

Green, Efficient Detection and Removal of Hg^{2+} by Water-soluble Fluorescent Pillar[5]arene Supramolecular Self-assembly

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Experimental Characterizations

The UV-Vis absorption spectra were recorded using a Helios Alpha UV-Vis scanning spectrophotometer with a 1 cm quartz cell. Fluorescence spectra were quantitatively measured by FluoroMax-4 spectrofluorometer with a xenon lamp and 0.5 cm quartz cells. High-resolution mass spectra were carried on LCQ Fleet LC-MS System (Thermo Fisher Scientific). Mass spectra were recorded on Waters ACQUITY TQD liquid chromatograph-mass spectrometer using APCI ionization. ¹H NMR and ¹³C NMR spectra were carried on a Bruker spectrometer. Compounds **P5A2** and **DPP-Br** were prepared according to the previous method, respectively [S1, S2].

Synthesis of host molecule **H** and guest molecule **G**

Synthesis of compound **H**

Compound **P5A2** (735 mg, 0.5 mmol) was dispersed in ethanol (50 mL). Then, NaOH solution (400 mg NaOH in 0.5 mL of deionized H₂O) was added to the mixture. The mixture was stirred at 80 °C under an N₂ atmosphere for 8 h, during which a white precipitate was formed. After cooling to room temperature, the precipitate was filtered and washed with a mixed solution of ethanol and water (100/1, v/v) to afford pure compound **H** as a white solid (85% yield, 600 mg). ¹H NMR (D₂O, 500 MHz, δ , ppm): 6.70 (s, 10 H), 4.46-4.43 (d, J = 16 Hz, 10 H), 4.17-4.14 (d, J = 16 Hz, 10 H), 3.74 (s, 10 H). ¹³C NMR (125 MHz, D₂O) δ 177.50, 149.17, 128.48, 114.35, 67.62, 28.96.

Synthesis of compound **G**

Compound **DPP-Br** (220 mg, 0.351 mmol) and trimethylamine (83 mg, 1.404 mmol) were dissolved in chloroform (10 mL). The mixture was stirred at 65 °C under an N₂ atmosphere for 10 h, during which a red precipitate was formed. After cooling, the precipitate was filtered and washed with chloroform to result in a red solid **G** (98% yield, 250 mg). ¹H NMR (500 MHz, D₂O) δ 8.33-8.32 (d, J = 3.8 Hz, 2 H), 7.78-7.77 (d, J = 4.9 Hz, 2 H), 7.19-7.17 (t, J = 4.4 Hz, 2 H), 3.55-3.51 (t, J = 7.9 Hz, 4 H), 3.25-3.21 (m, 4 H), 3.08 (s, 18 H), 1.72-1.67 (m, 8 H), 1.43-1.40 (m, 4 H), 1.26 (s, 8 H). ¹³C NMR (125 MHz, D₂O) δ 160.97, 140.21, 135.18, 133.06, 128.69, 106.35, 66.48, 52.84, 41.85, 28.51, 25.45, 24.92, 22.27.

The host-guest complexation by ¹H NMR titration experiment

The **G** solution in D₂O (8.3 mM) was firstly prepared. Then, different concentration of **H** in D₂O (up to 33.2 mM) was added. After 5 min, the ¹H NMR spectrum was recorded.

Experimental procedure of **H**⊃**G** for Hg^{2+} detection

The **H₂G** (10 μ M) in water was mixed with different concentrations of Hg^{2+} aqueous solution at 25 $^{\circ}\text{C}$ for 1 min. Individual samples for spectral data were recorded. The resulting individual solution was shaken well for absorption and fluorescence spectral analysis.

The emission color change of **H₂G** loaded filter paper in presence of Hg^{2+} and following S^{2-}

A volume of 200 μL of water stock solution of the **H₂G** (1 mM) was drop-casted onto the Whatman filter paper, followed by evaporation to dry. The **H₂G** loaded filter paper was exposed to Hg^{2+} aqueous solutions for 1 min, and following treatment with S^{2-} . Then the emission color change under 365 nm irradiation was measured with a camera.

Measurement of detection limit

The detection limit was gained from the fluorescence titration data. On the basis of the results of the emission titrating experiment, a good linear relationship between the emission at 560 nm of **H₂G** and Hg^{2+} concentrations ranging from 10 to 40 μM was obtained. A limit of detection (LOD) was calculated by means of Eq. (1):

$$\text{Detection limit} = (3 \times \sigma) / k \quad (1)$$

Where σ is the standard deviation of blank measurements, k is the slope between emission at 560 nm versus Hg^{2+} concentration.

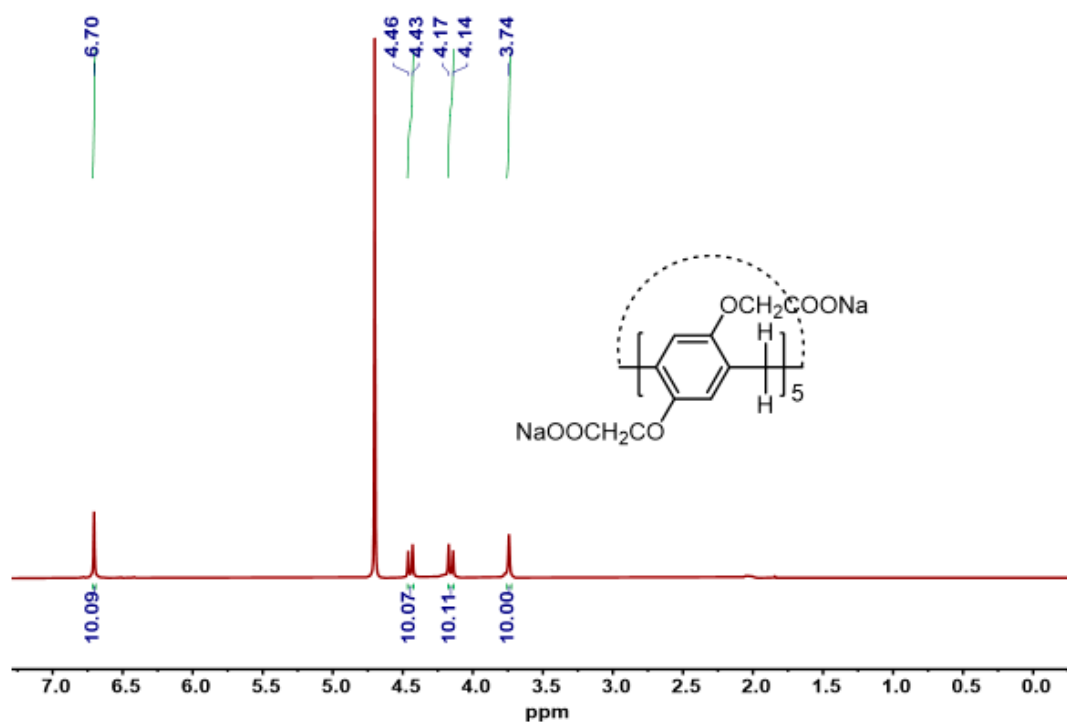


Figure S1. ^1H NMR spectrum (500 MHz, D_2O) of **H₂G**.

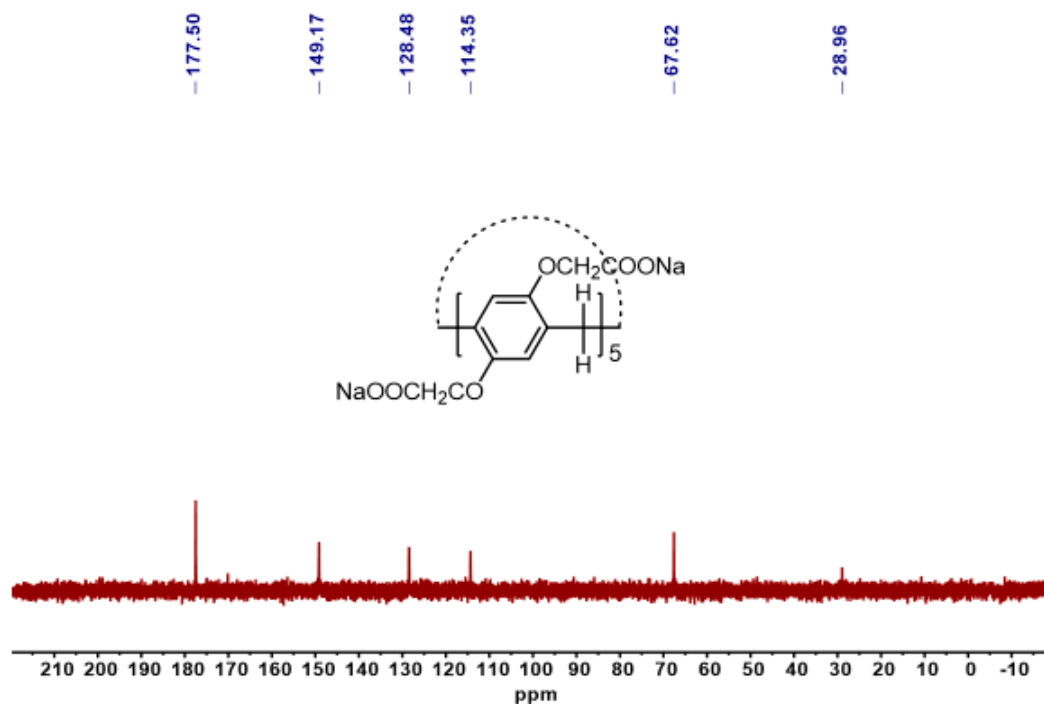


Figure S2. ^{13}C NMR spectrum (125 MHz, D_2O) of compound H.

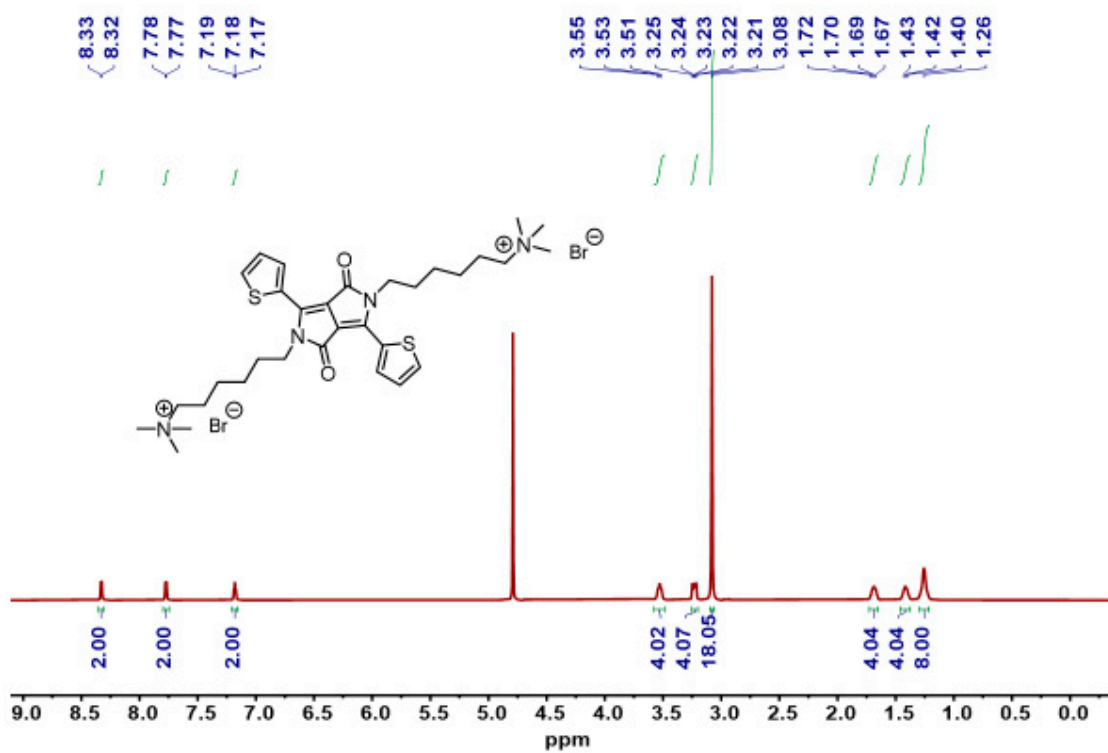


Figure S3. ^1H NMR spectrum (500 MHz, D_2O) of G.

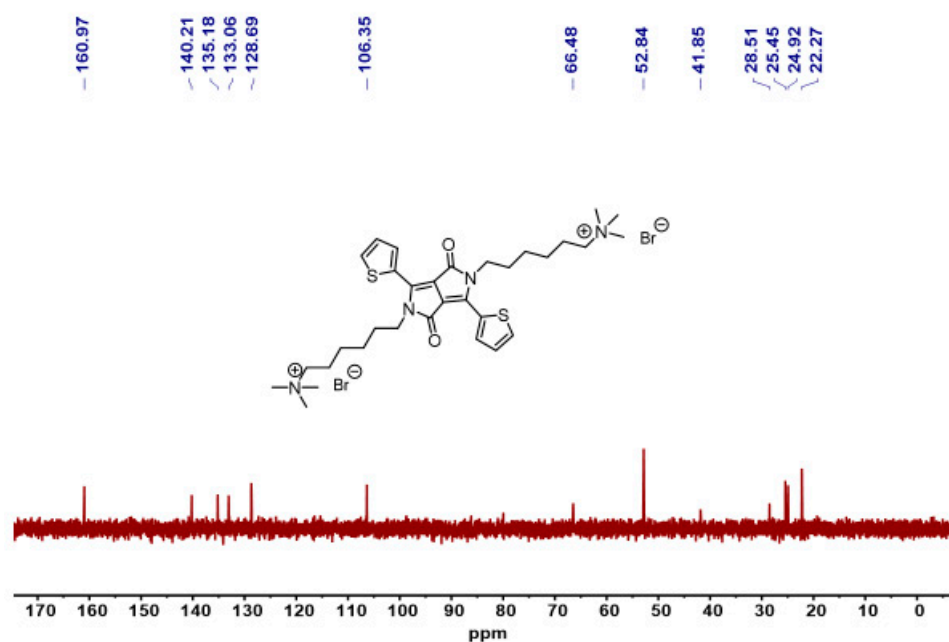


Figure S4. ^{13}C NMR spectrum (125 MHz, D_2O) of **G**.

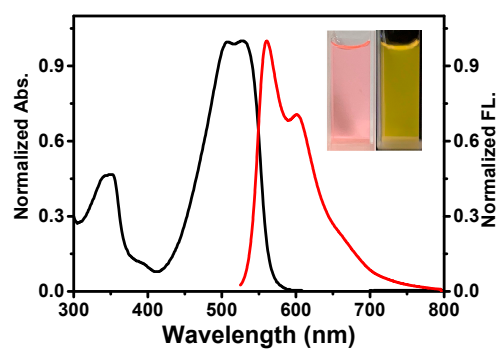


Figure S5. Normalized UV-vis emission spectra of **G** in aqueous solution (insert: photographs of aqueous solutions of **G** under daylight and 365 nm light irradiation [G]= 10^{-5} M).

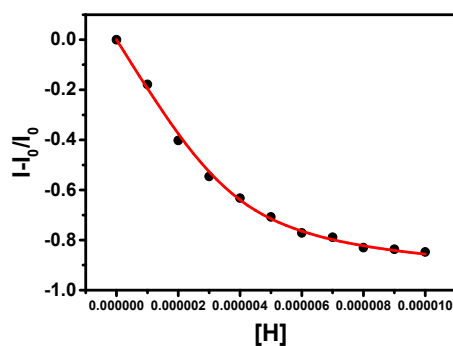


Figure S6. Binding isotherm of the H_2G complex fitted with a 1:2 binding model according to fluorescence titration experiment ($[\text{G}]=10^{-5}$ M, $\lambda_{\text{ex}} = 510$ nm).

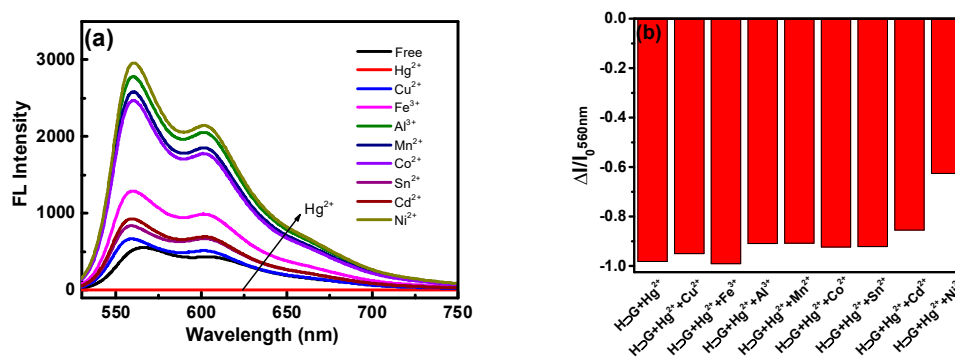


Figure S7. (a) The emission spectra of **H₂G** in presence of different metal ions. (b) Plot of fluorescence intensity changes at 560 nm ($\Delta I/I_0$) in presence of with the addition of 50.0 equiv. in the presence of 50.0 equiv. of other cations in aqueous solution (Hg^{2+} , Cu^{2+} , Fe^{3+} , Al^{3+} , Mn^{2+} , Co^{2+} , Sn^{2+} , Cd^{2+} , Ni^{2+}).

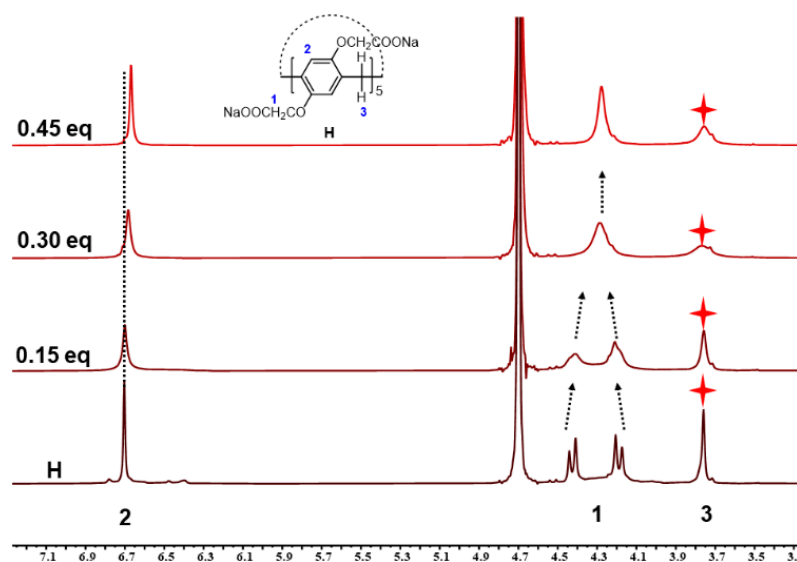


Figure S8. ^1H NMR titration spectra (500 MHz, D_2O) of **H** ($[\text{H}] = 8 \text{ mM}$) with different equivalents of Hg^{2+} .

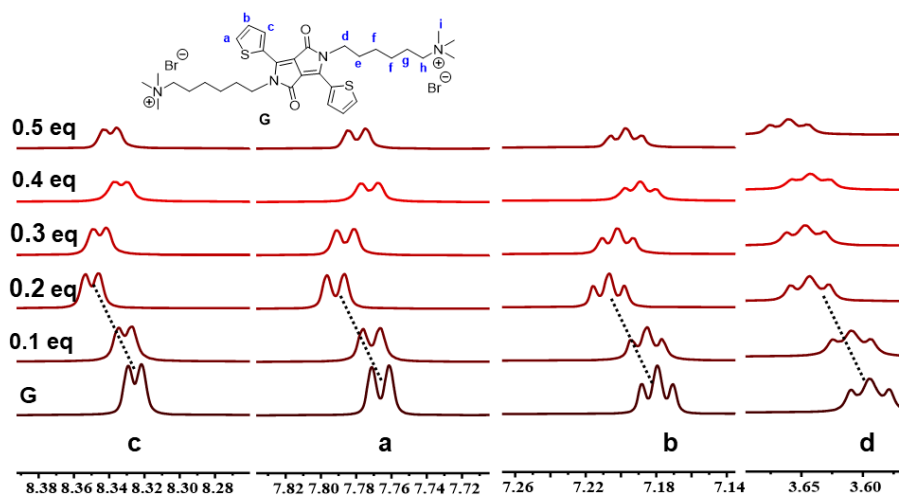


Figure S9. Partial ^1H NMR titration spectra (500 MHz, D_2O) of **G** ($[\text{G}] = 8 \text{ mM}$) upon addition of Hg^{2+} .

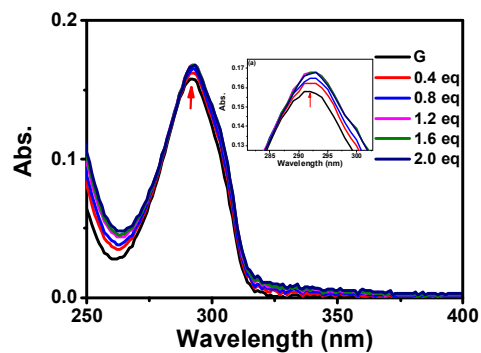


Figure S10. UV-vis spectra of **H** upon addition of Hg^{2+} ($[\text{H}]=10^{-5}$ M).

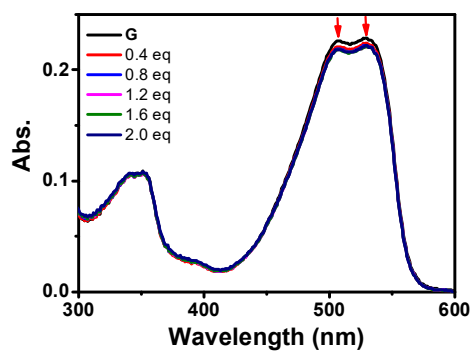


Figure S11. UV-vis spectra of **G** upon addition of Hg^{2+} ($[\text{G}]=10^{-5}$ M).

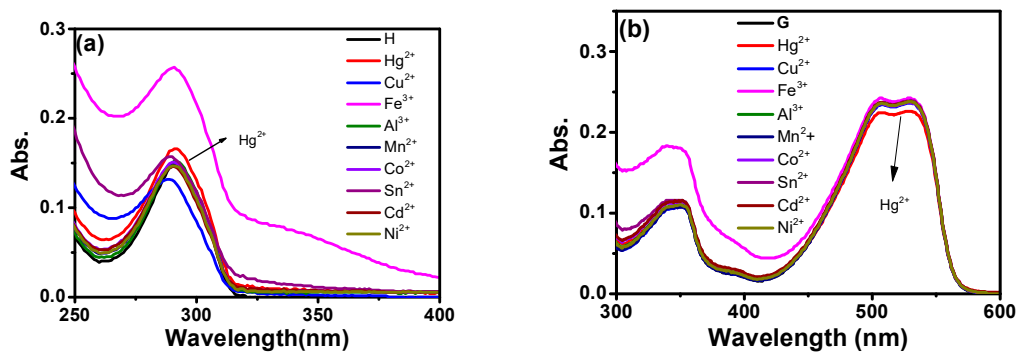


Figure S12. UV-vis spectra of (a) **G** and (b) **H** upon addition of 5 equiv. of different metal ions ($[\text{G}] = [\text{H}] = 10^{-5}$ M).

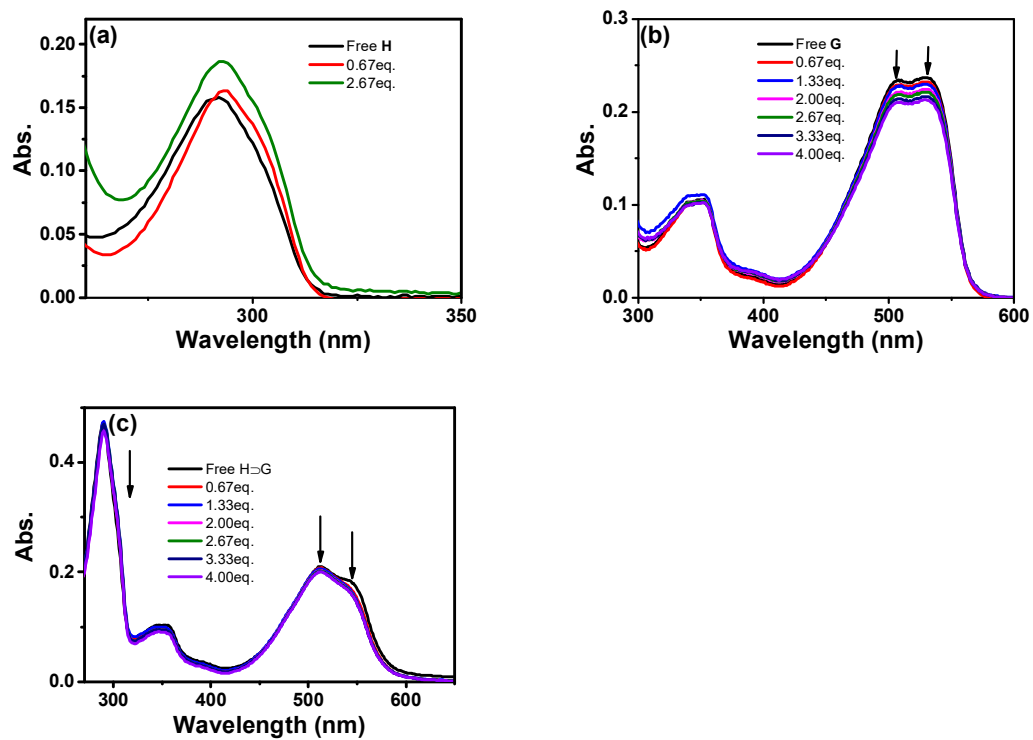


Figure S13. UV-vis spectra of (a) **G**, (b) **H** and (c) **H₂G** upon addition of various amount of S^{2-} ($[G] = [H] = 10^{-5}$ M, for **H₂G**, $[H] = 10^{-5}$ M, $[G] = 2 \times 10^{-5}$ M)