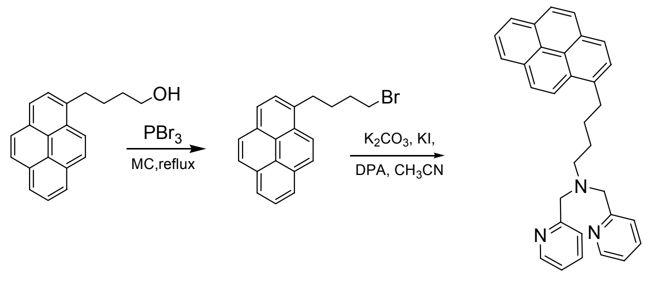
Supporting Information

1. Synthesis



1

Synthesis of 1

Commercially available 4-pyrenyl-l-butanol (211 mg, 0.769 mmol) was dissolved in methylene chloride (10 mL). After cooling to 0 °C, PBr_3 (208 mg, 0.769 mmol) was slowly added to 4-pyrenyl-l-butanol solution with vigorous stirring. The mixture was refluxed for 12 hr and cooled to room temperature. After evaporating solvent, the residue was purified by column chromatography (silica gel; hexane:ethylacetate = 50:1 v/v) to provide 1-(4-bromobutyl)pyrene as a white solid (194 mg, 0.575 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.27 (d, J = 9.3 Hz, 1H), 8.21~8.12 (m, 4H), 8.06~7.97 (m, 3H), 7.90 (d, J = 7.8 Hz, 1H), 3.50 (t, J = 6.3 Hz, 2H), 3.40 (t, J = 7.0 Hz, 2H), 2.07~2.04 (m, 4H).

1-(4-Bromobutyl)pyrene (50.0 mg, 0.148 mmol), potassium carbonate (41 mg, 0.296 mmol), di(2-picolyl)amine (DPA; 28.0 µl , 0.155 mmol) and potassium iodide (49.0 mg, 0.296 mmol) were dissolved in acetonitrile and stirred vigorously at ambient temperature for 2 days. After solvent evaporation, the residue was diluted with water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was concentrated and purified by column chromatography (silica gel; ethylacetate) to give a pale yellow oil (49 mg, 0.107 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.54 (d, J = 4.2 Hz, 2H), 8.25~8.16 (m, 3H), 8.10~7.99 (m, 5H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 5.7 Hz, 2H), 3.86 (s, 4H), 3.29 (t, *J* = 7.2 Hz, 2H), 2.68 (t, *J* = 6.9 Hz, 2H), 1.87 (m, 2H), 1.74 (m, 2H); ^{13}C NMR (60 MHz, $CDCl_3$): δ (ppm) 149.17, 136.84, 131.61, 131.08, 129.96, 128.75, 127.69, 127.39, 127.35, 126.76, 125.99, 125.20, 125.03, 124.95, 124.86, 123.86, 123.57, 122.61, 60.04, 54.18, 33.30, 32.93, 29.89, 29.36, 21.36, 26.57 ; ESI-MS: *m/z* 456.7 [M+H$^+$].

Synthesis of **1**-Zn

To a solution of **1** (15.0 mg, 0.0329 mmol) in 15 mL of MeOH-THF (1:1) was added dropwise aqueous solution of $ZnClO_4 \cdot 6H_2O$ (1 eq., 0.2 mL), and the mixture was stirred for 30 min at room temperature. After solvent evaporation, the solid was collected to give **1**-Zn (98%) without further purification. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ (ppm) 8.59 (s, 2H), 8.30~8.26 (m, 3H), 8.21~8.04 (m, 8H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.58 (m, 4H), 4.28 (d, *J* = 16.2 Hz, 2H), 3.94 (d, *J* = 16.2 Hz, 2H), 3.35 (s, 4H), 2.73 (s, 2H), 1.55 (s, 4H); ^{13}C NMR (60 MHz, DMSO-*d*$_6$): δ (ppm) 184.14, 147.48, 140.58, 140.56, 136.40, 130.88, 130.36, 129.28, 127.99, 127.44, 127.28, 126.56, 126.20, 125.02, 124.93, 124.81, 124.60, 124.29, 124.22, 124.12, 82.80, 56.98, 32.54, 29.11 ; HRMS (FAB$^+$, m-NBA,): *m/z* found 618.1128, calcd for [M+ClO_4^+] 618.1138.

2. Fluorescence Spectra

All stock solutions were prepared in DMSO, then diluted with 10 mM HEPES buffer (pH=7.4) solution to prepare samples. Total volume percent of DMSO in a sample is below 0.1%. Fluorescence spectra were recorded on a Jasco FP-750 spectrophotometer.

Fluorescence quantum yields were calculated according to the following equation. In this equation, Φ_{sample} and Φ_{std} are the quantum yields of sample and standard, respectively; I_{sample} and I_{std} are the integrated emission intensities of the sample and the standard, respectively; A_{sample} and A_{std} are the absorbance of the sample and standard, respectively; and n_{sample} and n_{std} are the refractive indexes of the sample and standard solutions, respectively.

$$\Phi_{\mathrm{sample}} = \Phi_{\mathrm{std}}\,[I_{\mathrm{sample}}/I_{\mathrm{std}}][A_{\mathrm{std}}/A_{\mathrm{sample}}][n_{\mathrm{sample}}/n_{\mathrm{std}}]^2$$

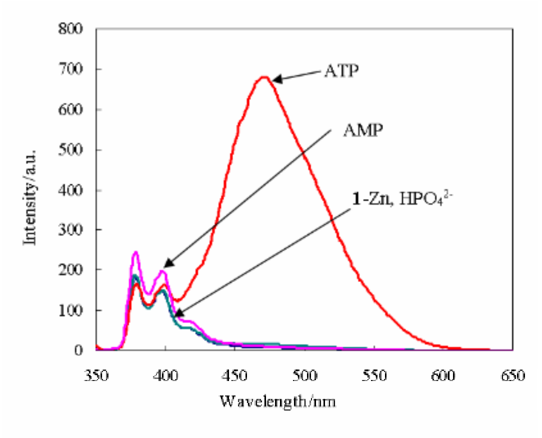


Figure S1. Fluorescence spectra of **1**-Zn (0.02 mM) in aqueous solvent of 10 mM HEPES buffer (pH=7.4) in the presence of various anions (0.4 equiv). Excitation wavelength, 343 nm.

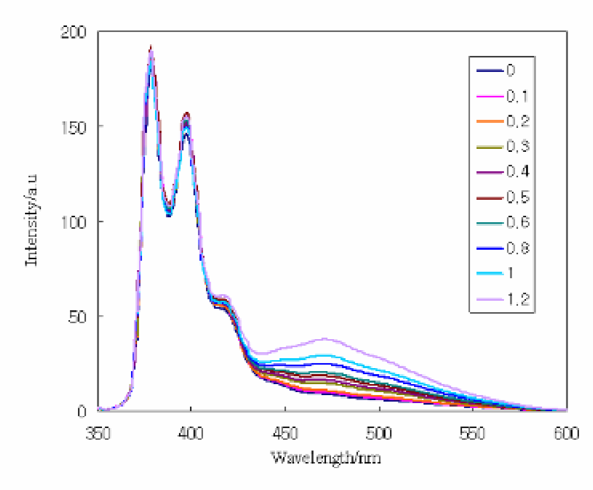


Figure S2. Fluorescence titration spectra of **1**-Zn upon addition of HPO_4^{2-} (sodium salt, equiv). [**1**-Zn] = 0.02 mM in aqueous HEPES buffer (pH=7.4). [HPO_4^{2-}] = 0 ~ 1.2 eqiuv of **1**-Zn. Excitation wavelength, 343 nm.

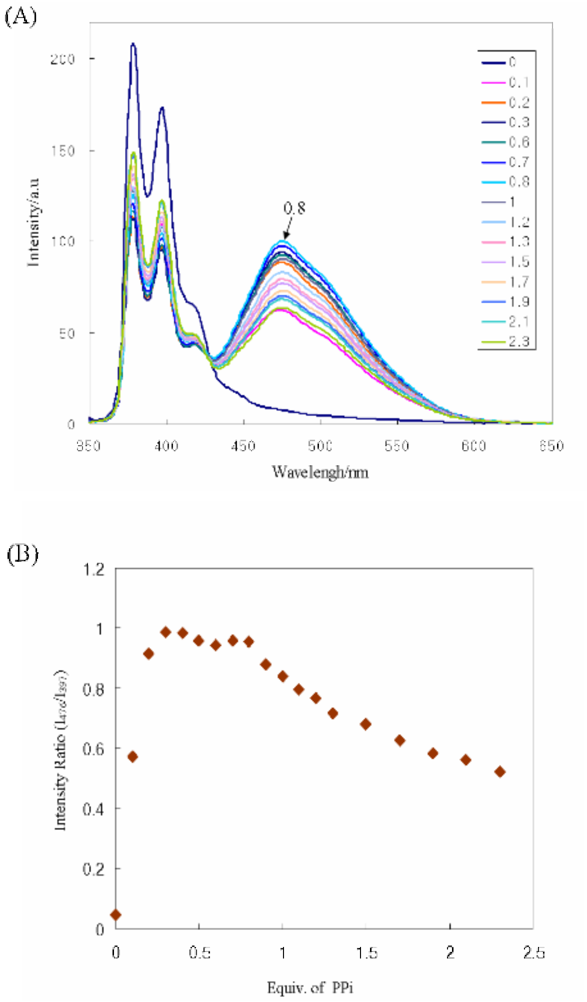


Figure S3. (A) Fluorescence spectra of **1**-Zn in the presence of 10 equiv of ATP upon addition of PPi (sodium salt, equiv). [**1**-Zn] = 0.02 mM in aqueous HEPES buffer (pH=7.4). [PPi] = 0 ~ 2.3 equiv of **1**-Zn. Excitation wavelength, 343 nm.

(B) Dependence of I_{476}/I_{397} in the presence of 10 equiv of ATP on the concentration of PPi (sodium salt, equiv).

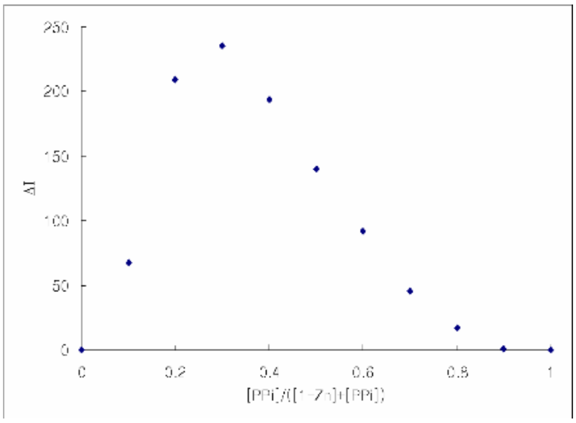


Figure S4. Job's plot for the binding between **1**-Zn and PPi. [**1**-Zn] + [PPi] = 0.02 mM.

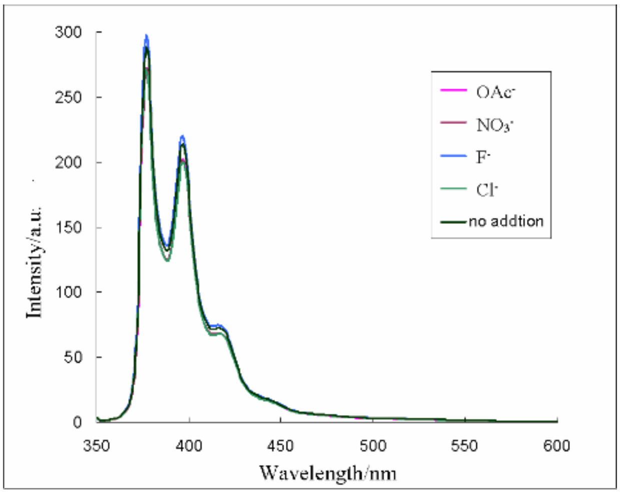


Figure S5. Fluorescence spectra of **1**-Zn (0.02 mM) in aqueous solvent of 10 mM HEPES buffer (pH=7.4) in the presence of various anions (1 equiv). Excitation wavelength, 343 nm. Additon of 0.5 eq. and further addition over 10 eq. of these anions did not affect the spectral change.

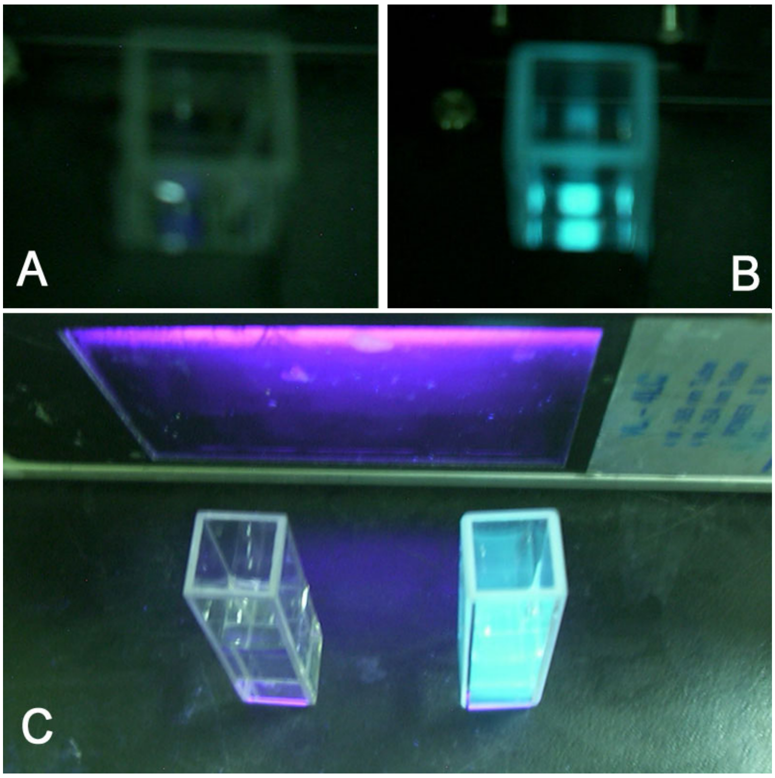


Figure S6. Photographs of light emission of **1**-Zn solution before (**A**) and after (**B**) addition of PPi in PL spectrophotometer (excitation wavelength = 343 nm); photographs of light emission of **1**-Zn solution before (left) and after (right) addition of PPi under UV lamp (365 nm) (**C**).