

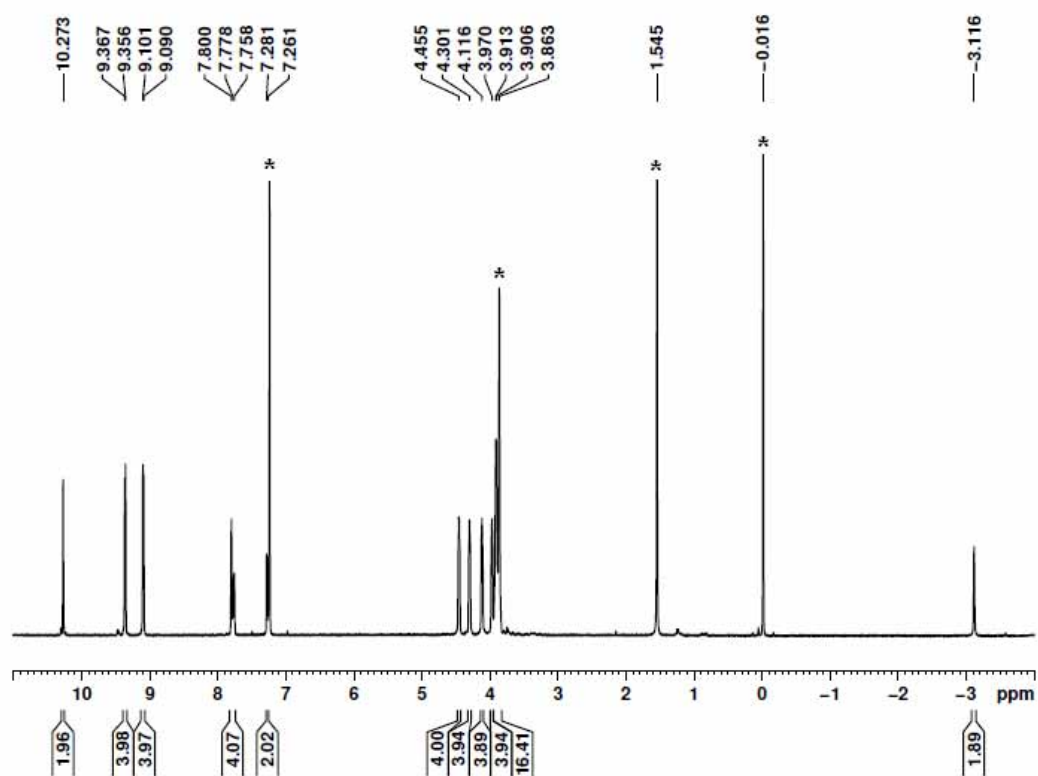
## **Supporting Information**

### **Azacrown[N, S, O]-modified Porphyrin Sensor for Detection of Ag<sup>+</sup>, Pb<sup>2+</sup> and Cu<sup>2+</sup>**

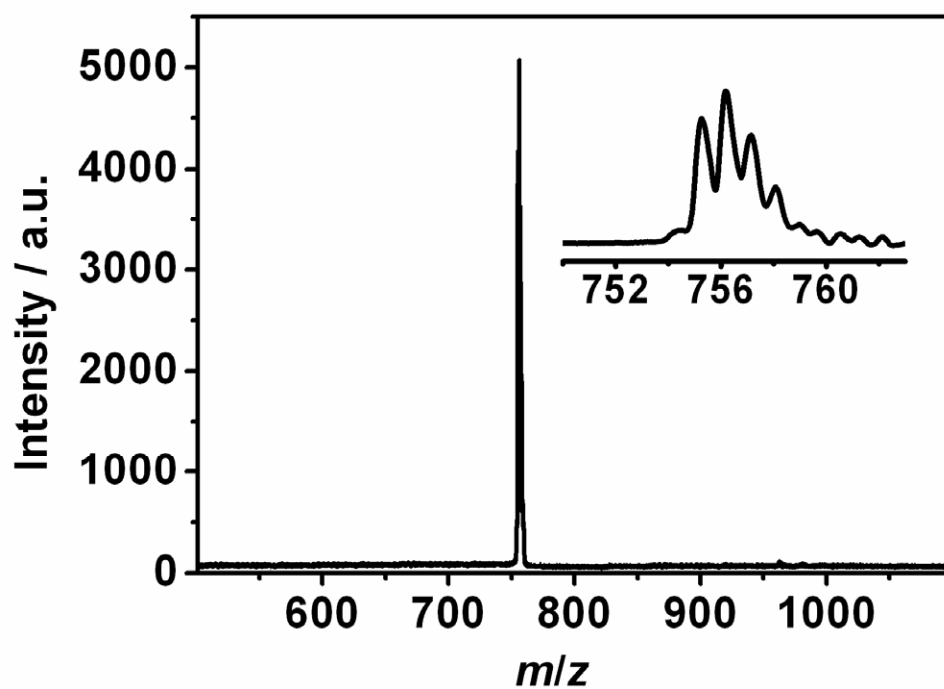
**Yuting Chen,\* and Kaili Wang**

## Content

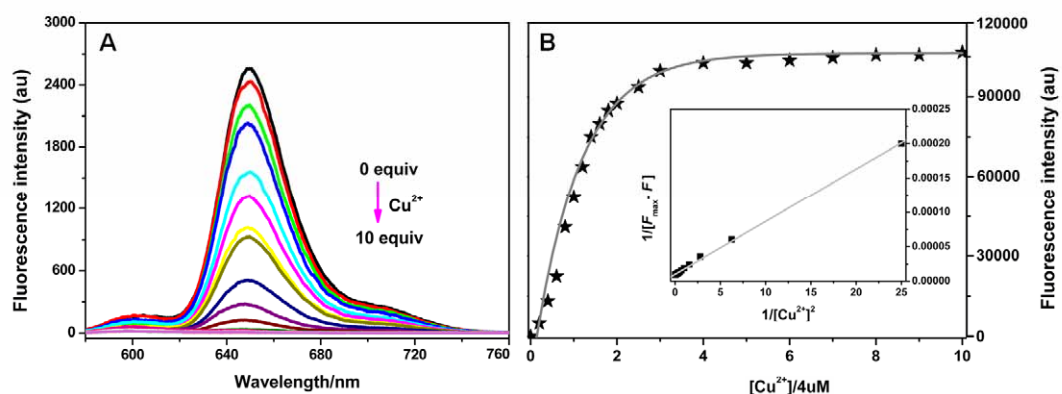
1.  $^1\text{H}$  NMR and MALDI-TOF mass spectra of  $\text{H}_2\text{Por-azacrown}$  (**1**), pages S3-4.
2. The fluorescence titration experiments of **1** with  $\text{Cu}^{2+}$ , page S5
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4. The fluorescence titration and absorption Job's plot of **1** with  $\text{Pb}^{2+}$ , page S7.
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7.  $^1\text{H}$  NMR data ( $\delta$ ) for  $\text{H}_2\text{Por-azacrown}$  (**1**) in  $\text{CDCl}_3$ , pages S12.



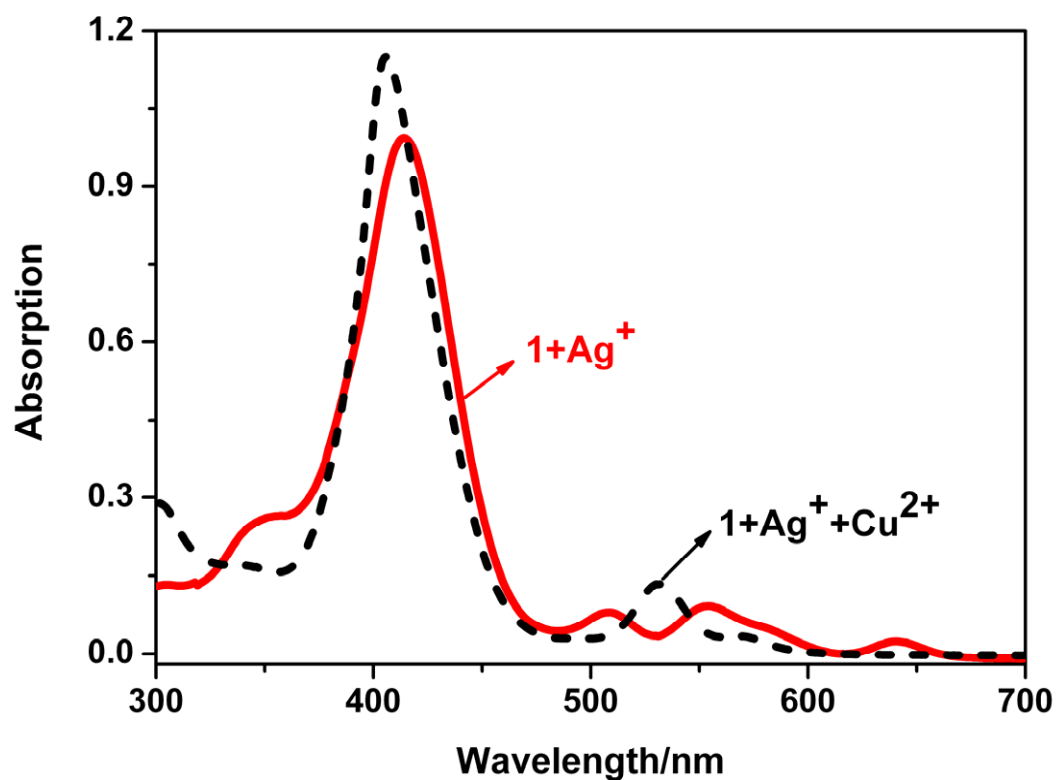
**Figure S1.**  $^1\text{H}$  NMR of  $\text{H}_2\text{Por-azacrown}$  (1) in  $\text{CDCl}_3$ . \* indicates the solvent impurities such as residual solvent signal band, MeOH and  $\text{H}_2\text{O}$ , respectively.



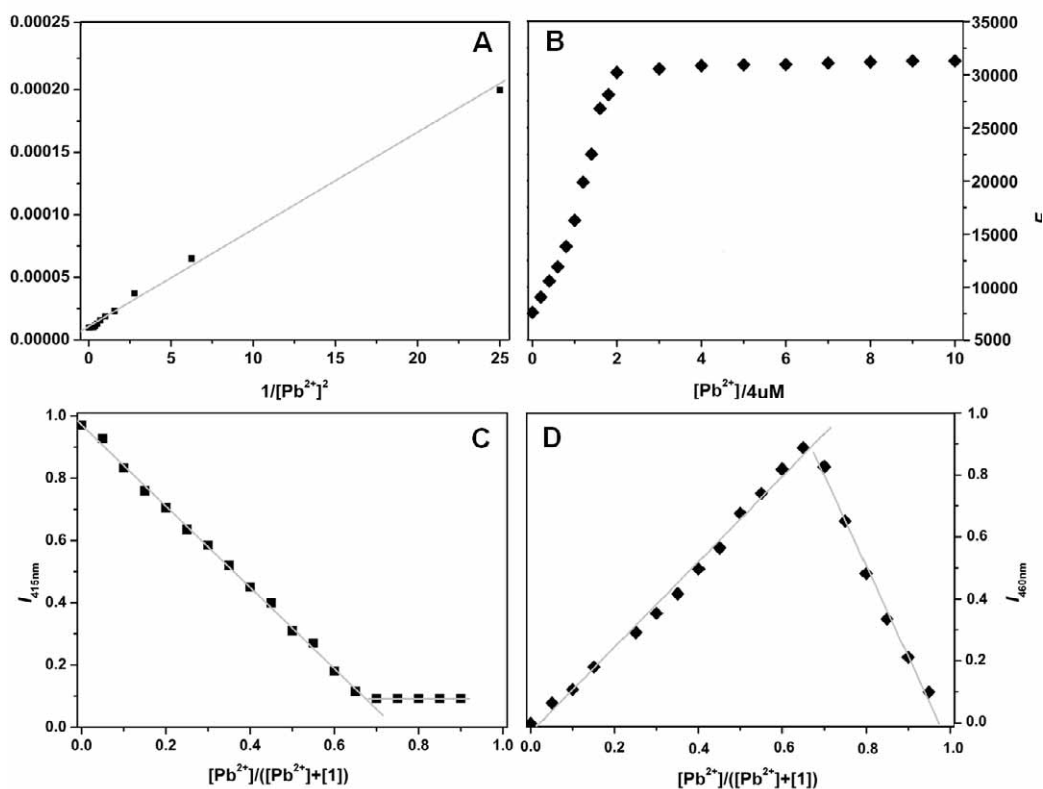
**Figure S2.** Experimental isotopic pattern for the molecular ion of the compound H<sub>2</sub>Por-azacrown (**1**) shown in the MALDI-TOF mass spectrum.



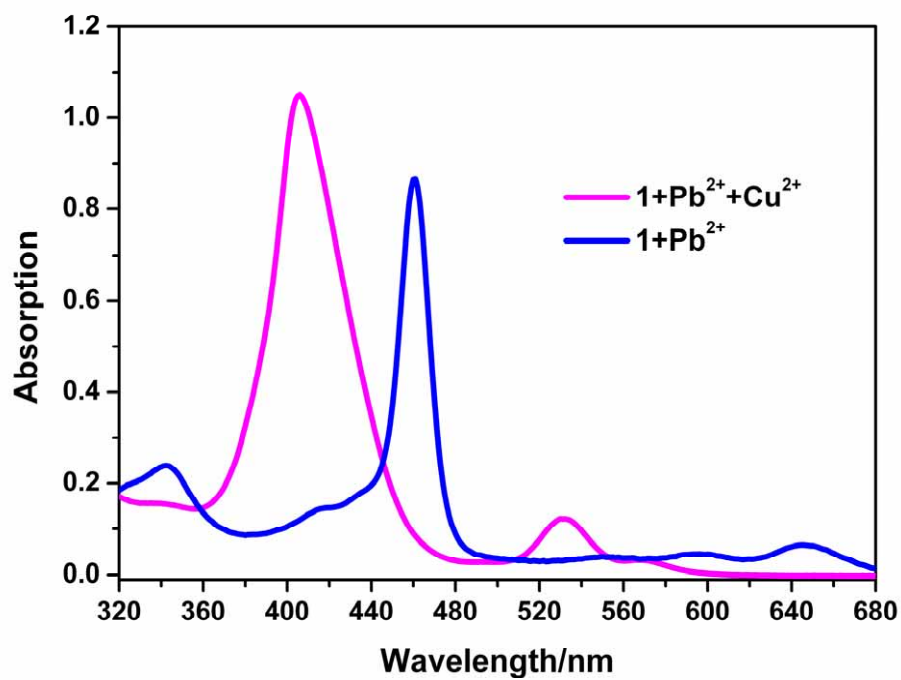
**Figure S3** The fluorescent emission spectra of **1** at the concentration of 4  $\mu\text{M}$  in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (3:2) upon addition of increasing amount (0-10 equiv) of  $\text{Cu}^{2+}$  (A), and Relative fluorescence intensities ( $F_{\text{max}} - F$ ) of **1** in the range from 580 to 750 nm as a function of the concentration of  $\text{Cu}^{2+}$  together with the inset showing assuming 1:2 stoichiometry for association between **1** and  $\text{Cu}^{2+}$  (B), with the excitation of 420 nm.



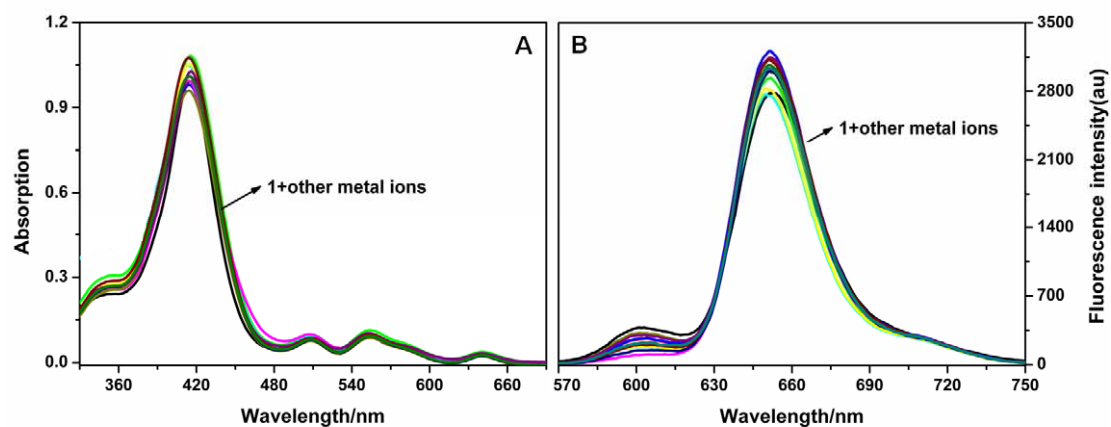
**Figure S4.** The electronic absorption spectrum of **1**-Ag<sup>+</sup> (1:10) at the concentration of 4  $\mu$ M in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (3:2) upon adding Cu<sup>2+</sup> (10 equiv).



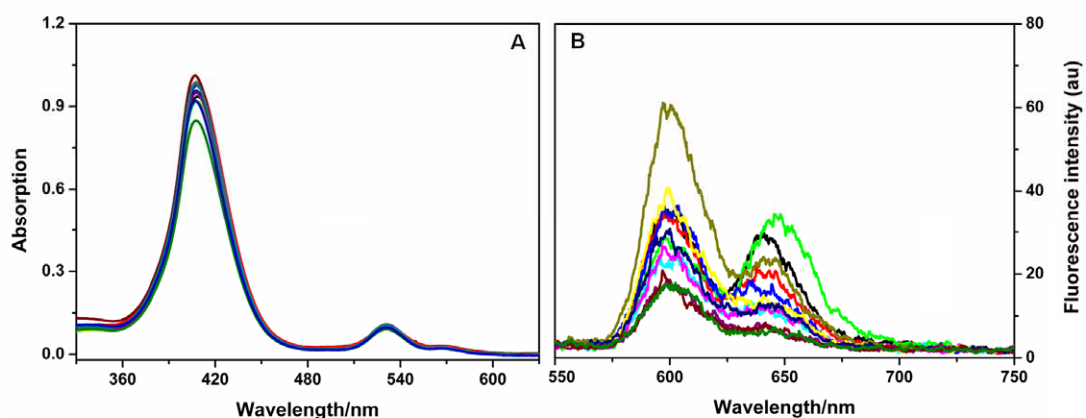
**Figure S5.** The linear relation between  $1/F_{\text{max}} - F$  and  $1/[\text{Pb}^{2+}]^2$  according to Benesi-Hildebrand equation with the emission at 650 nm (A) and the change of fluorescence emission at 600 nm along with the increasing amount of  $\text{Pb}^{2+}$  (0-10 equiv) (B); the absorption Job's plot with the absorption at 415 nm (C) and 460 nm (D), respectively, indicating the 1:2 binding stoichiometry between **1** and  $\text{Pb}^{2+}$ .



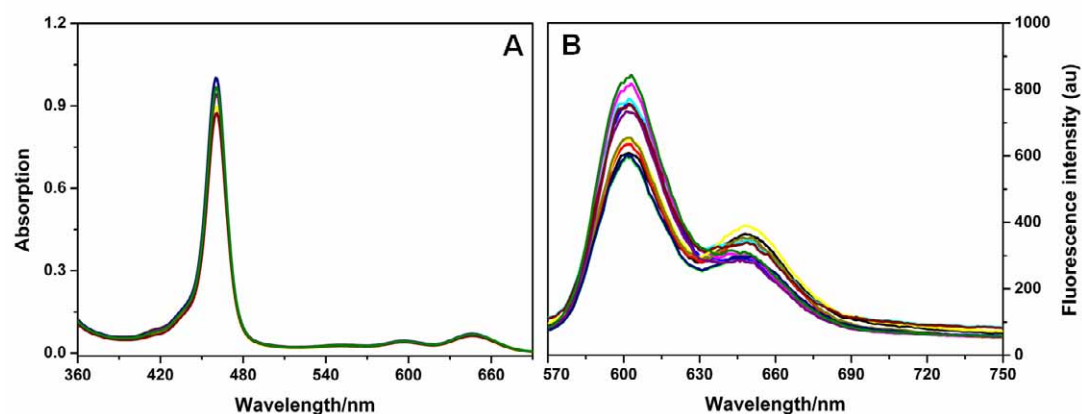
**Figure S6.** The electronic absorption spectrum of **1**-Pb<sup>2+</sup> complex upon addition of Cu<sup>2+</sup> (10 equiv).



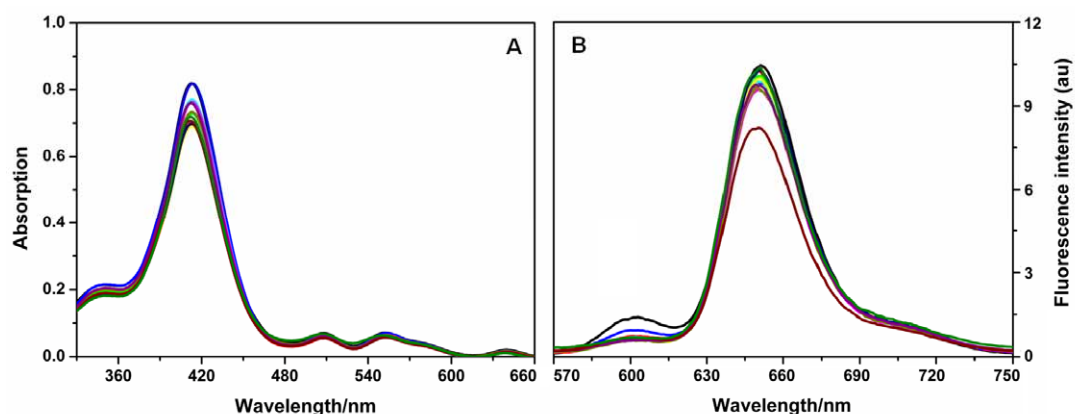
**Figure S7.** The electronic absorption (A) and fluorescence emission spectra (B) of **1** (4  $\mu$ M) in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (3:2) upon addition of Fe<sup>3+</sup>, Co<sup>2+</sup>, Hg<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Mg<sup>2+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, or K<sup>+</sup> (10 equiv), respectively, with the excitation of 420 nm.



**Figure S8.** The electronic absorption (A) and fluorescence emission spectra (B) of **1-Cu<sup>2+</sup>** (1:10) in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (3:2) upon addition of K<sup>+</sup>, Li<sup>+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Ba<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Hg<sup>2+</sup>, or Zn<sup>2+</sup> (10 equiv), respectively, with the excitation of 420 nm.



**Figure S9.** The electronic absorption (A) and fluorescence emission spectra (B) of **1-Pb<sup>2+</sup>** (1:10) in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (3:2) upon addition of K<sup>+</sup>, Li<sup>+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Ba<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Hg<sup>2+</sup>, or Zn<sup>2+</sup> (10 equiv), respectively, with the excitation of 420 nm.



**Figure S10.** The electronic absorption (A) and fluorescence emission spectra (B) of **1-Ag<sup>+</sup>** (1:10) in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (3:2) upon addition of K<sup>+</sup>, Li<sup>+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Ba<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Hg<sup>2+</sup>, or Zn<sup>2+</sup> (10 equiv), respectively, with the excitation of 420 nm.

**Table S1.** <sup>1</sup>H NMR data (δ) for H<sub>2</sub>Por-azacrown (**1**) in CDCl<sub>3</sub>.

| Por-meso-H     | pyrrole-H     | Por-Ph-H                     | Aza-crown-H                     | CH <sub>3</sub>         | metal-free H   |
|----------------|---------------|------------------------------|---------------------------------|-------------------------|----------------|
| 10.27 (s, 2 H) | 9.37 (d, 4 H) | 7.80 (t, 4 H)                | 4.46 (s, 4 H)                   | 3.92-3.86               | -3.12 (s, 2 H) |
|                | 9.10 (d, 4 H) | 7.28 (t, 4 H) <sup>[a]</sup> | 4.30 (s, 4 H)                   | (m, 6 H) <sup>[b]</sup> |                |
|                |               |                              | 4.12 (s, 4 H),                  |                         |                |
|                |               |                              | 3.97 (s, 4 H),                  |                         |                |
|                |               |                              | 3.92~3.86(m, 4H) <sup>[b]</sup> |                         |                |

<sup>[a]</sup> Two proton signals are overlapped by the bands of the residual solvent CHCl<sub>3</sub>,  
 MeOH; <sup>[b]</sup> These signals are overlapped by the bands of MeOH.