Supplementary Material (ESI) for Chemical Communications

Water Soluble Benzo- and Naphtho-thiadiazole Bistriazoles And Their Metal-Binding Properties

*Scott M. Brombosz, Anthony Lucas Appleton, Andrew J. Zappas II and Uwe H. F. Bunz**

School of Chemistry and Biochemistry, Georgia Institute of Technology, 901 Atlantic Drive, Atlanta, GA 30332. Fax: 404-385-1795; Tel: 404-510-2443;

E-mail: uwe.bunz@chemistry.gatech.edu

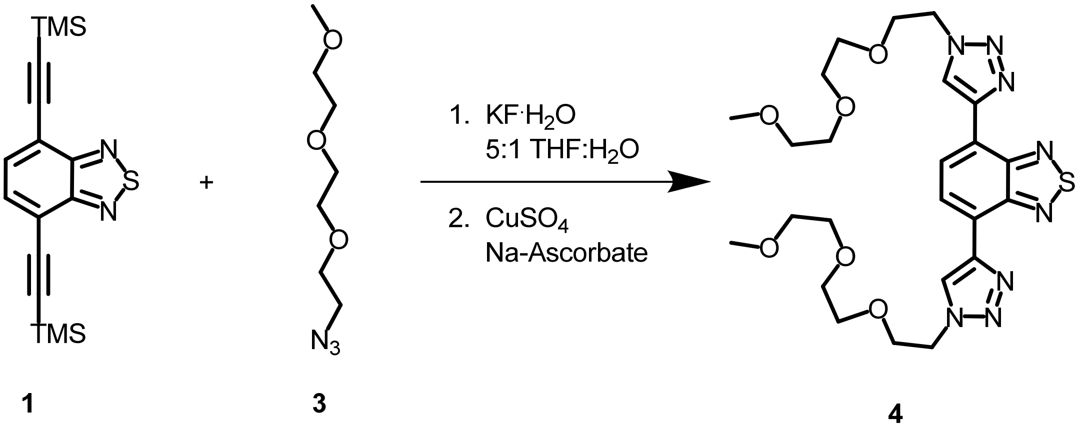
Table of Contents:

Methods and Materials

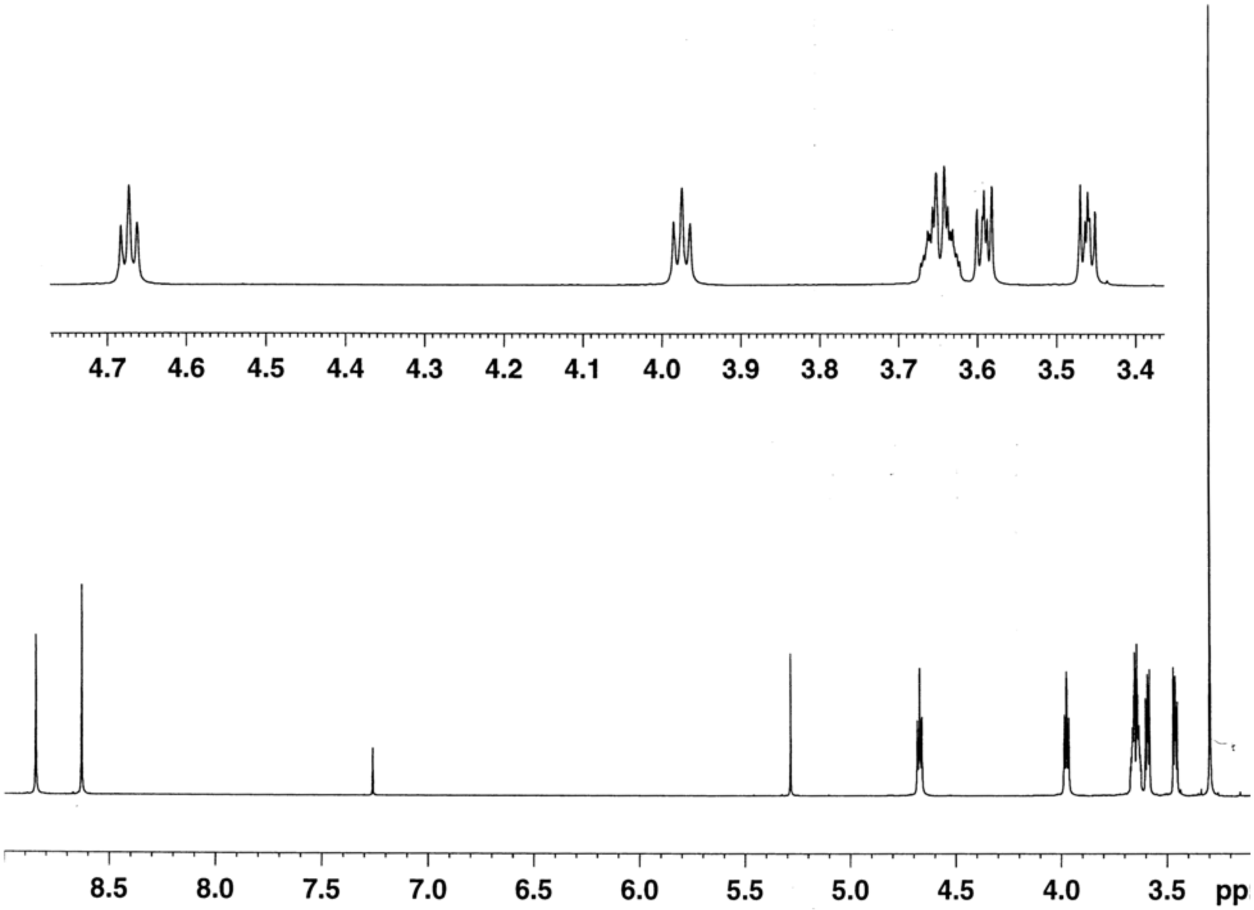
All chemicals were purchased and used without purification unless otherwise specified. Column chromatography was performed using Standard Grade silica gel 60 Å, 32-63 μm (230 x 450 mesh) and the indicated eluent. Elution of compounds was readily monitored using a handheld UV lamp (365 nm). Unless otherwise specified, NMR spectra were recorded at 298 K (500 or 300 MHz). Chemical shifts are reported in parts per million (ppm), using residual solvent (chloroform-*d*) as an internal standard. Data reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant, and integration. Lifetime measurements were obtained utilizing a 372 nm laser diode. Compounds **3** and **7** were synthesized according to modified procedures described in the literature.[1,2]

Section 1: 4,7-bis(1-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-1H-1,2,3-triazol-4-yl)benzo[c][1,2,5]thiadiazole.

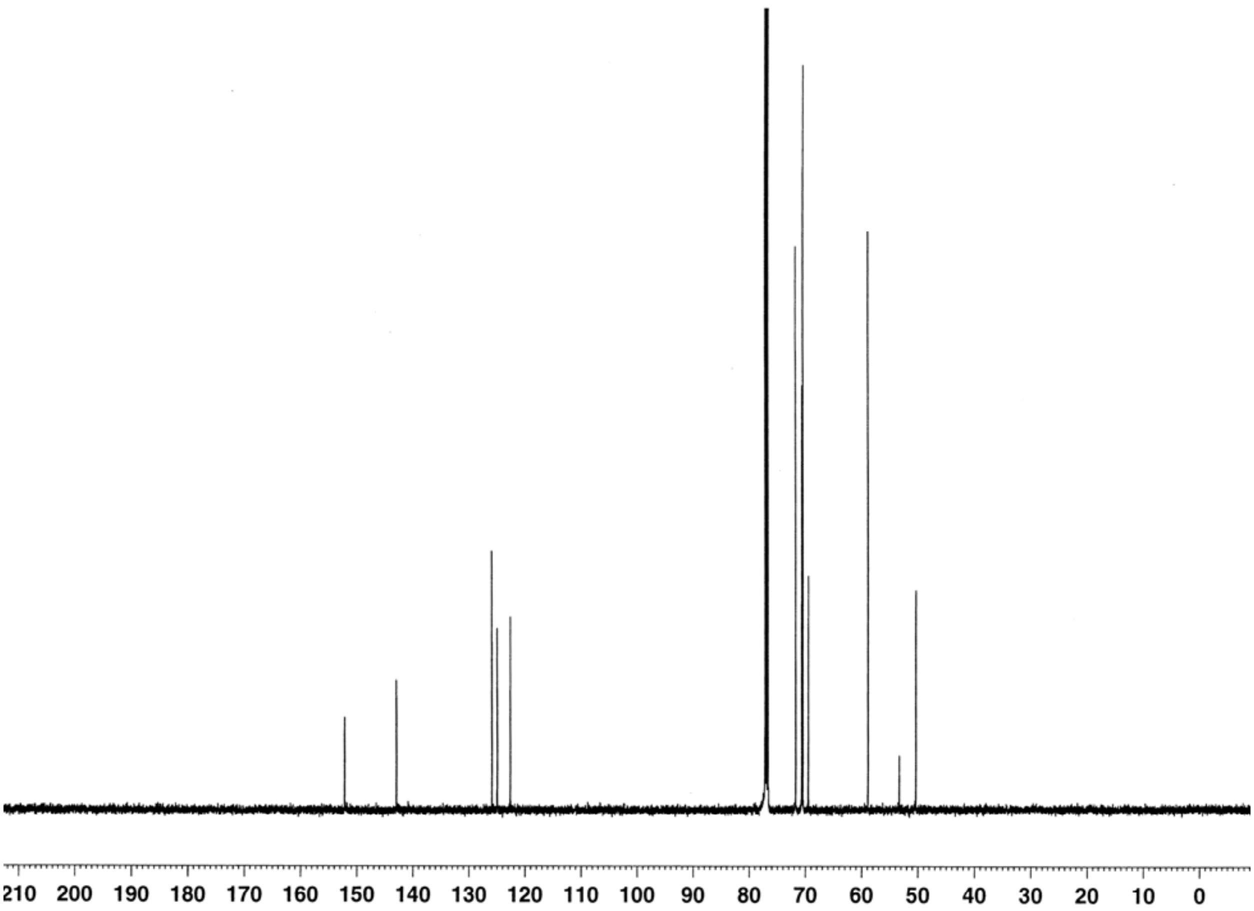
Synthesis:



To a stirring solution of 0.150 g (1.0 eq, 4.57x10^{-4} mol) of 4,7-bis((trimethylsilyl) ethynyl)benzo[c][1,2,5]thiadiazole (**1**) in 10 mL of 5:1 THF:H_2O was added 0.139 g (4.0 eq, 1.826x10^{-3} mol) of KF hydrate was added and the solution was allowed to stir for 30 minutes. After the addition of 0.216 g (2.5 eq, 1.14x10^{-3} mol) of **3** the solution was freeze-pump-thawed three times to remove any oxygen. While under a flow of N_2, 0.182 g (2.5 eq, 1.14x10^{-3} mol) of copper sulfate and 0.226 g (2.5 eq, 1.14x10^{-3} mol) of sodium ascorbate was added. After stirring overnight, the crude mixture was filtered through celite with dichloromethane. The solvent was removed under vacuum. The product was filtered through a short silica column with dichloromethane followed by ethyl acetate as the eluent to elute any thiadiazole starting material. The product (**4**) was then eluted with acetone. After concentration, the recovered oil was dissolved in water and lyophilized for two days to yield a yellow/green solid in 55% yield (0.141 g). ^{1}H-NMR (500 MHz, $CDCl_3$) 3.30 (s, 6H), 3.46 (m, 4H), 3.59 (m, 4H), 3.65 (m, 8H), 3.98 (t, 4H J=5 Hz), 4.68 (t, 4H J=5 Hz), 8.63 (s, 2H), 8.85 (s, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) 50.44, 58.95, 69.56, 70.54, 70.73, 71.83, 122.67, 125.02, 125.97, 143.00, 152.25; IR (KBr) $\tilde{\nu}$ 3500 (w), 3175 (m), 3113 (w), 2870 (s), 2291 (w), 1946 (w), 1580 (w), 1539 (w), 1456 (s), 1366 (s), 1271 (s), 1227 (s), 1142 (s), 1045 (s), 981 (s), 879 (s), 825 (s), 692 (s), 619 (s), 500 (s); HRMS Calc. for $C_{24}H_{35}O_6N_8S$ (FAB **4** + H) 563.24003, found 563.24070.



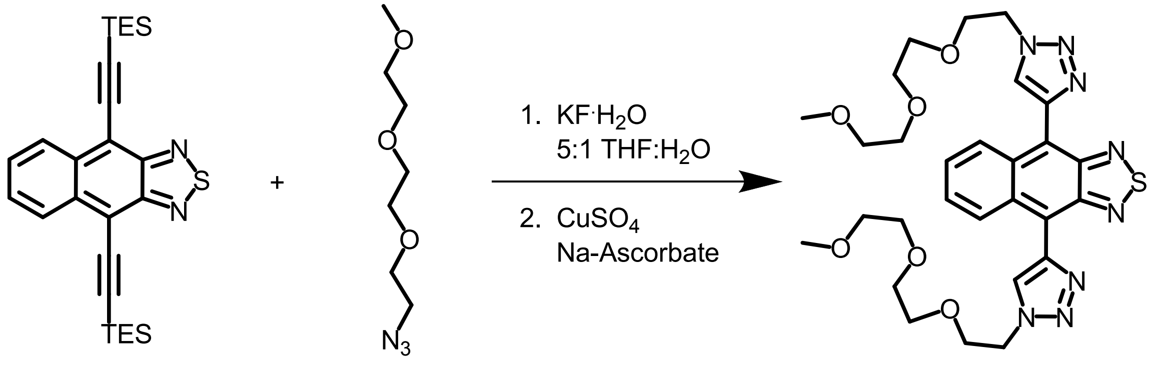
SI Figure 1. ^{1}H-NMR Spectrum ($CDCl_3$) of **4**.



SI Figure 2. ^{13}C-NMR Spectrum ($CDCl_3$) of **4**.

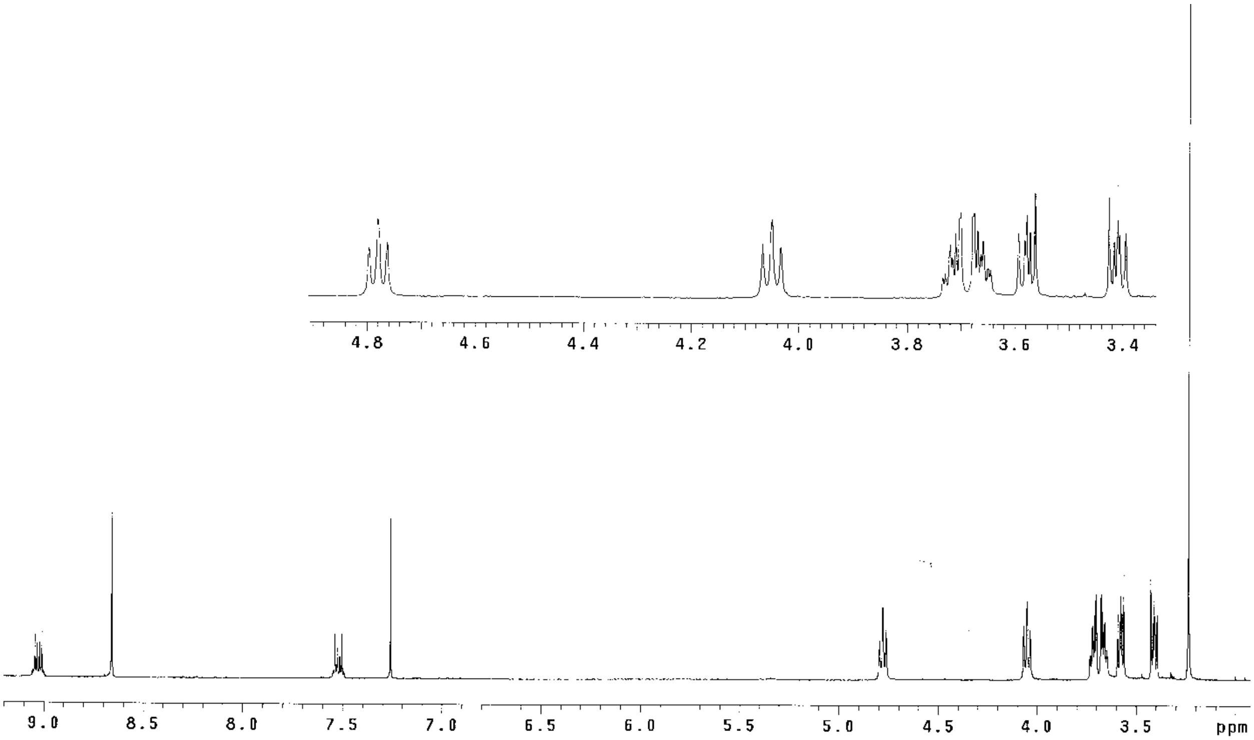
Section 2: 4,9-bis(1-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-1H-1,2,3-triazol-4-yl)naphtho[c][1,2,5]thiadiazole.

Synthesis:



2 **3** **5**

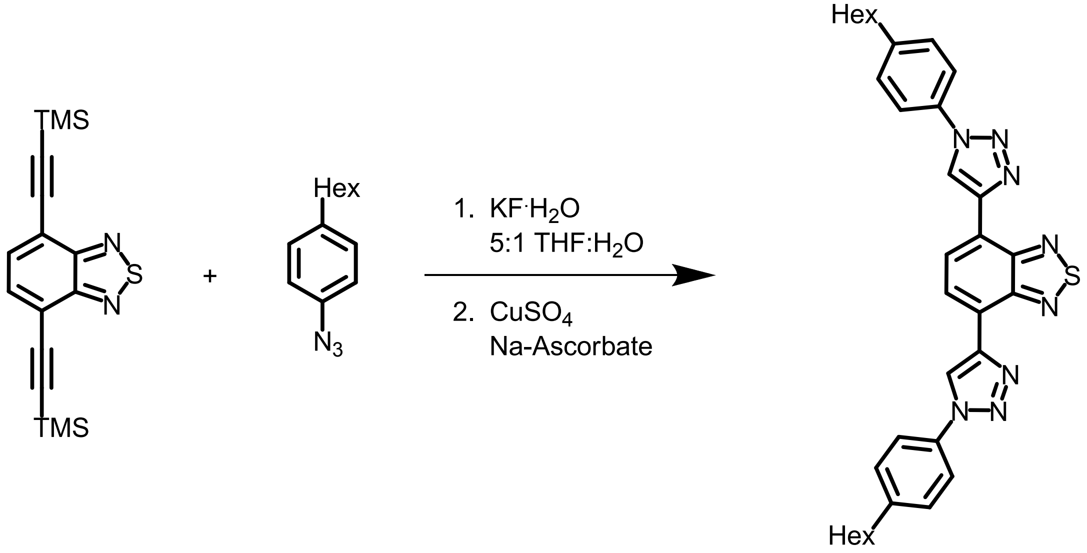
To a stirring solution of 0.150 g (1.0 eq, 3.24×10^{-4} mol) of 4,9-bis((triethylsilyl)ethynyl)naphtho[2,3-c][1,2,5]thiadiazole (**2**) in 10 mL of 5:1 THF:H_2O was added 0.099 g (4.0 eq, 1.3×10^{-3} mol) of KF hydrate was added and the solution was allowed to stir for 30 minutes. After the addition of 0.153 g (2.5 eq, 8.10×10^{-4} mol) of **3** the solution was freeze-pump-thawed three times to remove any oxygen. While under a flow of N_2, 0.129 g (2.5 eq, 8.10×10^{-4} mol) of copper sulfate and 0.161 g (2.5 eq, 8.10×10^{-4} mol) of sodium ascorbate was added. After stirring overnight, the crude mixture was filtered through celite with dichloromethane. The solvent was removed under vacuum. The product was filtered through a short silica column with dichloromethane followed by ethyl acetate as the eluent to elute any thiadiazole starting material. The product (**5**) was then eluted with 20% acetone in ethyl acetate. After concentration, the recovered oil was dissolved in water and lyophilized for two days to yield a red solid in 60% yield (0.119 g). ^{1}H-NMR (500 MHz, $CDCl_3$) 3.24 (s, 6H), 3.41 (m, 4H), 3.58 (m, 4H), 3.69 (m, 8H), 4.05 (t, 4H J=5 Hz), 4.78 (t, 4H J=5 Hz), 7.52 (dd, 2H J=6Hz), 8.66 (s, 2H), 9.03 (dd, 2H J=6Hz); IR (KBr) $\tilde{\nu}$ 3497 (w), 3148 (m), 2870 (s), 1950 (w), 1647 (w), 1533 (w), 1458 (s), 1352 (s), 1259 (s), 1109 (s), 1051 (s), 893 (s), 822 (s), 765 (s), 721 (s), 529 (s); HRMS Calc. for $C_{28}H_{37}O_6N_8S$ (FAB **5** + H) 613.25568, found 613.25273.



SI Figure 3. ^{1}H-NMR Spectrum ($CDCl_3$) of **5**.

Section 3: 4,7-bis(1-(4-hexylphenyl)-1H-1,2,3-triazol-4-yl)benzo[c][1,2,5]thiadiazole.

Synthesis:

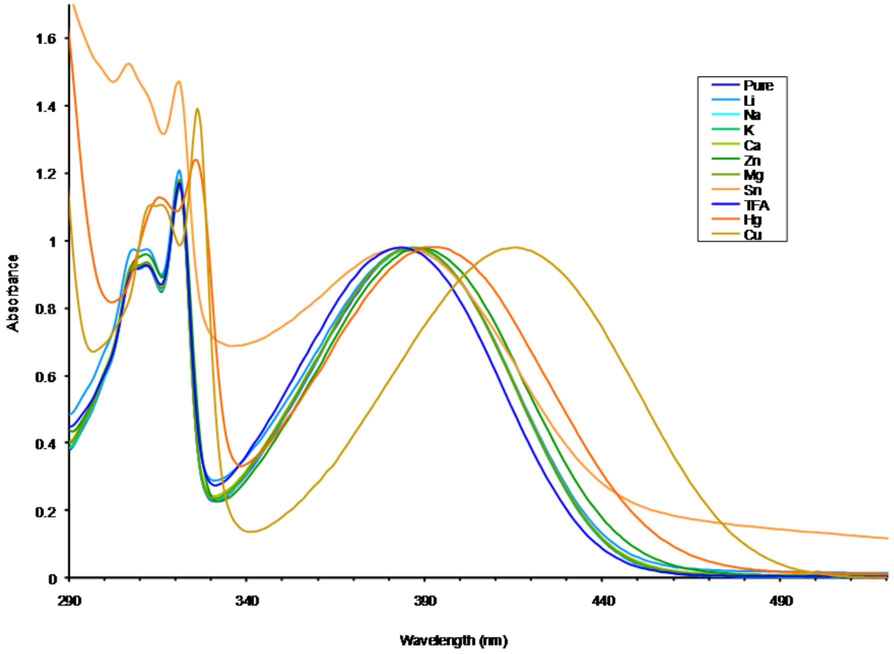


1 **7** **6a**

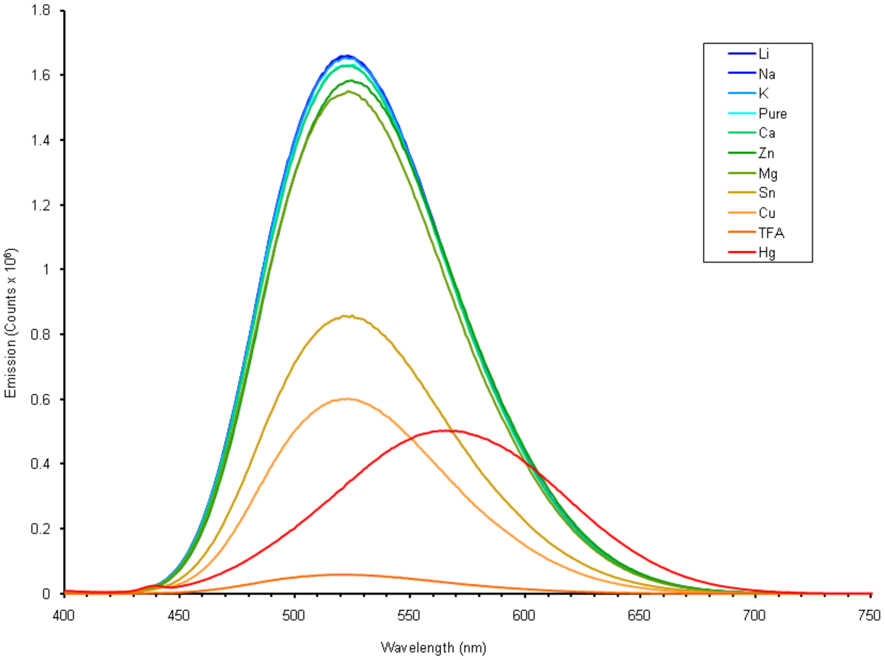
To a stirring solution of 0.150 g (1.0 eq, $4.57x10^{-4}$ mol) of 4,7-bis((trimethylsilyl) ethynyl)benzo[c][1,2,5]thiadiazole (**1**) in 10 mL of 5:1 THF:H_2O was added 0.139 g (4.0 eq, $1.826x10^{-3}$ mol) of KF hydrate was added and the solution was allowed to stir for 30 minutes. After the addition of 0.232 g (2.5 eq, $1.14x10^{-3}$ mol) of **7** the solution was freeze-pump-thawed three times to remove any oxygen. While under a flow of N_2, 0.182 g (2.5 eq, $1.14x10^{-3}$ mol) of copper sulfate and 0.226 g (2.5 eq, $1.14x10^{-3}$ mol) of sodium ascorbate was added. After stirring overnight, the crude mixture was filtered through celite with dichloromethane. The solvent was removed under vacuum. The product was filtered through a short silica column with dichloromethane to elute any thiadiazole starting material. The product (**4**) was then eluted with 5% ethyl acetate in DCM. Concentration under reduced pressure provided **6a** as a yellow solid (0.070g, 26% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) 0.89 (t, 6H), 1.32 (m, 12H), 1.63 (m, 4H), 2.65 (t, 4H), 7.29 (d, 4H J=5 Hz), 7.68 (d, 4H =5 Hz), 8.59 (s, 2H), 9.00 (s, 2H); ^{13}C-NMR

(125 MHz, $CDCl_3$) 14.41, 22.85, 29.14, 31.54, 31.92, 35.73, 120.44, 121.77, 122.49, 126.13, 129.76, 134.91, 143.54, 144.08, 152.16; IR (KBr) $\tilde{\nu}$ 3167 (m), 3051 (w), 2955 (s), 2924 (s), 2853 (s), 2280 (w), 1909 (m), 1728 (m), 1580 (m), 1517 (s), 1466 (m), 1410 (m), 1240 (s), 1177 (m), 1040 (s), 989 (s), 885 (s), 837 (s), 802 (s), 519 (s); HRMS Calc. for $C_{34}H_{38}N_8S$ (EI **6b** + H) 590.2940, found 590.2925.

Section 4: Addition of Triflate Metal Salts to **4** in Water.

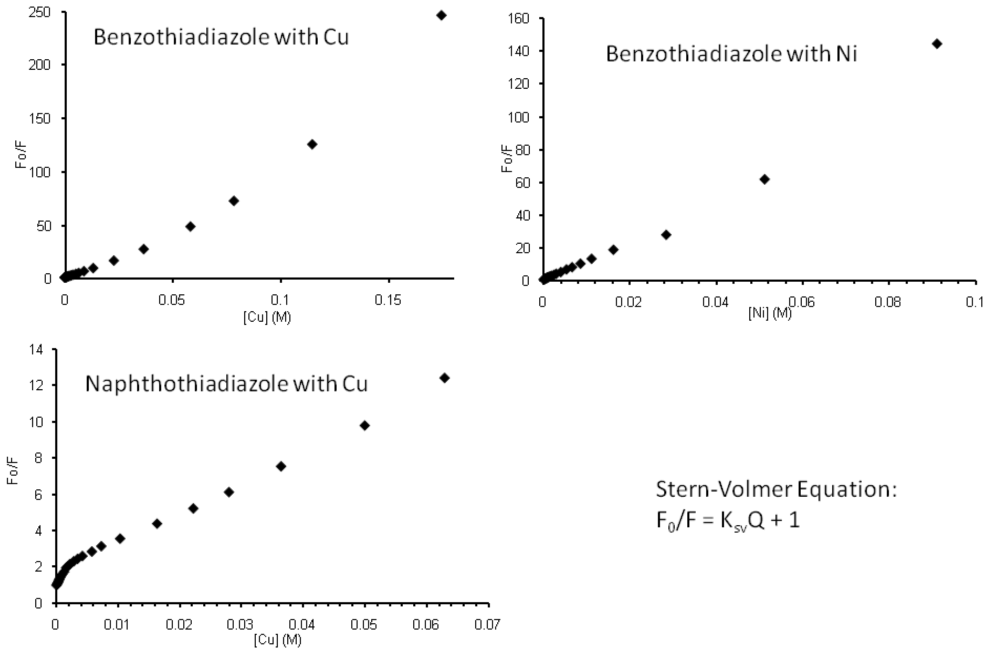


SI Figure 4. Absorption spectra of **4** before and after the addition of metal triflates and TFA in water. All fluorophore concentrations were at 89 μM.



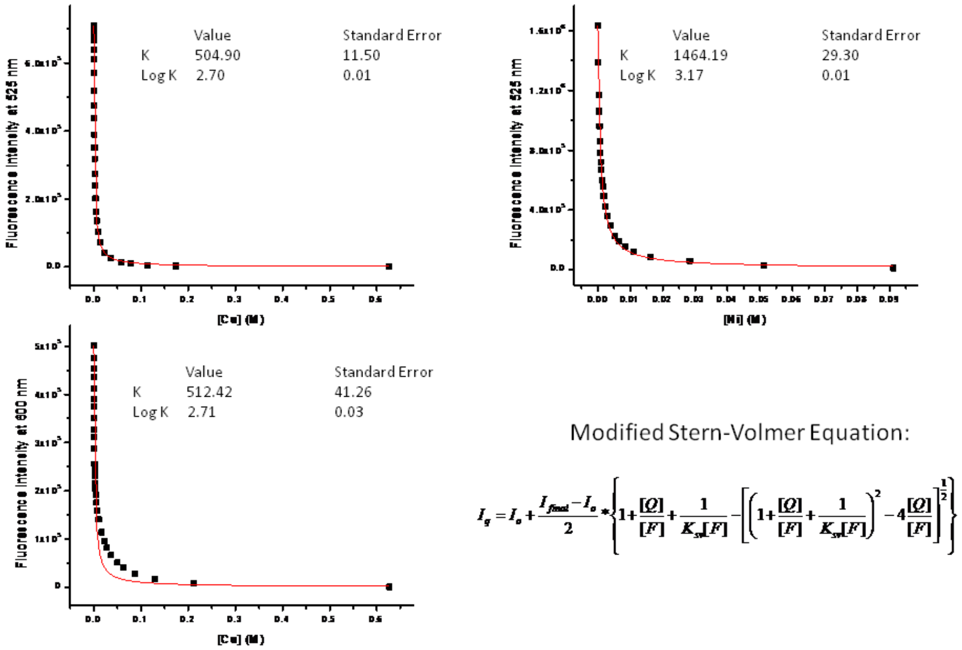
SI Figure 5. Emission spectra of **4** before and after the addition of metal triflates and TFA in water. All fluorophore concentrations were at 89 μM.

Section 5: Stern-Volmer Plots of **4** and **5**.



Stern-Volmer Equation:
$F_0/F = K_{sv}Q + 1$

SI Figure 6. Emission quenching data plotted according to the standard Stern-Volmer equation showing the non-linear behavior of the quenching.

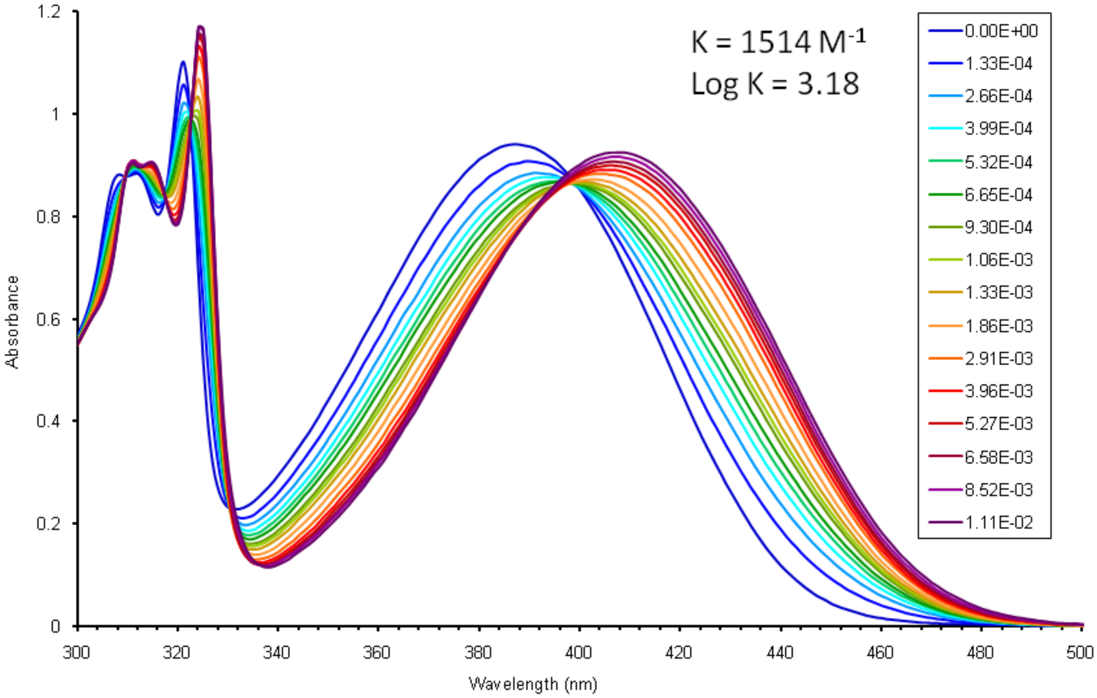


Modified Stern-Volmer Equation:

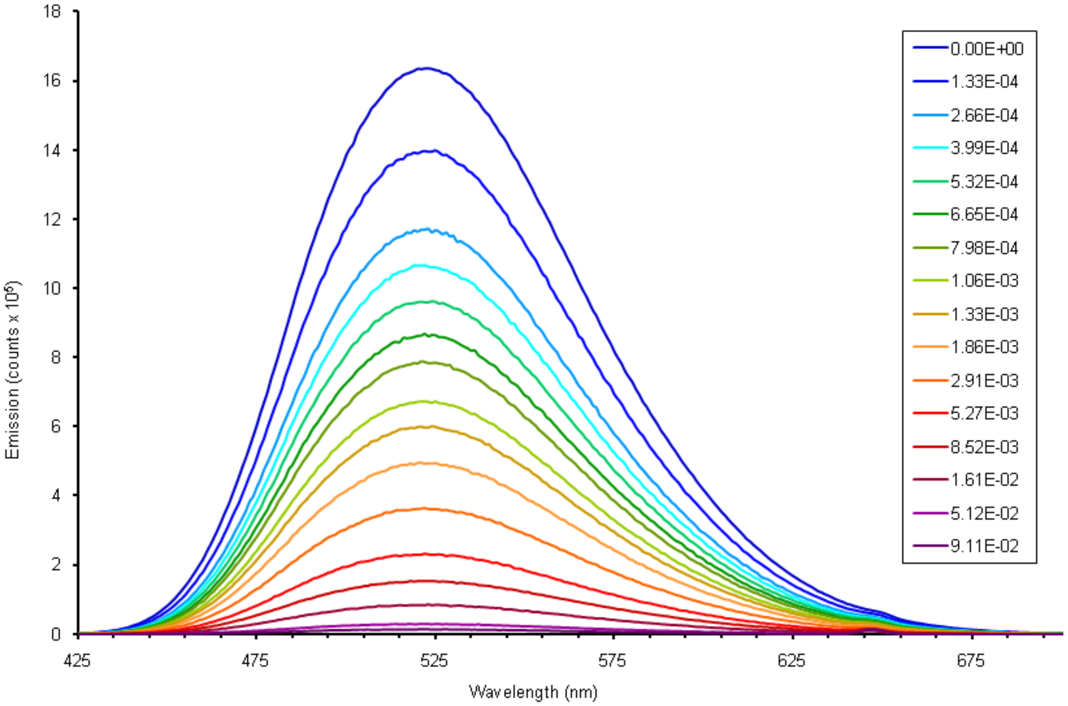
$$I_g = I_o + \frac{I_{final} - I_o}{2} * \left\{ 1 + \frac{[Q]}{[F]} + \frac{1}{K_{sv}[F]} - \left[\left(1 + \frac{[Q]}{[F]} + \frac{1}{K_{sv}[F]} \right)^2 - 4\frac{[Q]}{[F]} \right]^{\frac{1}{2}} \right\}$$

SI Figure 7. Emission quenching data plotted according to the modified Stern-Volmer equation.

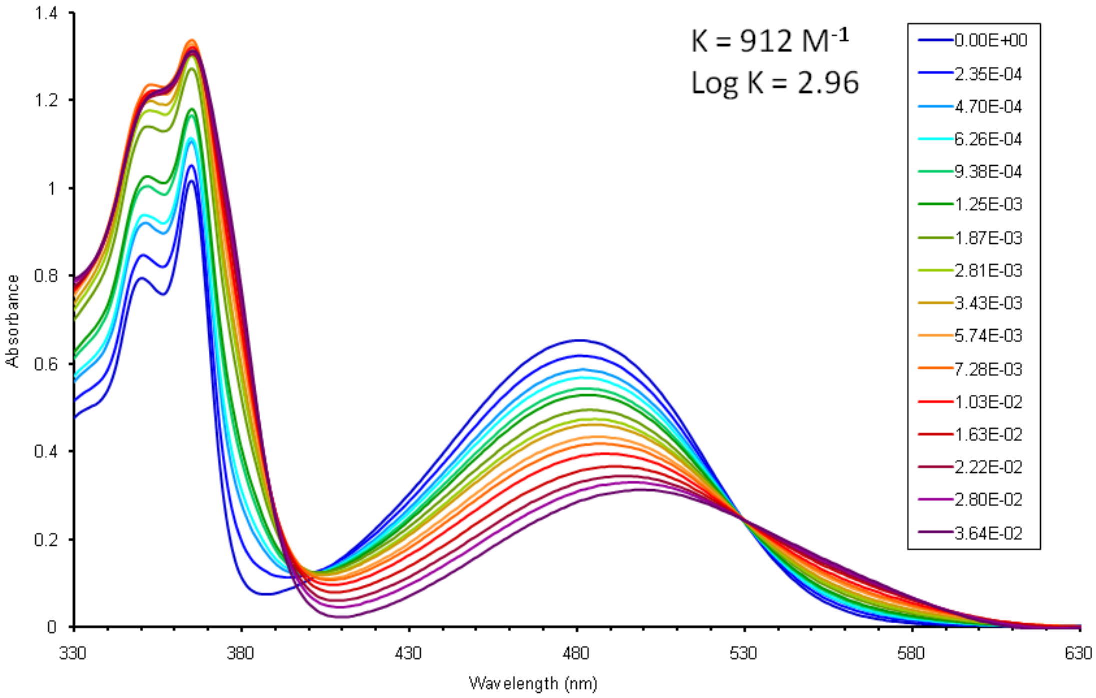
Section 6: Absorption and Emission Spectra of the Titration of **4** and **5**.



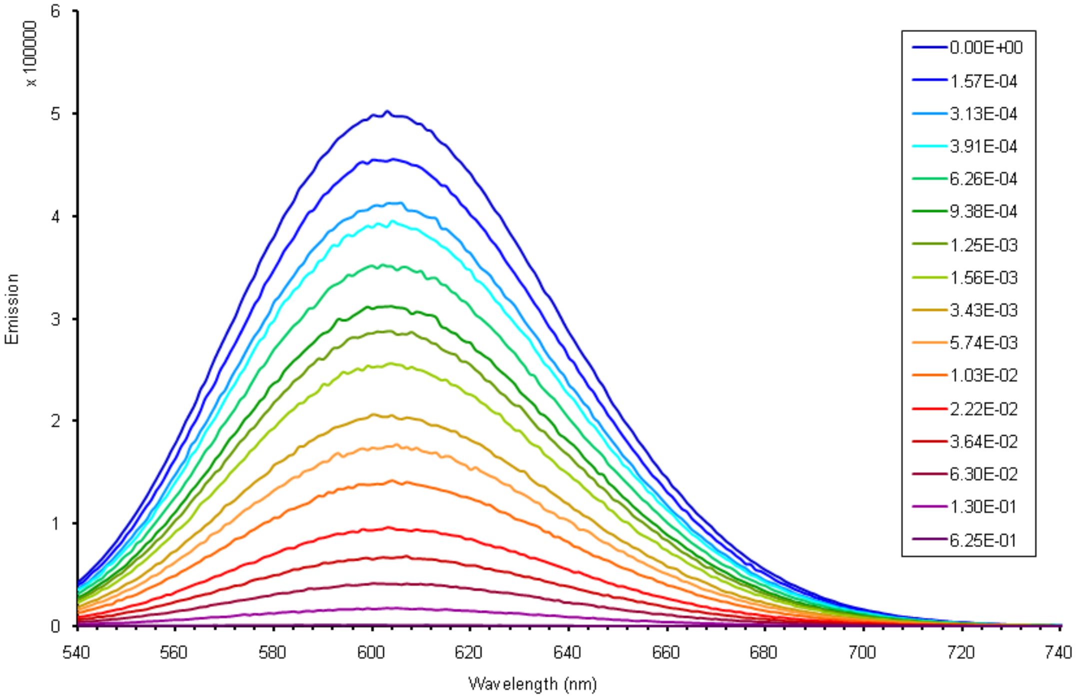
SI Figure 8. Absorption spectra of the titration of **4** (151 μM) with $NiSO_4$ in water.



SI Figure 9. Emission spectra of the titration of **4** (151 μM) with $NiSO_4$ in water.



SI Figure 10. Absorption spectra of the titration of **5** (166 μM) with $CuSO_4$ in water.



SI Figure 11. Emission spectra of the titration of 5 (166 μM) with $CuSO_4$ in water.

Section 7: References.

1. D. A. Neumayer, J. A. Belot, R. L. Feezel, C. Reedy, C. L. Stern, T. J. Marks, *Inorg. Chem.*, 1998, **37** (21), 5625.
2. M. Hu, J.i Li, S. Q. Yao, *Org. Lett.*, 2008, **10** (24), 5529.