

Electronic Supplementary Information

“Turn-On” Fluorescent Sensor for the Selective Detection of Zinc Ion by a Sterically-Encumbered Bipyridyl-Based Receptor

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Experimental

Reagents and General Methods. Reagents were obtained from Acros, Aldrich Chemical Co., TCI America, or Alfa Aesar and used without further purification except for solvents, which were purified by passage through alumina columns under a N₂ atmosphere employing an MBraun solvent purification system. Air sensitive operations were carried out in an MBraun dry box or using standard Schlenk techniques under an atmosphere of N₂. The materials 2,6-dimesitylbenzaldehyde¹ and 5,5'-bis(diethylphosphonylmethyl)-2,2'-bipyridine² were prepared by literature procedures and their ¹H, ¹³C, and ³¹P NMR spectra are provided in Figures S1-S4. Proton and ¹³C NMR spectra were obtained using a Bruker Avance 300 spectrometer operating at 300 MHz for proton, 75 MHz for ¹³C, and 121 MHz for ³¹P nuclei. All spectra were collected at 25 °C and referenced to TMS or residual solvent signals for ¹H and ¹³C and to 85% phosphoric acid for ³¹P. Absorption spectra were recorded using a Cary 50 spectrophotometer and photoluminescence (PL) spectra were recorded using a Varian Eclipse spectrofluorimeter. Samples for fluorescence had a pathlength of 1 cm in quartz cuvettes, with optical density of <0.05 in degassed anhydrous solvent, and all samples were filtered through a 0.4 mm PTFE syringe filter immediately prior to use. Quantum yield determinations were performed in triplicate and are reported, with standard deviations, relative to quinine bisulfate in 0.1 N H₂SO₄(aq) ($\Phi = 0.546$).³

Preparation of 5,5'-bis-[2-(2,6-dimesitylphenyl)-vinyl]-2,2'-bipyridinyl (TAB). To a stirred solution of the materials 4-bromo-3,5-dimesitylbenzaldehyde (1.36 g, 3.84 mmol) and 5,5'-bis(diethylphosphonylmethyl)-2,2'-bipyridine (0.876 g, 1.92 mmol) in 25 mL THF was added dropwise a solution of KO^tBu (0.768 g, 4.22 mmol) in 20 mL THF at room temperature. Upon addition, the color of the mixture changed progressively from colorless to brown. After 24 hours

stirring at room temperature, the solution was removed from the dry box and poured into 100 mL of 10% HCl in methanol. All volatiles were removed under reducer pressure to afford the crude material as a tan solid. Analytically pure material was obtained by crystallization from ethyl acetate/dichloromethane to yield feathery yellow **TAB**·(ethyl acetate), which was dried in vacuo to give solvent-free **TAB** (1.28 g, 78%). mp 242-245 °C. ¹H NMR (CDCl₃, 300 MHz): δ 2.01 (s, 12H), 2.37 (s, 6H), 5.78 (d, 2H, J = 17 Hz), 6.65 (d, 2H, J = 17 Hz), 6.98 (s, 4H), 7.05-7.16 (m, 3H), 7.39 (t, 2H, J = 8 Hz), 7.96-8.06 (m, 4H). ¹³C NMR (CDCl₃, 75.5 MHz): δ 20.5, 21.1, 120.3, 127.4, 127.7, 127.9, 128.3, 129.1, 133.0, 133.3, 133.7, 135.6, 136.8, 138.4, 140.8, 147.51, 154.1. **TAB**·(ethyl acetate): Anal. Calcd for C₆₆H₆₈N₂O₂: C, 86.05; H, 7.44; N, 3.04. Found: C, 86.44; H, 6.96; N, 3.32. NMR spectra are provided in Figures S5-S6.

Optical Response of TAB to Metal Ions.

PL Response of TAB to excess Metal Ions. For each metal ion tested, a 3 mL aliquot of **TAB** (1 μM in THF) was placed in a cuvette and an initial PL spectrum collected. A 30 μL (20 equiv) aliquot of a 100 μM solution of the requisite metal salt was then added, and the cell was capped. After the cuvette was inverted several times to affect mixing, another PL spectrum was acquired. This set of experiments was carried out twice, once with λ_{ex} = 370 nm and once with λ_{ex} = 420 nm. Figure S7 shows the PL spectra for all trials. The relative impact of each metal ion on integrated emission intensity is provided visually in Figure S13.

Absorption Response of TAB to excess Metal Ions. For each metal ion tested, a 3 mL aliquot of **TAB** (10 μM in THF) was placed in a cuvette, and an initial UV-vis spectrum was collected. A 30 μL (20 equiv) aliquot of a 1 mM solution of the requisite metal salt was then added, and the

cell was capped. After the cuvette was inverted several times to affect mixing, another PL spectrum was acquired. Results of these trials are shown in Figure 1a in the main text.

Fluorescence titration of TAB with metal ions. A 1 μM solution of **TAB** was prepared in anhydrous THF under an atmosphere of nitrogen. The solution was filtered, and a 3 mL aliquot of this solution was added to the cell and an initial PL spectrum was acquired with an excitation wavelength of 420 nm. Small (3 μL) aliquots of a 100 μM solution of metal ion salts in THF were added, where each 3 μL aliquot represents 0.10 equiv of metal ion with respect to **TAB**. A total of 60 μL of the solution was added, and progressive change in fluorescence with added metal ion was monitored. Spectra associated with the Zn^{2+} titration are provided in Figure 2 in the main text, while spectra for fluorescence titrations are provided in Figures S8-S11.

Absorption spectroscopic titration of TAB with $\text{Zn}(\text{ClO}_4)_2$. 3 mL of anhydrous THF was added to a cuvette and scanned, to be used as the background sample for the experiment. A 10 μM solution of **TAB** was prepared in anhydrous THF under an atmosphere of nitrogen. The solution was filtered and 3 mL of the prepared solution was added to the cuvette and scanned. Small aliquots (3 μL) of $\text{Zn}(\text{ClO}_4)_2$ (1 mM) in THF were added, where each 3 μL aliquots represents 0.10 equivalents of Zn^{2+} with respect to **TAB**. A significant red shift was observed with increasing additions of Zn^{2+} (Figure 1b in the main text).

Figure S1. Dennis and Smith

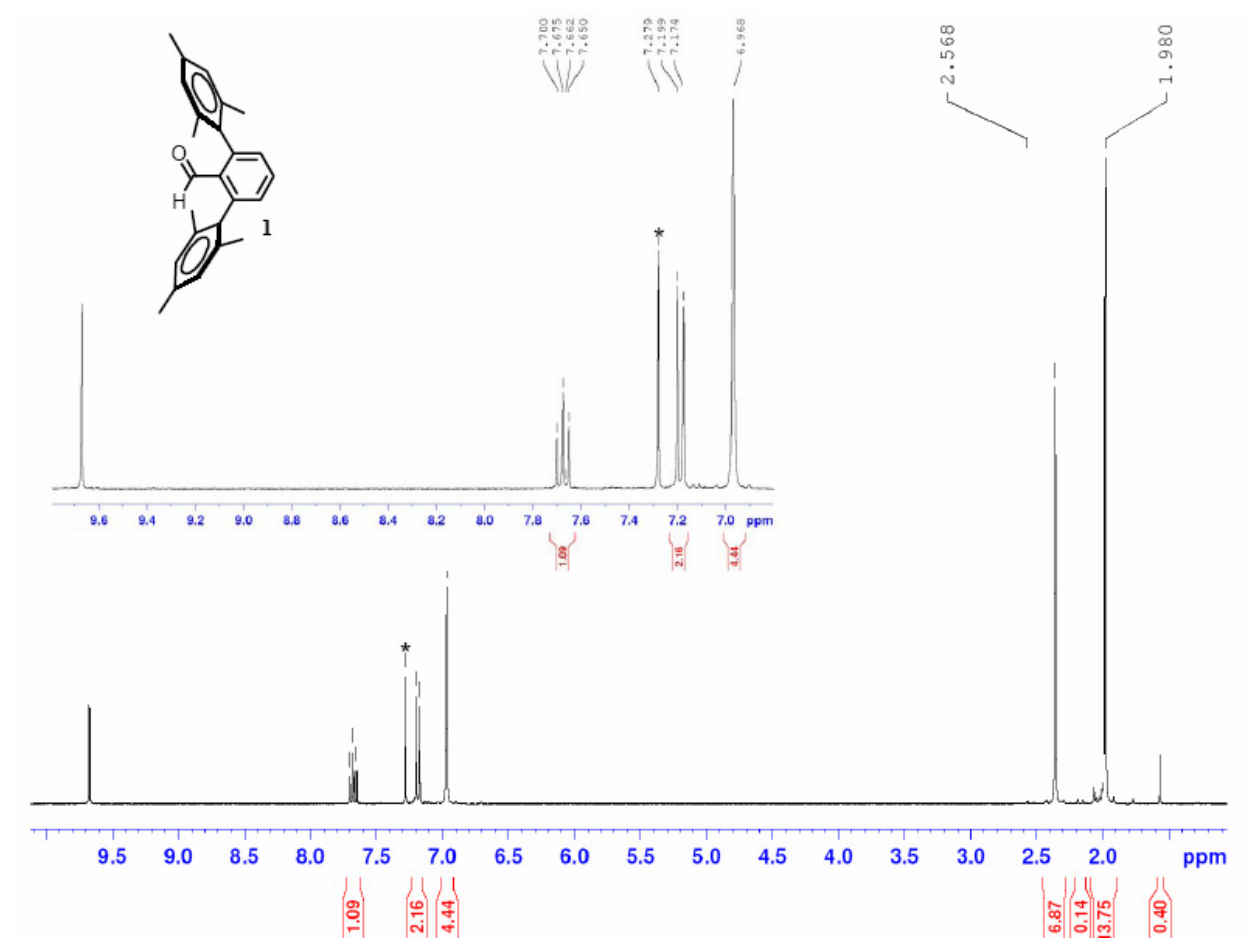


Figure S1. Proton NMR Spectrum of **1** (CDCl₃, 300 MHz). Peaks marked with an asterisk correspond to residual solvent signals.

Figure S2. Dennis and Smith

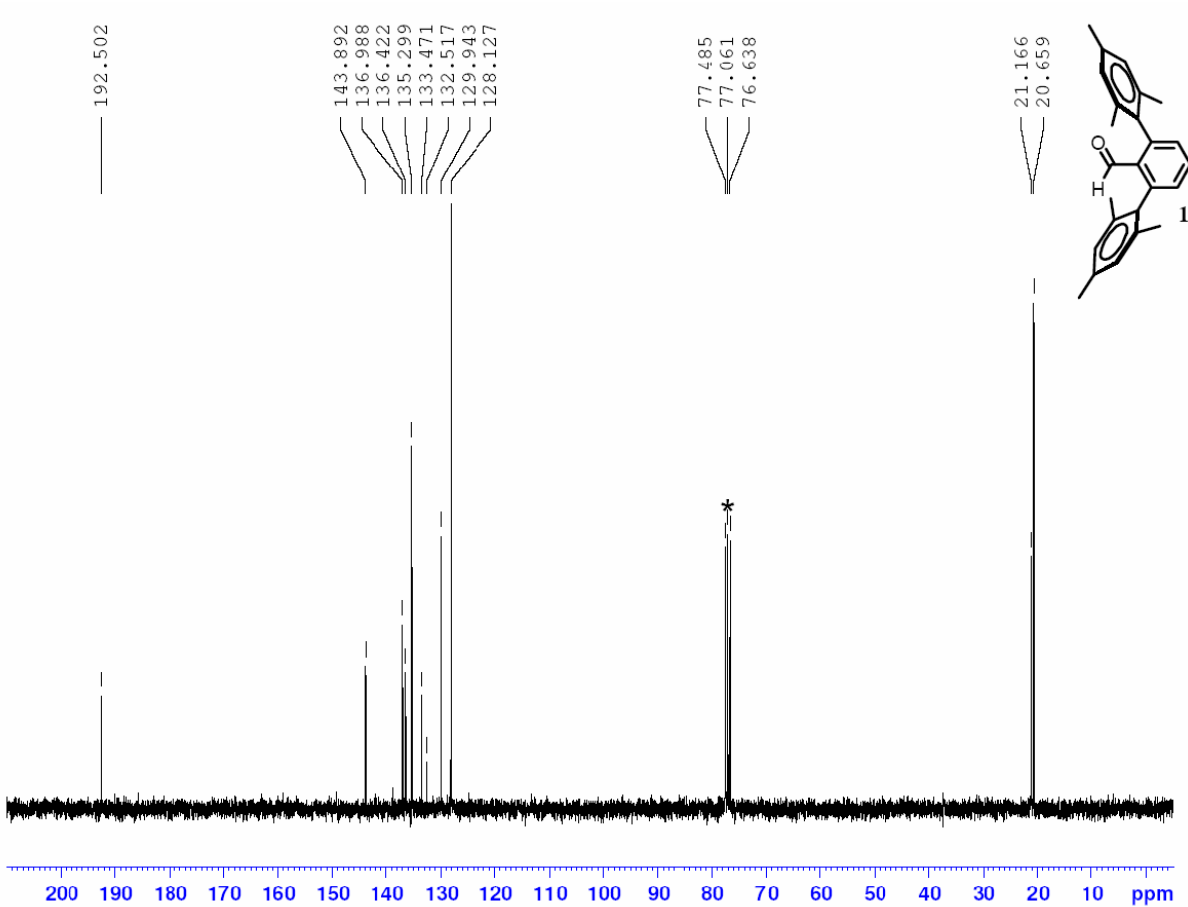


Figure S2. Carbon-13 NMR Spectrum of **1** (CDCl_3 , 75 MHz). Peaks marked with an asterisk correspond to residual solvent signals.

Figure S3. Dennis and Smith

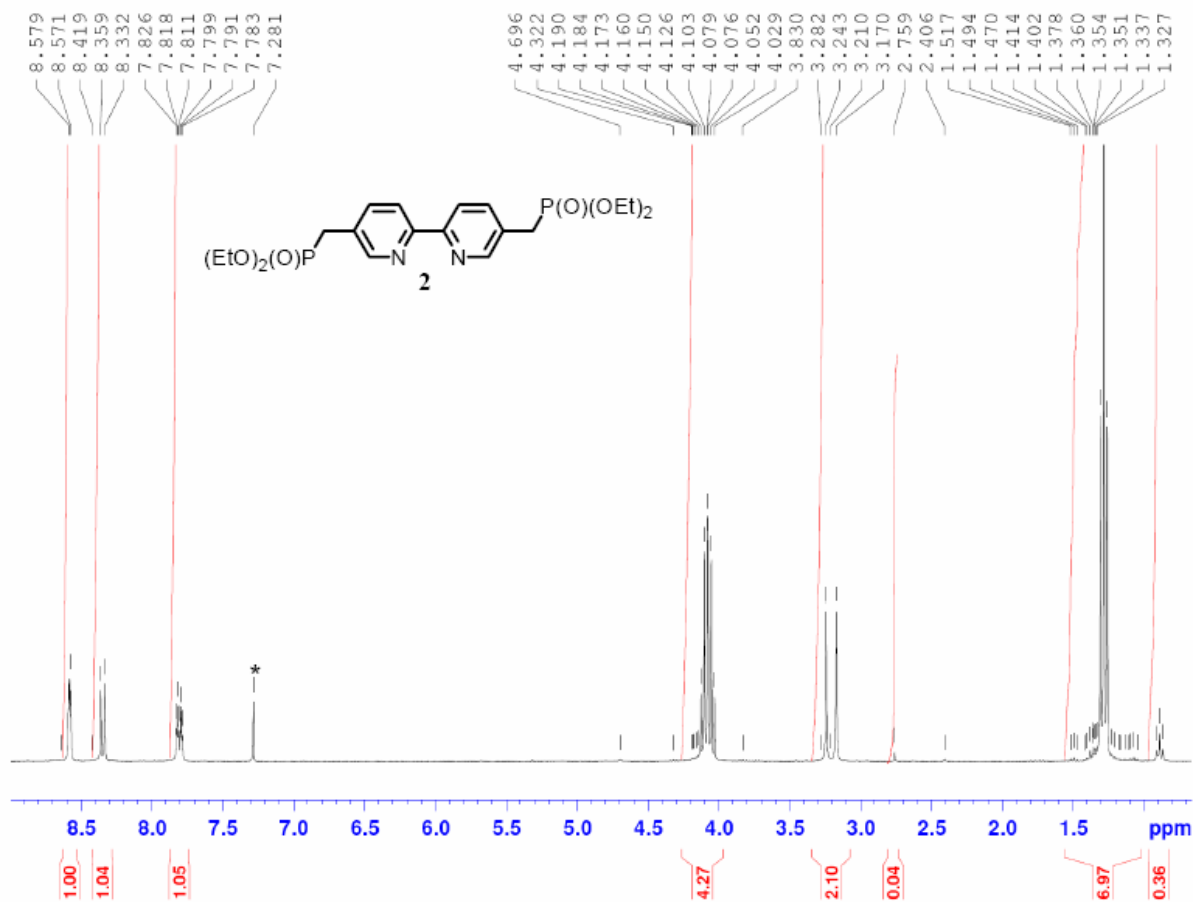


Figure S3. Proton NMR of 2 (CDCl₃, 300 MHz). Peaks marked with an asterisk correspond to residual solvent signals.

Figure S4. Dennis and Smith

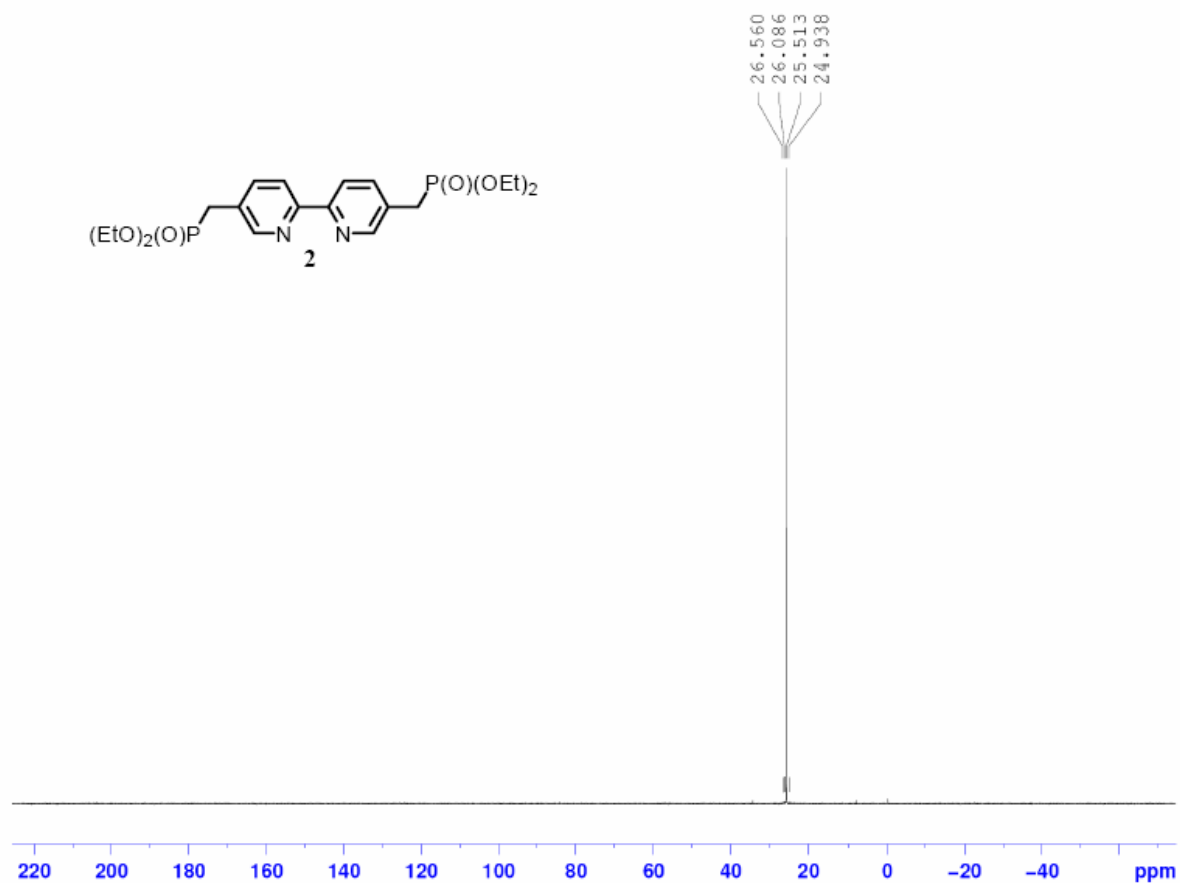


Figure S4. Phosphorous NMR of **2** (CDCl_3 , 121.5 MHz). Peaks marked with an asterisk correspond to residual solvent signals.

Figure S5. Dennis and Smith

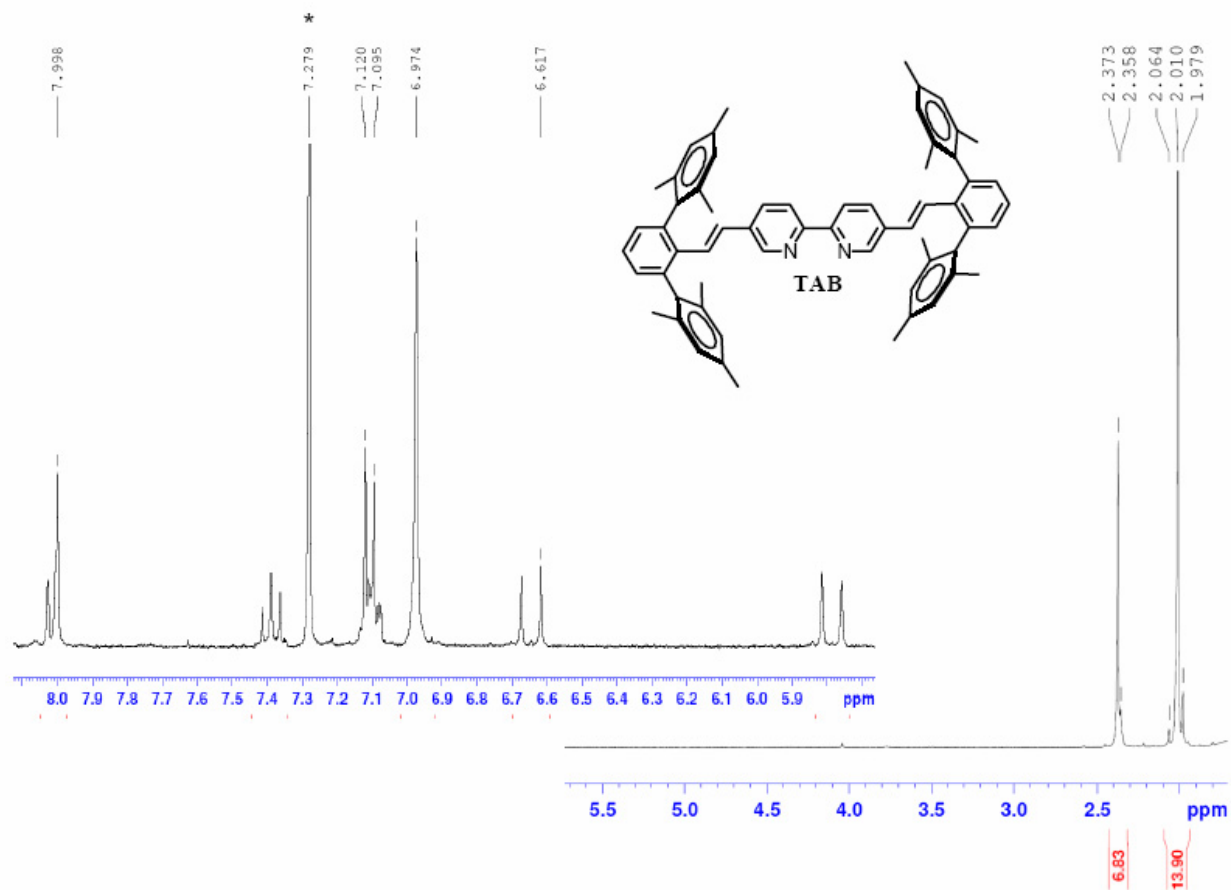


Figure S5. Proton NMR of TAB (CDCl₃, 300 MHz). Peaks marked with an asterisk correspond to residual solvent signals.

Figure S6. Dennis and Smith

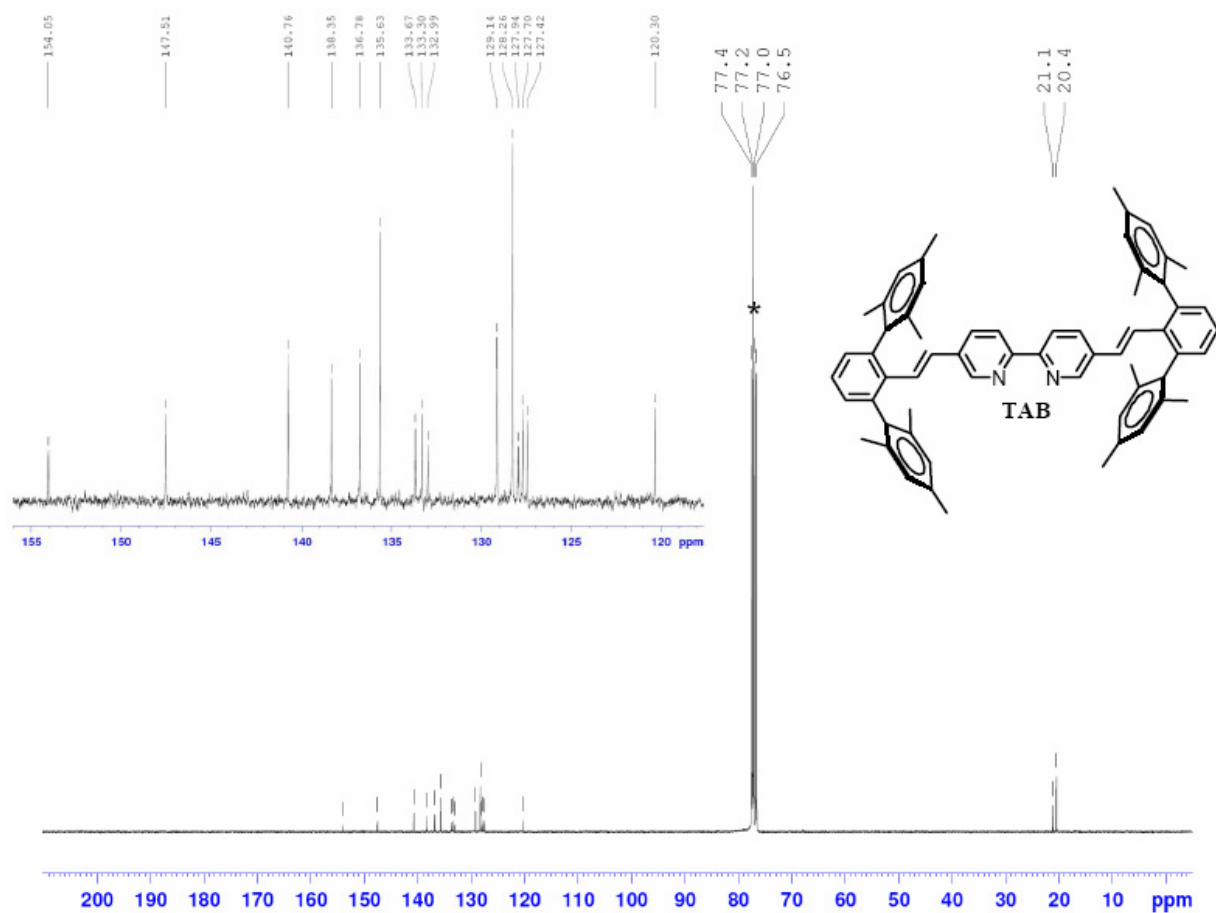


Figure S6. Carbon-13 NMR of **TAB** (CDCl₃, 75 MHz). Peaks marked with an asterisk correspond to residual solvent signals.

Figure S7. Dennis and Smith

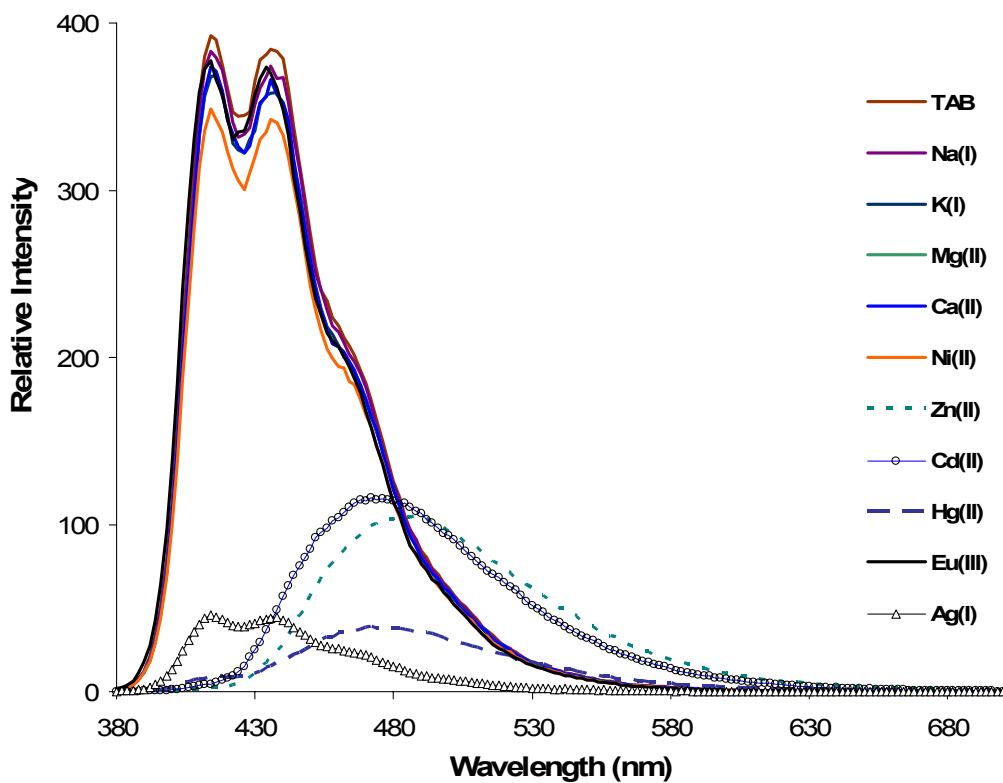


Figure S7. PL response of **TAB** (1 μM in THF) to 10 equiv of various metals ($\lambda_{\text{ex}} = 370 \text{ nm}$).

The spectra for Cu^{1+} , Cu^{2+} , Co^{2+} and Fe^{2+} were in the baseline, and are not shown.

Figure S8. Dennis and Smith

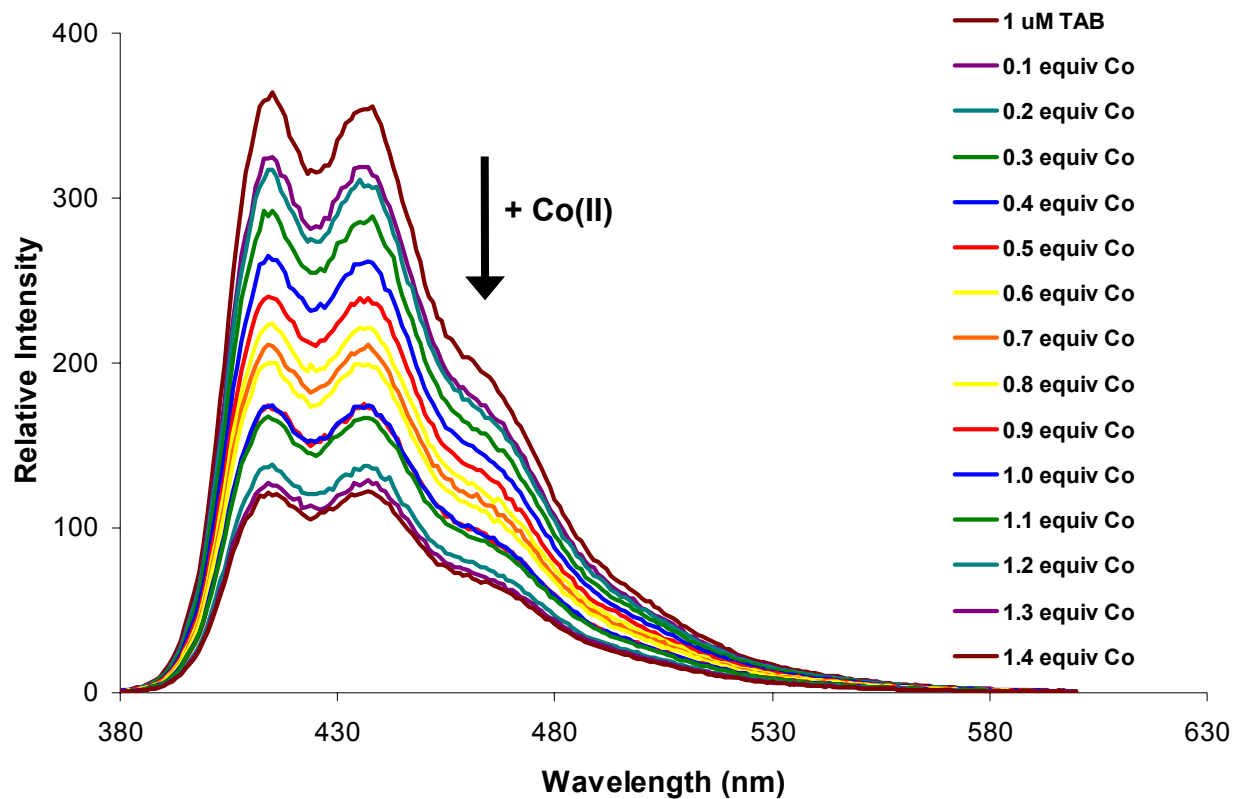


Figure S8. Titration of TAB (1 μM in THF) with Co²⁺ ($\lambda_{\text{ex}} = 370 \text{ nm}$).

Figure S9. Dennis and Smith

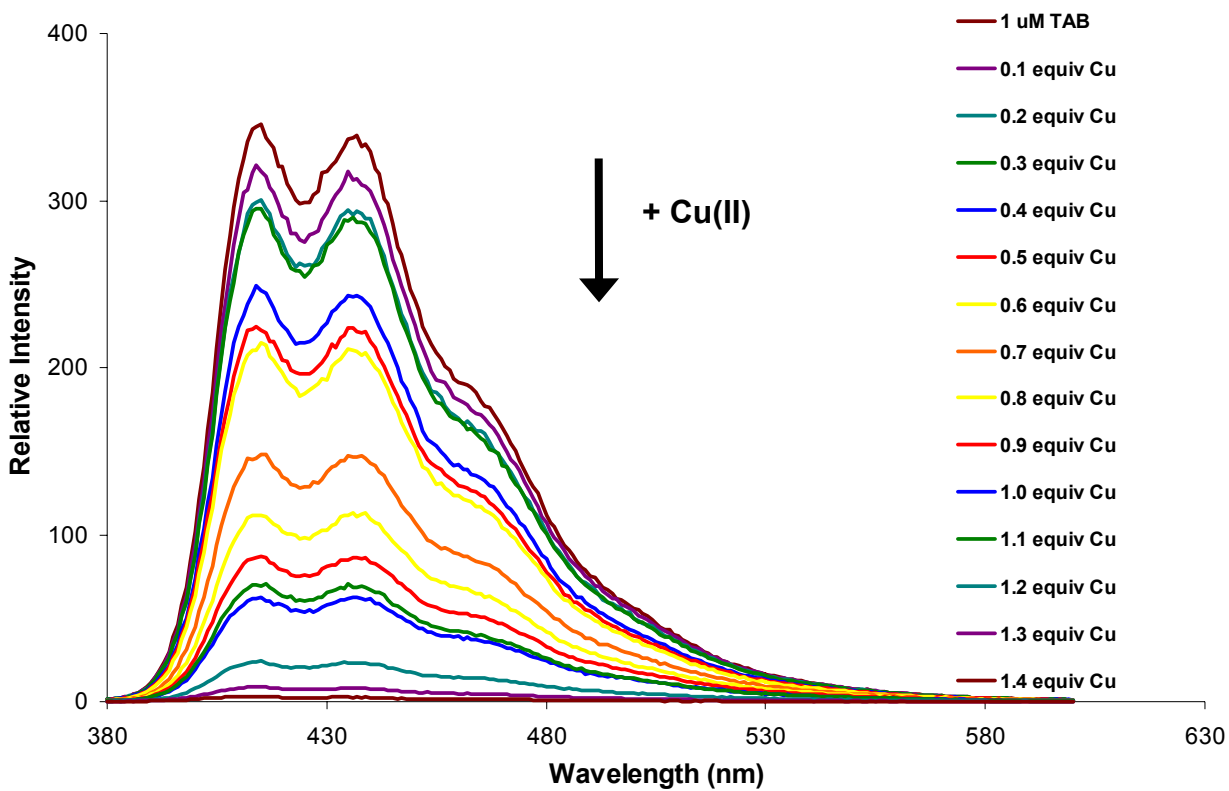


Figure S9. Titration of TAB (1 μM in THF) with Cu^{2+} ($\lambda_{\text{ex}} = 370 \text{ nm}$)

Figure S10. Dennis and Smith

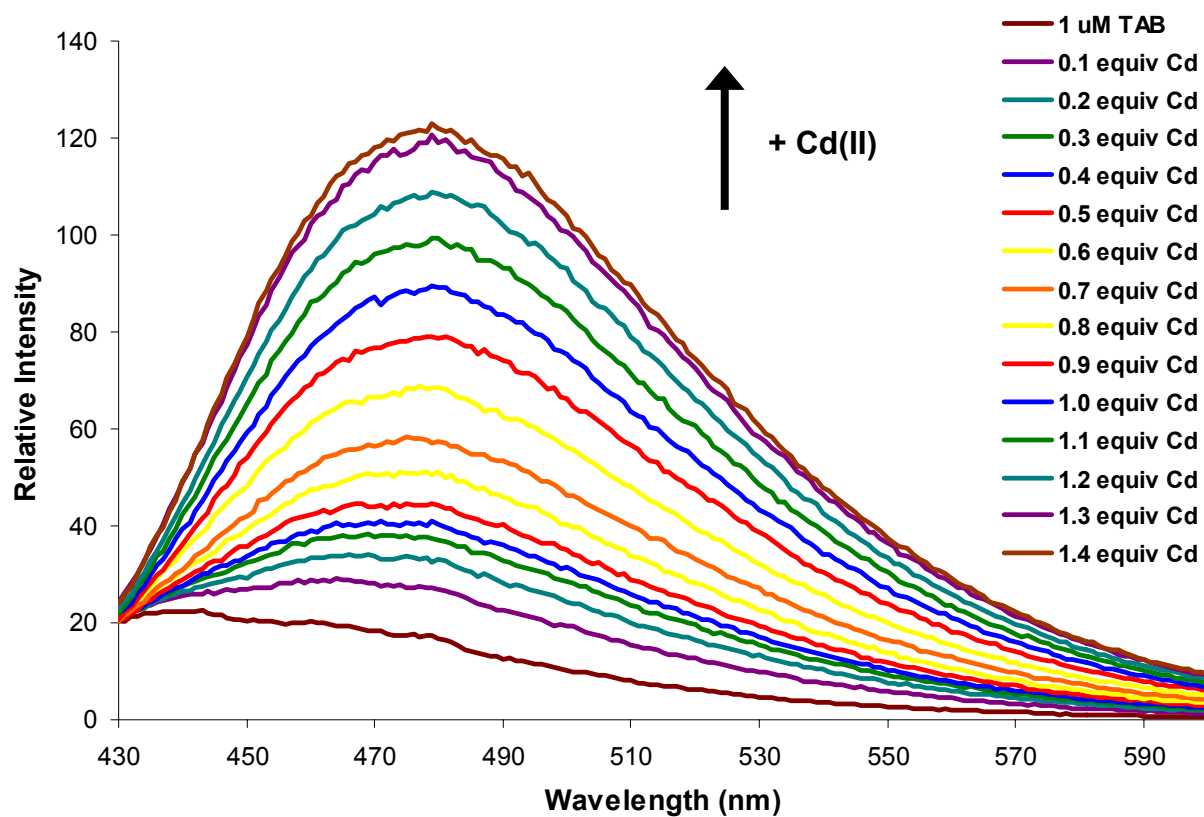


Figure S10. Titration of TAB (1 μM in THF) with Cd^{2+} ($\lambda_{\text{ex}} = 420 \text{ nm}$)

Figure S11. Dennis and Smith

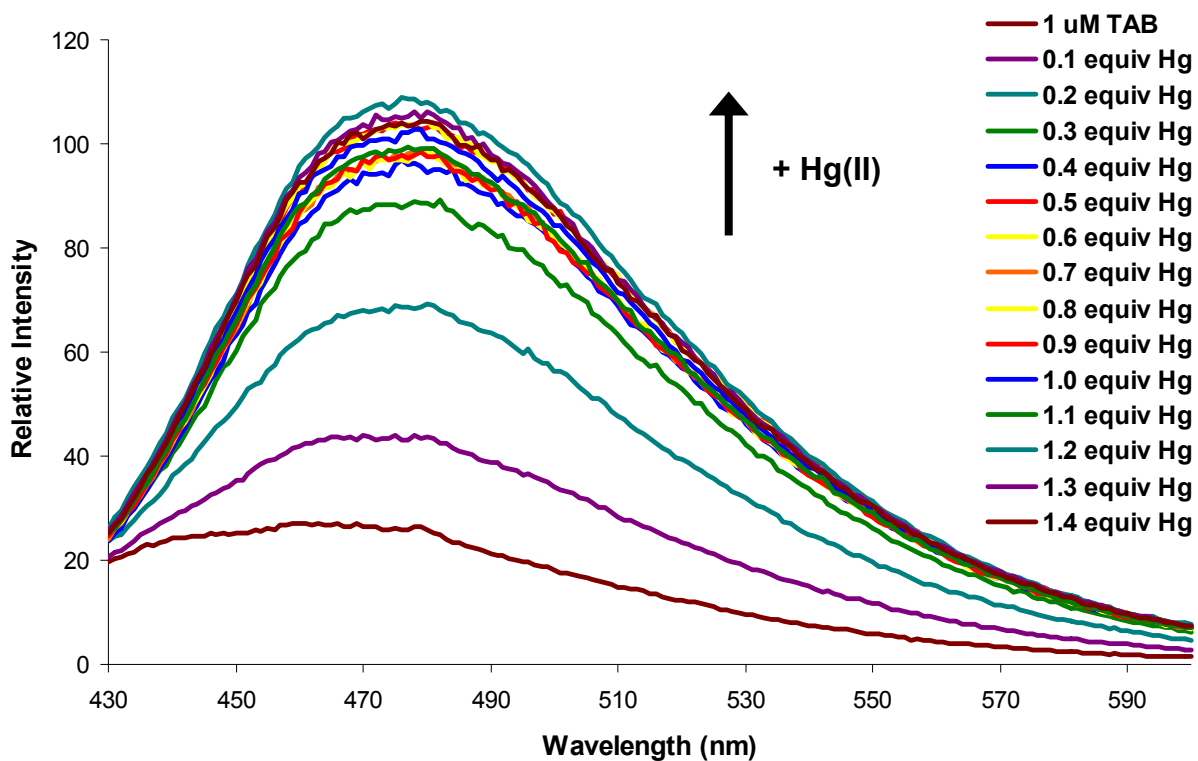


Figure S11. Titration of TAB (1 μM in THF) with Hg²⁺ ($\lambda_{\text{ex}} = 420 \text{ nm}$)

Figure S12. Dennis and Smith

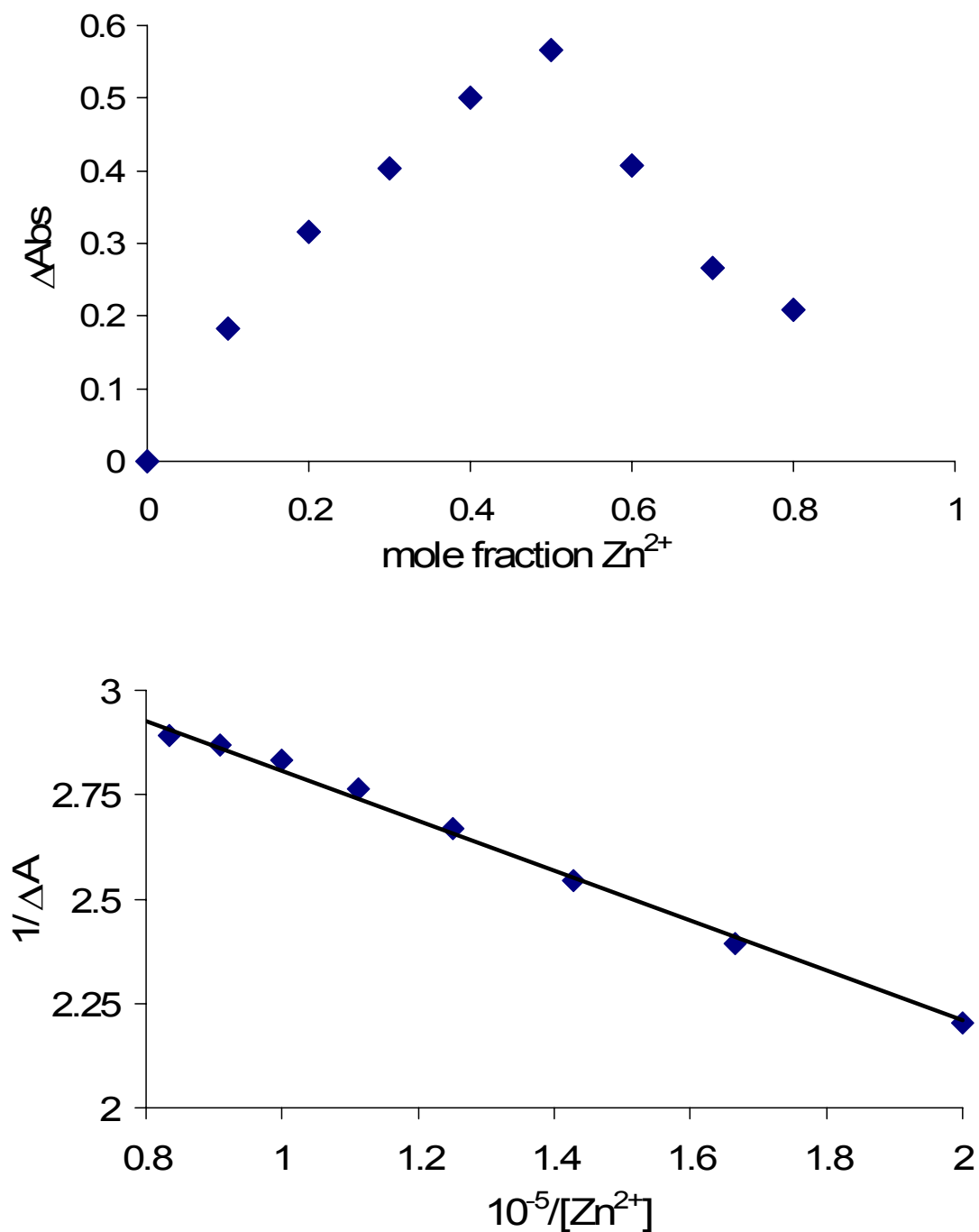


Figure S12. Job plot indicating the desired 1:1 complex formation (top) and Benesi-Hildebrand plot used to determine dissociation constant (bottom), both derived from titration of **TAB** with Zn^{2+} in THF. This form of the Benesi-Hildebrand plot employs equation 2d in ref. S4. The x axis has been multiplied by 10^{-5} for clarity.

Figure S13. Dennis and Smith

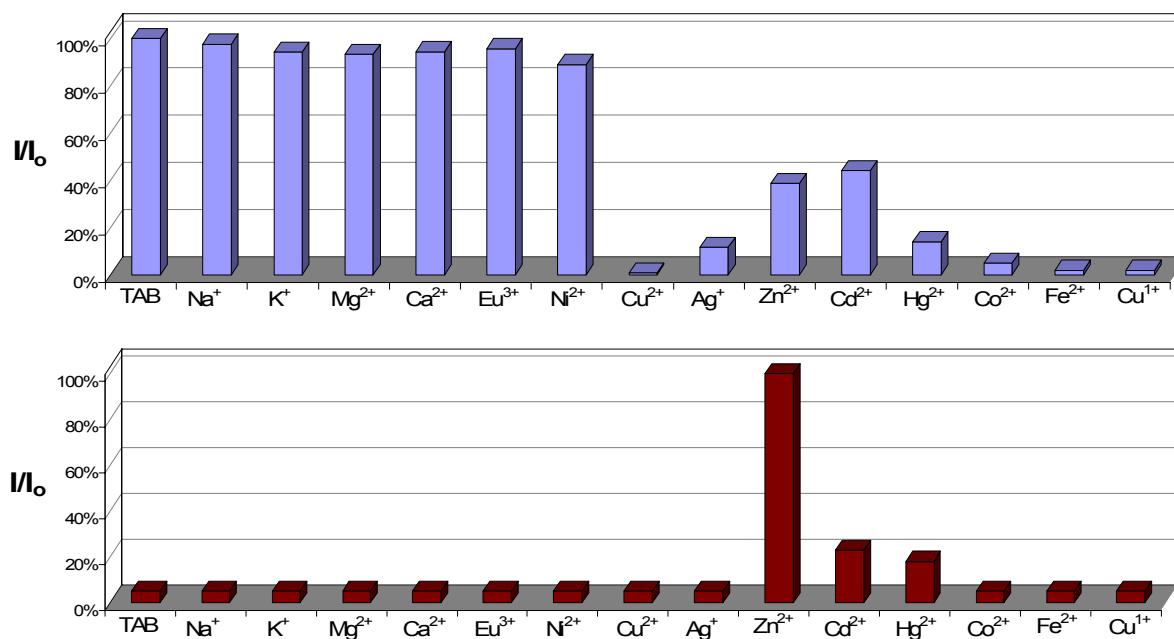


Figure S13. Relative metal ion-induced emission normalized to **TAB** with $\lambda_{\text{ex}} = 370$ (top) and normalized to **TAB-Zn²⁺** with $\lambda_{\text{ex}} = 420$ nm (bottom). In each case the emission is normalized to the most emissive species (set at 100%) at the given excitation wavelength for clarity.

Supporting Information References

- (S1) Smith, R. C.; Gleason, L. B.; Protasiewicz, J. D. *J. Mat. Chem.* **2006**, *16*, 2445-2452.
- (S2) Odobel, F.; Massiot, D.; Harrison, B. S.; Schanze, K. S. *Langmuir* **2003**, *19*, 30-39.
- (S3) *Handbook of Photochemistry*, 3rd Ed., (Eds: M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi), CRC Press, Boca Raton, 2006.
- (S4) Hammond, P. R. *J. Chem. Soc.* **1964**, 479-484.