Colorimetric Barbiturate Sensing with Hybrid Spin Crossover Assemblies

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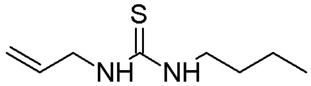
Electronic Supplementary Information

1. General Information

^{1}H and ^{13}C spectra were recorded on a Varian Inova 400 MHz or 500 MHz NMR spectrometer. Proton (^{1}H) chemical shifts are reported in parts per million (δ) with respect to tetramethylsilane (TMS, δ=0), and referenced internally with respect to the protio solvent impurity. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, Inc., Andover, MA, and used without further purification. UV/Vis spectroscopy was performed on a Cary 50 Photospectrometer using the Varian Scans program to collect data. All other materials were obtained from Aldrich Chemical Company, St. Louis, MO, or TCI, Tokyo, Japan and were used as received. Ligand **1**,[1] complexes **2** and **3**,[1] dioctyl barbiturate,[1] barbital,[2] and dibutyl barbiturate[3] were prepared according to previously published procedures.

2. Synthesis of Compounds



1-Allyl-3-butylthiourea (6):

Butylamine (1.05 mL, 10.6 mmol) was added to MeCN (10 mL), followed by addition of allyl isothiocyanate (1.00 mL, 10.2 mmol). This mixture was heat under reflux for 30 min, followed by cooling. The solvent and excess butylamine was evaporated *in vacuo* to give the desired product as a viscous yellow oil (1.45 g, 82%). ^{1}H NMR (400 MHz; $CDCl_3$) δ 6.64 (br s, 2H), 5.59 (ddd, *J* = 22.5, 10.5, 5.4 Hz, 1H), 4.94 (dt, *J* = 10.9 Hz, 5.4 Hz, 1H), 4.88 (dd, *J* = 10.2, 0.9 Hz, 1H), 3.85 (br s, 2H), 3.20 (br s, 2H), 1.29, (p, *J* = 7.3 Hz, 2H), 1.10 (sex, *J* = 7.4 Hz, 2H), 0.66 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz; $CDCl_3$) δ 180.8, 133.1, 116.0, 46.1, 43.8, 30.5, 19.4, 13.1. HRMS (ESI) m/z calcd for $C_8H_{17}N_2S$ ($[M+H]^+$) 173.1106, found 173.1321.

3. NMR Spectral Data

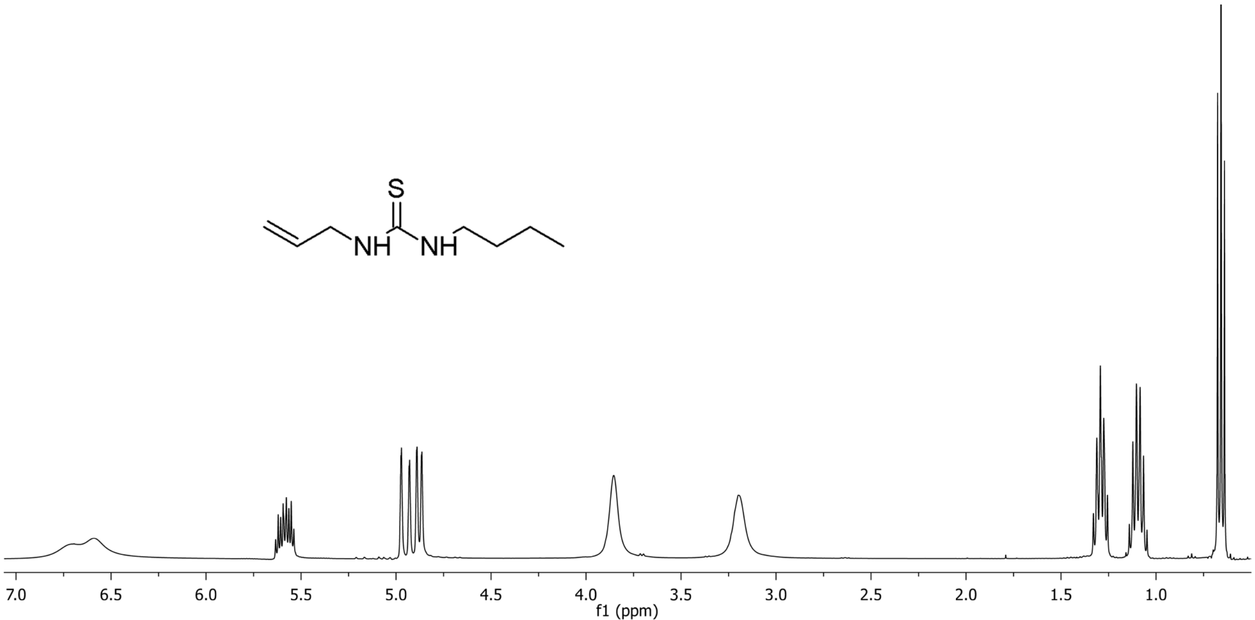


Figure S-1. ^{1}H NMR spectrum of **6** ($CDCl_3$, 400 MHz, 298 K).

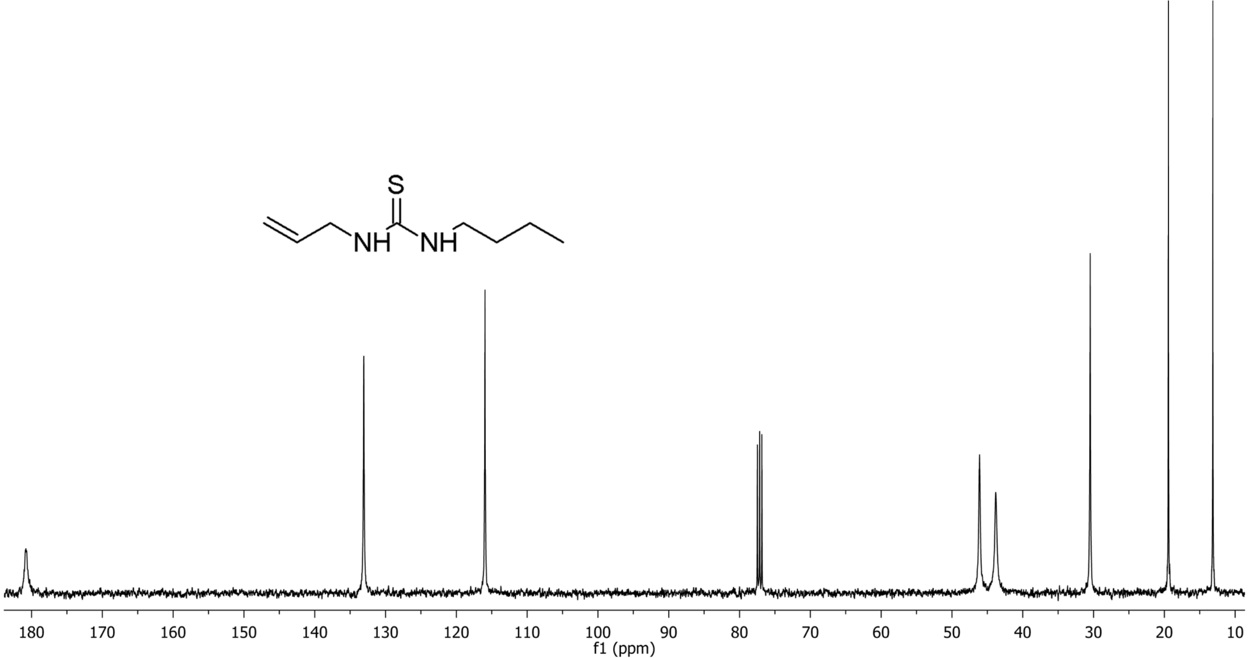


Figure S-2. ^{13}C NMR spectrum of **6** ($CDCl_3$, 100 MHz, 298 K).

4. Optical Spectroscopy Data

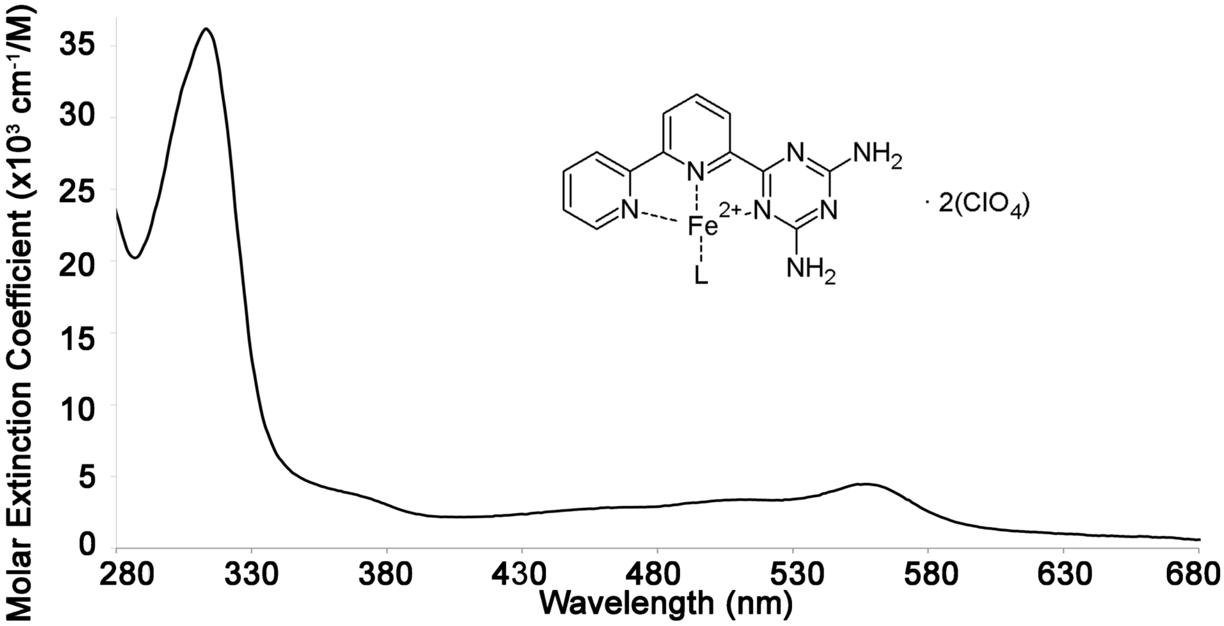


Figure S-3. UV/Vis absorbance spectrum of complex **2** (CH_3CN, 2.5 x 10^{-5} M).

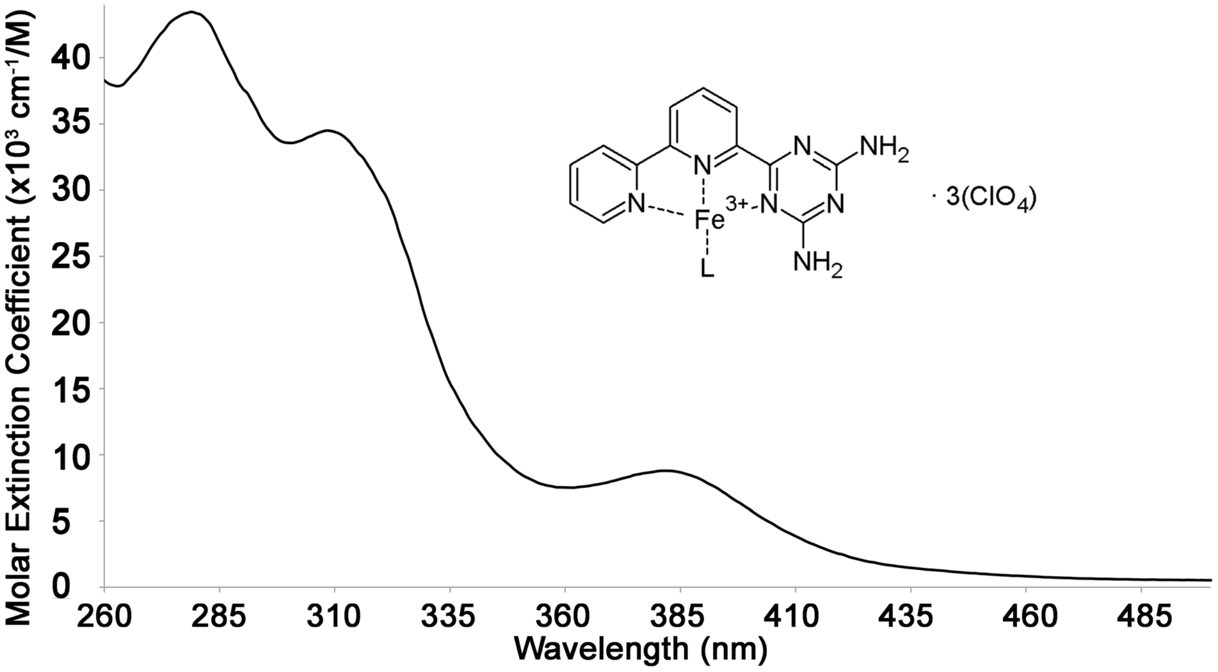


Figure S-4. UV/Vis absorbance spectrum of complex **3** (CH_3CN, 2.5 x 10^{-5} M).

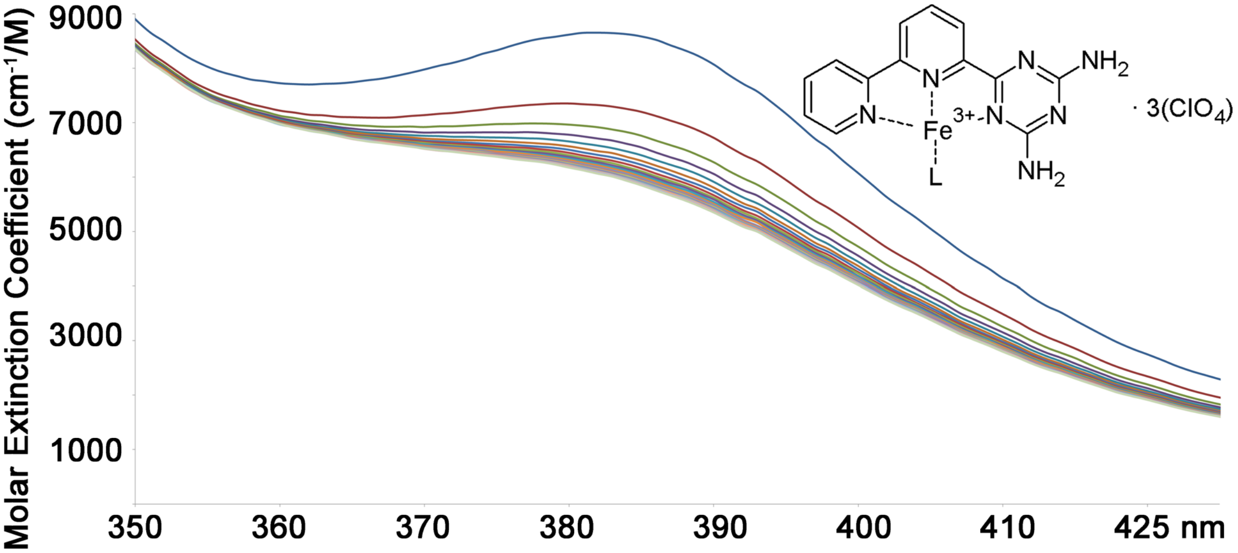


Figure S-5. Time dependent UV/Vis spectra of **3** treated with **4b** (2.4×10^{-5} M) monitored every minute for 20 min (CH_3CN, 1.15×10^{-4} M).

Figure S-6. Sensor fidelity when **2** is treated with **4b** (10 mM): a) After 4 d; b) After 10 d (CH_3CN, 1.15×10^{-4} M).

5. Compiled Spectral Data

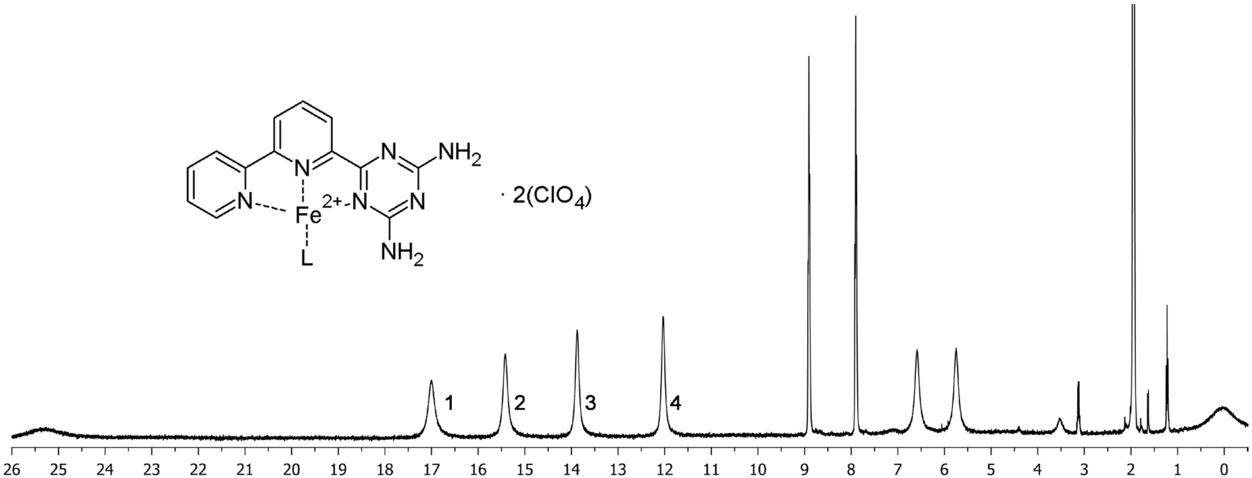


Figure S-7. ^{1}H NMR spectrum of **2** (CD$_3$CN, 400 MHz, 298 K).

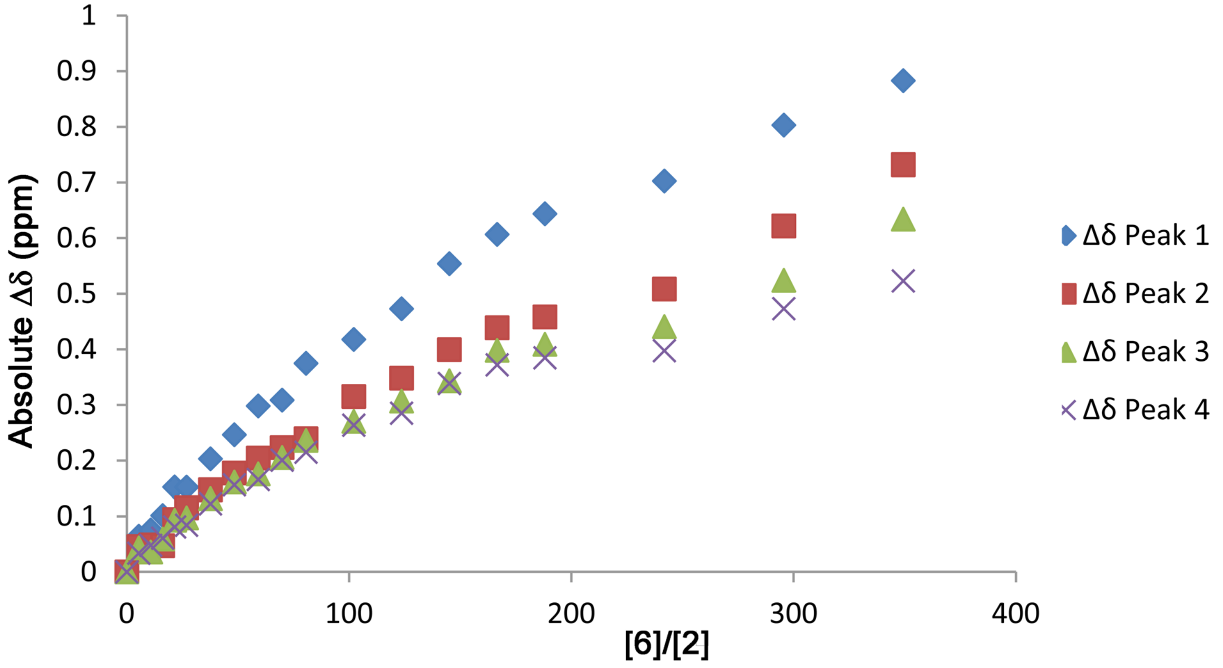


Figure S-8. Absolute change in the upfield chemical shift of selected proton resonances of **2** (see Figure *S*-7 for peak assignments) as a function of the concentration of **6** (CD$_3$CN, 400 MHz, 4.5 x 10^{-3} M).

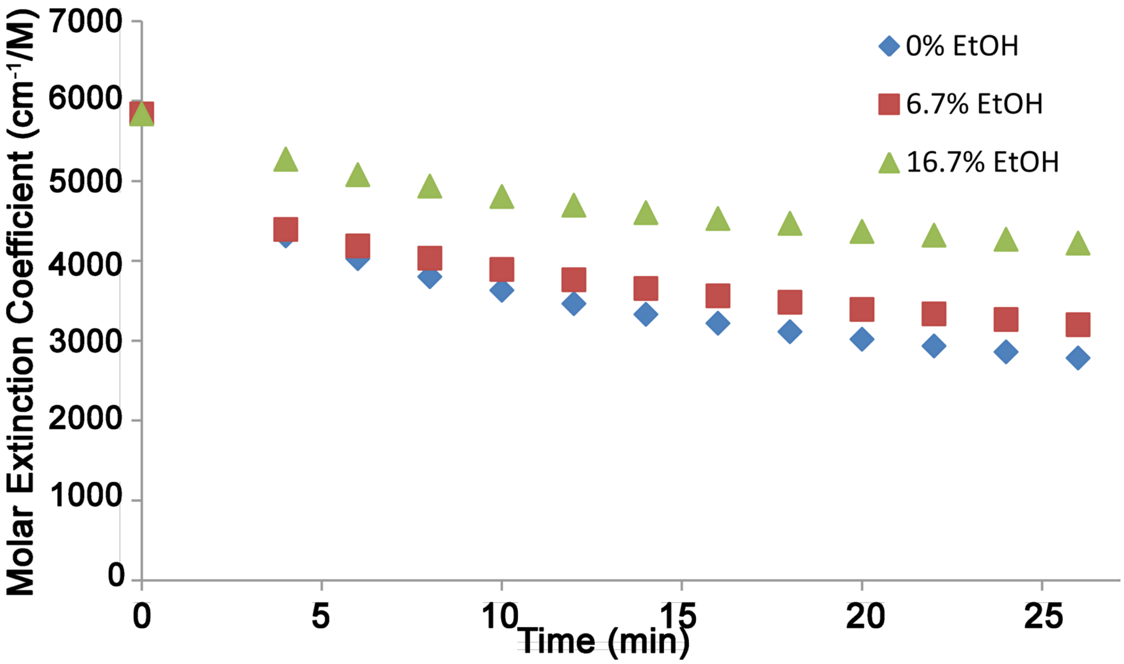


Figure S-9. Time dependent UV/Vis spectra of **2** combined with **4b** in the presence of varying amounts of EtOH (CH_3CN, 2.5 x 10^{-5} M).

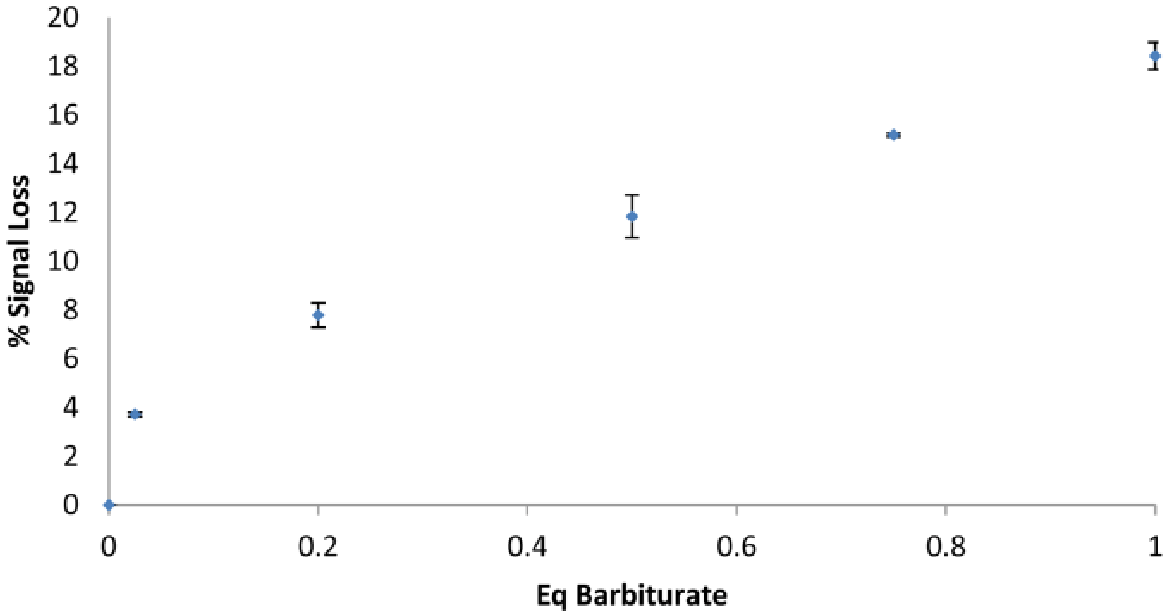


Figure S-10. Limit of detection data (CH_3CN, 5.0 x 10^{-5} M).

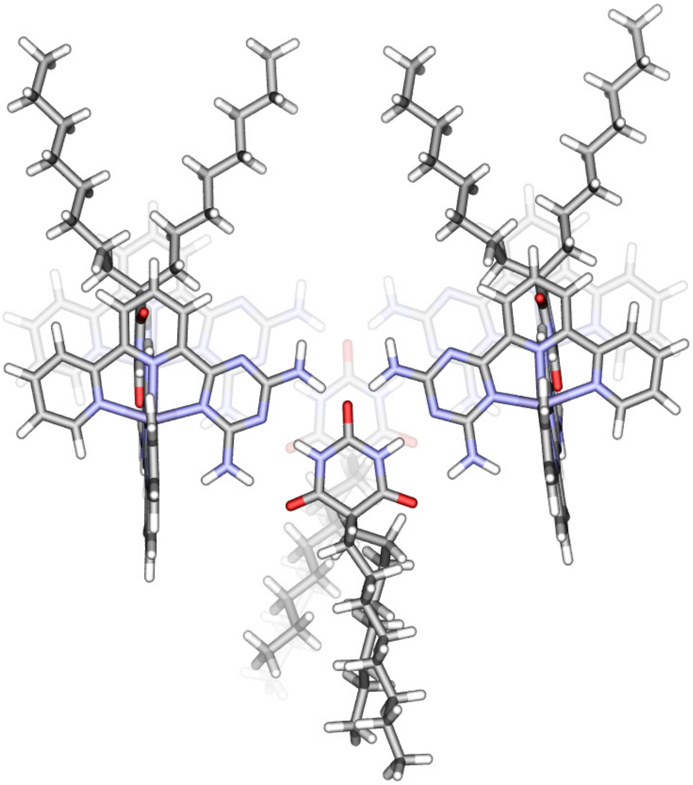


Figure S-11. Minimized structure of assembly **(2•4a)**$_4$ from a side view (SPARTAN**,** AM1 force field).

References

1) M. C. Young, E. Liew, J. Ashby, K. E. McCoy and R. J. Hooley, *Chem. Commun.*, 2013, **49**, 6331-6333.
2) A. Ashnagar, N. G. Naseri and B. Sheeri, *Chin. J. Chem.*, 2007, **25**, 382-384.
3) S. M. S. Chauhan and N. G. Giri, *Supramol. Chem.*, 2008, **20**, 743-752.