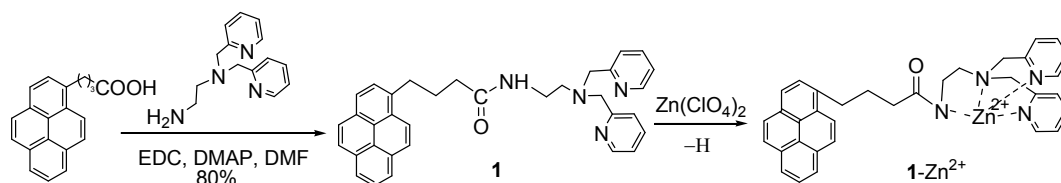
<sup>a</sup>Department of Chemistry, Beijing Normal University, Beijing 100875, China.

<sup>b</sup>Analytical and Testing Center, Beijing Normal University, Beijing, 100875, China.

<sup>c</sup>Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, College of Chemistry, Beijing Normal University, Beijing 100875, China

#### Experimental Section

**General.** All chemicals were purchased as reagent grade and used without further purification. The reactions were monitored by analytical thin-layer chromatography (TLC) on silica gel F<sub>254</sub> glass plates and visualized under UV light (254 and 365 nm) and/or by staining with ninhydrin. Flash column chromatography was performed on silica gel (200–300 mesh). <sup>1</sup>H NMR spectra were recorded with a Bruker Avance III 400 MHz NMR spectrometer at 20 °C. Chemical shifts (in ppm) were determined relative to tetramethylsilane ( $\delta = 0$  ppm) in deuteriated solvents. Coupling constants in Hz were measured from the one-dimensional spectra. <sup>13</sup>C NMR spectra were recorded with the 400 MHz NMR spectrometer (100 MHz) and calibrated with CDCl<sub>3</sub> ( $\delta = 77.23$  ppm). High-resolution mass spectra were recorded with Waters LCT Premier XE mass spectrometer. Low-resolution mass spectra were determined by Agilent 7890A GC-5975CMS. Emission spectra were recorded with a GBC Cintra 10e UV/Vis spectrophotometer and a Varian Cary Eclipse spectro-fluorimeter, respectively, in a quartz cell with a 1 cm path length.

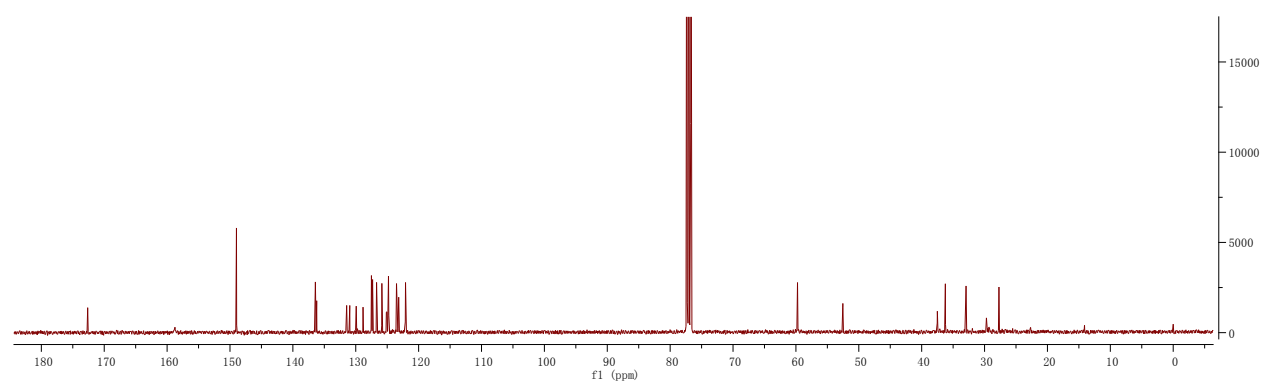
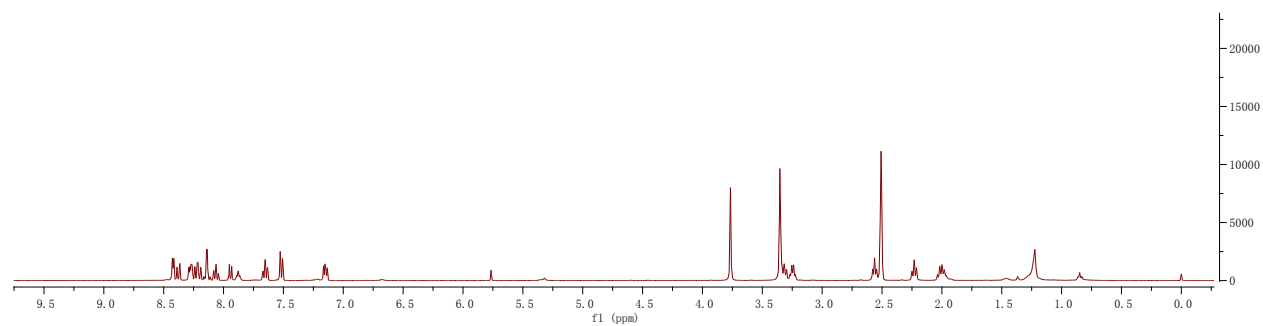


### Synthesis of Compound 1

1-Pyrenebutyric acid (85 mg, 0.295 mmol, 1.20 equiv.) was dissolved in DMF (2 ml), and BPEA (60 mg, 0.248 mmol, 1.00 equiv.) and EDC (85 mg, 0.494 mmol, 2.00 equiv.) were added. The reaction mixture was stirred in a 60 °C oil bath until the starting material had been completely consumed as detected by TLC. The solution was then allowed to cool to room temperature, and the DMF was evaporated under vacuum to leave a yellowish oil. The crude oil was then diluted with DCM (150 mL), washed with saturated NaCl solution, and dried over  $\text{MgSO}_4$ . After removal of the solvent, the mixture was purified by column chromatography ( $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH} = 30/1$ ) to give **1** (102 mg, 0.199 mmol, 80%) as a colorless solid. Mp. 193–194 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  8.42 (d,  $J = 4.7$  Hz, 2 H), 8.38 (d,  $J = 9.2$  Hz, 1 H), 8.26–8.29 (m, 2 H), 8.19–8.24 (m, 2 H), 8.11–8.16 (m, 2 H), 8.06 (t,  $J = 7.6$  Hz, 1 H), 7.94 (d,  $J = 7.8$  Hz, 1 H), 7.88 (t,  $J = 5.4$  Hz, 1 H), 7.65 (td,  $J = 7.7$  Hz,  $J = 1.4$  Hz, 2 H), 7.52 (d,  $J = 7.8$  Hz, 2 H), 7.15 (t,  $J = 5.2$  Hz, 2 H), 3.77 (s, 4 H), 3.32 (t,  $J = 7.8$  Hz, 2 H), 3.22–3.27 (m, 2 H), 2.56 (t,  $J = 6.4$  Hz, 2 H), 2.23 (t,  $J = 7.4$  Hz, 2 H), 1.98–2.04 (m, 2 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.6, 149.0, 136.4, 136.2, 131.4, 131.0, 129.9, 128.8, 127.50, 127.46, 127.3, 126.7, 125.9, 125.1, 125.0, 124.9, 124.79, 124.75, 123.5, 123.2, 122.1, 59.8, 52.5, 37.5, 36.2, 32.9, 29.7, 27.7. HRMS(ESI):  $m/z$  calcd for  $\text{C}_{34}\text{H}_{33}\text{N}_4\text{O}$  ( $[\text{M}+\text{H}]^+$ ): 513.2649; found: 513.2642.

**Spectroscopic Materials and Methods:** Stock solutions (0.5 mM) of zinc perchlorate were prepared in HEPES buffer (10 mM HEPES, pH = 7.4). Stock solutions (1.0 mM) of **1** were prepared in DMSO. **1-Zn<sup>2+</sup>** complex solutions were prepared *in situ* by mixing of stock solutions (0.5 mM) of zinc perchlorate (2.0 mL) and stock solutions (1.0 mM) of **1** (1.0 mL), and then diluted to 100 mL. All the fluorescence spectra of probes were also measured in HEPES buffer (10 mM HEPES, pH = 7.4, 1% (v/v) DMSO) and the excitation wavelength was 350 nm with excitation and emission slit widths of 5 nm at room temperature.

**NMR Materials and Methods:** Stock solutions (46.8 mM) of ATP, ADP, AMP and PPI were prepared in  $\text{D}_2\text{O}$ . Stock solutions (9.36 mM) of **1** were prepared in  $\text{DMSO-d}_6$ . **1-Zn<sup>2+</sup>** complex solutions were prepared *in situ* by mixing of stock solutions of **1** (9.36 mM, 5 mL) and equivalent  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (17.4 mg). **1-Zn<sup>2+</sup>-ATP** (ADP, AMP) solutions were prepared *in situ* by mixing of stock solutions (9.36 mM) of **1-Zn<sup>2+</sup>** (0.5 mL) and stock solutions (46.8 mM) of ATP (ADP, AMP and PPI) (0.05 mL).



**Fig. S1**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of **1**.

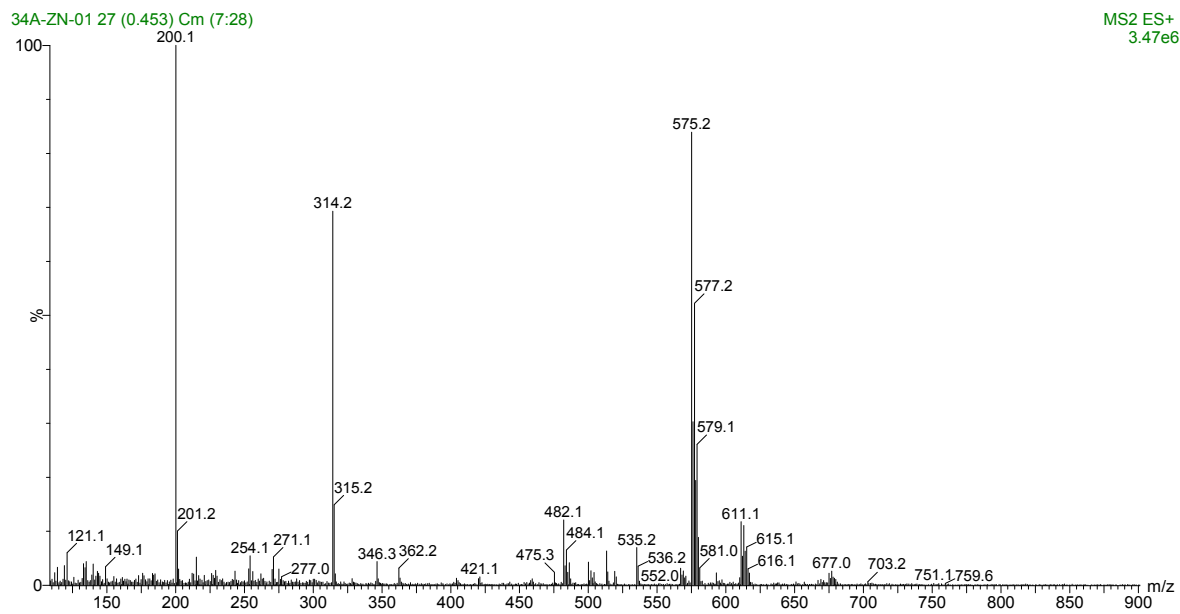


Fig. S2 ESI-MS spectrum of  $1\text{-Zn}^{2+}$ .

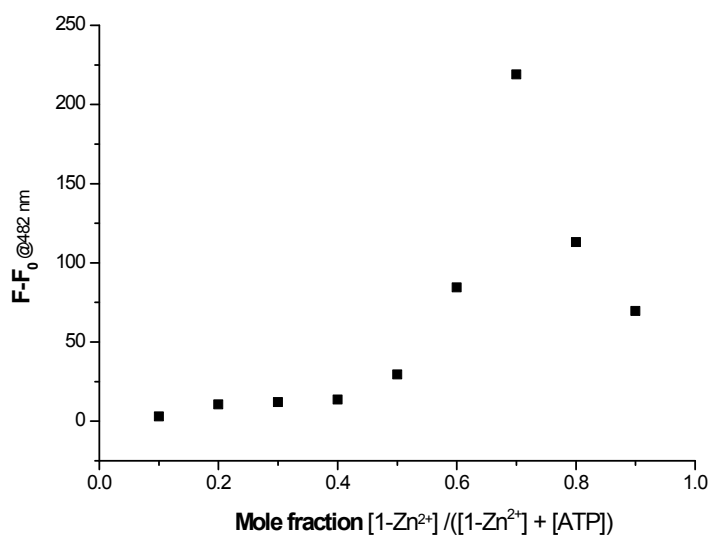


Fig. S3 Job's plot for the binding between **1**-Zn<sup>2+</sup> and ATP, [1-Zn<sup>2+</sup>] + [ATP] = 0.01 mM.

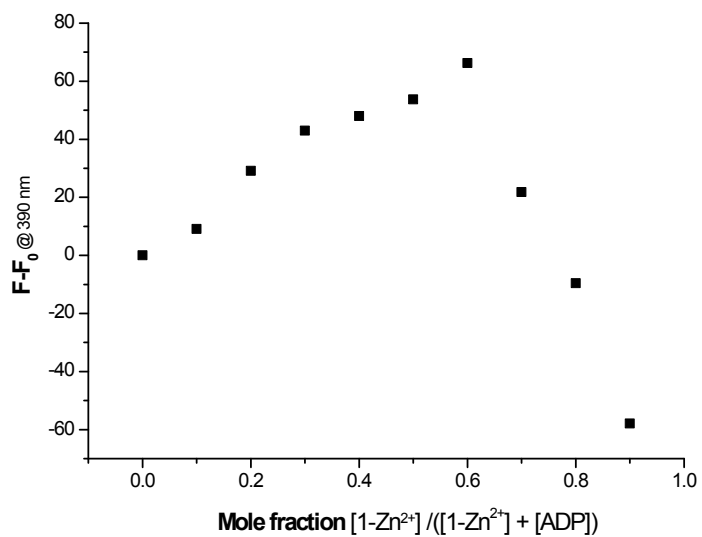
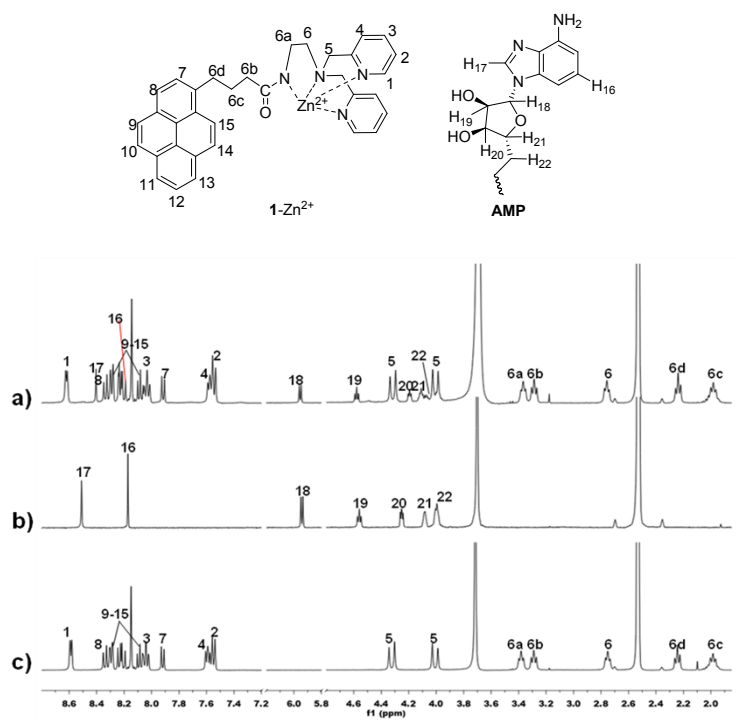


Fig. S4 Job's plot for the binding between **1**-Zn<sup>2+</sup> and ADP, [1-Zn<sup>2+</sup>] + [ADP] = 0.01 mM.



**Fig. S5** Regions from the 400 MHz <sup>1</sup>H NMR spectra for a) **1-Zn<sup>2+</sup>** + AMP (0.5 equiv.), b) AMP, c) **1-Zn<sup>2+</sup>** in DMSO-*d*<sub>6</sub>.