

Supplementary Material

A novel magnetic fluorescent chemosensor for Cu²⁺ based on self-assembled systems of azobenzene and α -cyclodextrin

1. Synthesis of iron oxide nanoparticles

Iron oxide magnetic nanoparticles (Fe₃O₄) were prepared through a hydrothermal reaction. Briefly, FeCl₃·6H₂O (1.35 g, 5 mmol) was dissolved in ethylene glycol (40 mL) to form a clear solution under magnetic stirring. Then, NaOAc (3.6 g) were added to the solution. Afterwards, the mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). The autoclave was maintained at 200 °C for 12 h, and allowed to cool to room temperature. The black products were washed several times with ethanol and dried at 60 °C for 6 h.

2. Synthesis of Fe₃O₄@SiO₂

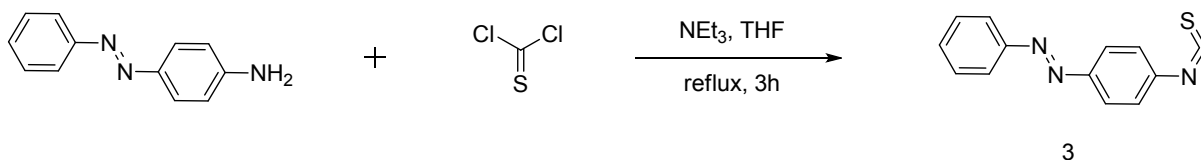
0.01 g Fe₃O₄ particles were treated with 0.1 M HCl aqueous solution (20 mL) by ultrasonication. After the treatment for 5 min, the magnetite particles were separated and washed with deionized water for two times, and then homogeneously dispersed in the mixture of ethanol (80 mL), deionized water (20 mL) and concentrated ammonia aqueous solution (1.0 mL, 25 wt.%), followed by the addition of tetraethylorthosilicate (TEOS, 0.1 mL). After stirring at room temperature for 12 h, the products were washed several times with ethanol.

3. Synthesis of Fe₃O₄@SiO₂- α -CD

The synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ - α -

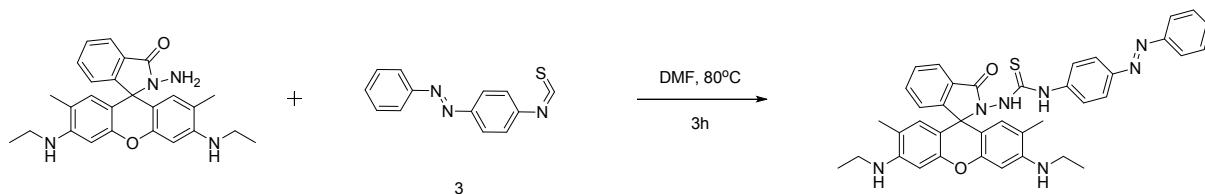
CD was the same steps in the procedure described in ref. 19. In the first step, α -CD (2.5 g) was dissolved in 50.0 mL of anhydrous DMF to which 0.5 g of NaH was added. The mixture was stirred at room temperature until no gas was emitted. Excess NaH was removed by filtration. 4.0 mL of KH-560 was added to the filtrate, which was allowed to react at 90°C under nitrogen protection for 5 h. After this process, α -CD moiety was bonded to the epoxy group of KH-560. Then 1.0g $\text{Fe}_3\text{O}_4@\text{SiO}_2$ was added to the aforementioned solution, with NH_3 (25% in H_2O) added dropwise. The reaction mixture was stirred for 12h under nitrogen atmosphere at room temperature. The product was collected and washed several times successively with anhydrous DMF, methanol, distilled water and acetone. Finally, the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -CD was dried under vacuum at 50°C.

4. Synthesis of ITCRh6G-Azo moiety.



p-Aminoazobenzene (0.280g, 1.44mmol) was dissolved in 80mL anhydrous THF in a three-neck flask of 250mL, then under N_2 protection NEt_3 (0.44mL, 3.17mmol) and thionyl chloride (0.11mL, 1.48mmol) were added dropwise to the system. Then the reaction mixture was stirred for 3h at 66°C before it was concentrated under reduced pressure, the mixture was then poured into 200mL dichloromethane and washed with deionized water twice (150mL \times 2), brine (200mL), then evaporated under reduced pressure. The residue was purified by a silica gel

column chromatography (petroleum ether/dichloromethane = 3/1) to give the orange crystalline 3 (0.327g, Yield 95%).



N-(Rhodamine 6G)lactam hydrazide (0.643g, 1.50mmol) and 3 (0.431g, 1.80mmol) were dissolved in 70mL anhydrous DMF, after stirred for 3h at 80°C the reaction mixture was poured into 300mL dichloromethane before washed with water for three times (200mL×3), dried with Na₂SO₄, evaporated under reduced pressure. The residue was then purified by a silica gel column chromatography (dichloromethane/methane = 500/1) to gave the light orange crystalline (0.851g, 85%).¹H NMR (400 MHz, DMSO-*d*₆, δ): 9.62 (s, 1H), 9.05 (s, 1H), 7.92 (d, *J* = 7.93 Hz, 1H), 7.86 (m, 3H), 7.73 (m, 3H), 7.54-7.66 (m, 7H), 7.40 (d, *J* = 7.41 Hz, 2H;), 7.06 (d, *J* = 7.07 Hz, 1H;), 6.22 (s, 2H;), 3.12 (m, 4H), 1.76 (m, 6H), 1.17 (m, 6H); ¹³C NMR (101 MHz, DMSO-*d*₆, δ): 181.25, 166.97, 152.47, 152.18, 151.71, 148.80, 148.24, 142.38, 134.19, 131.66, 129.91, 129.69, 129.04, 125.08, 125.05, 124.69, 123.39, 122.85, 122.52, 118.51, 104.27, 95.86, 37.86, 17.44, 14.69. HRMS (ESI, *m/z*): [M+H]⁺ calcd for C₃₉H₃₇N₇O₂S, 668.2808; found, 668.2441.

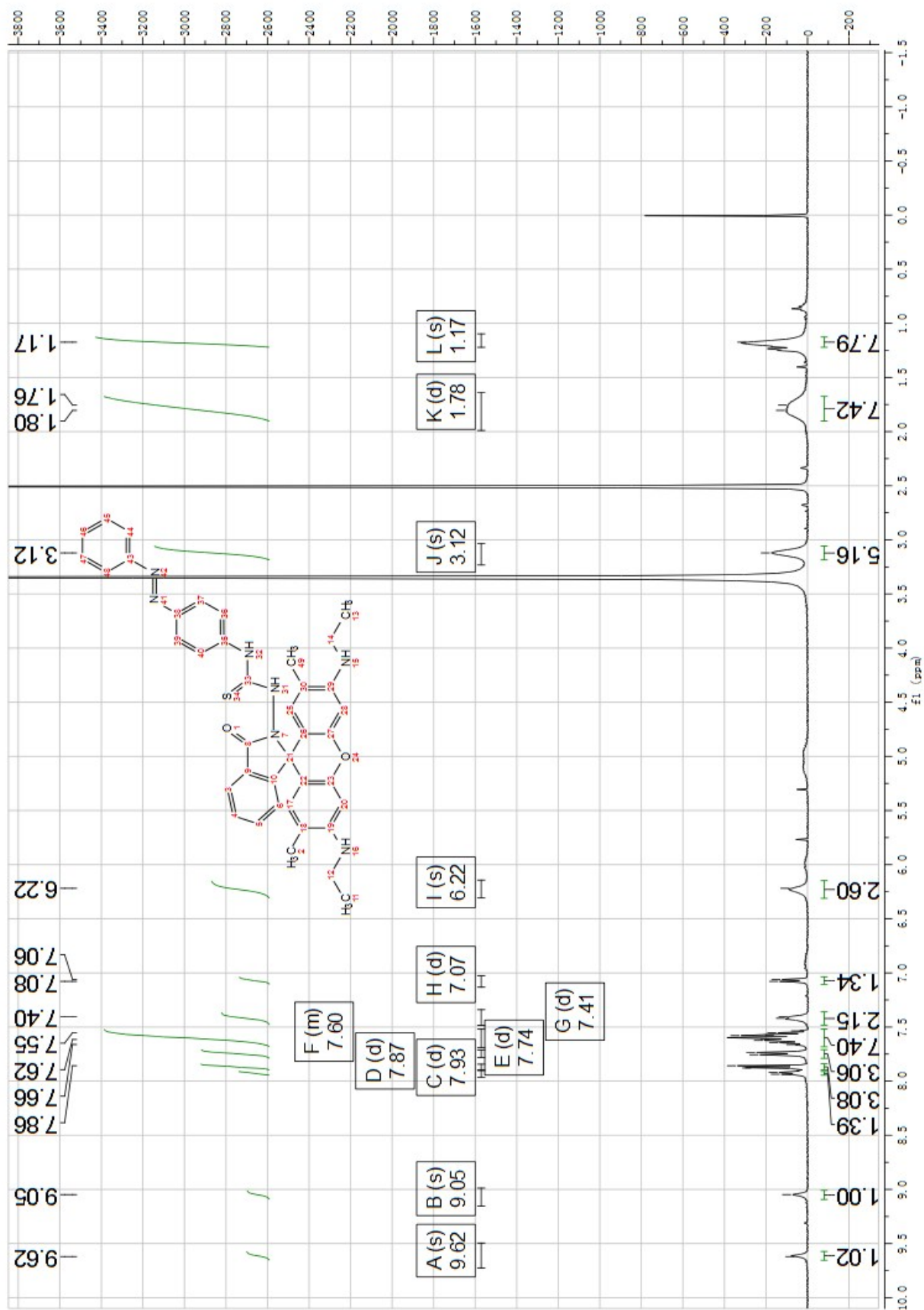


Fig S1. ^1H NMR spectrum of ITCRh6G-Azo in $\text{DMSO-}d_6$.

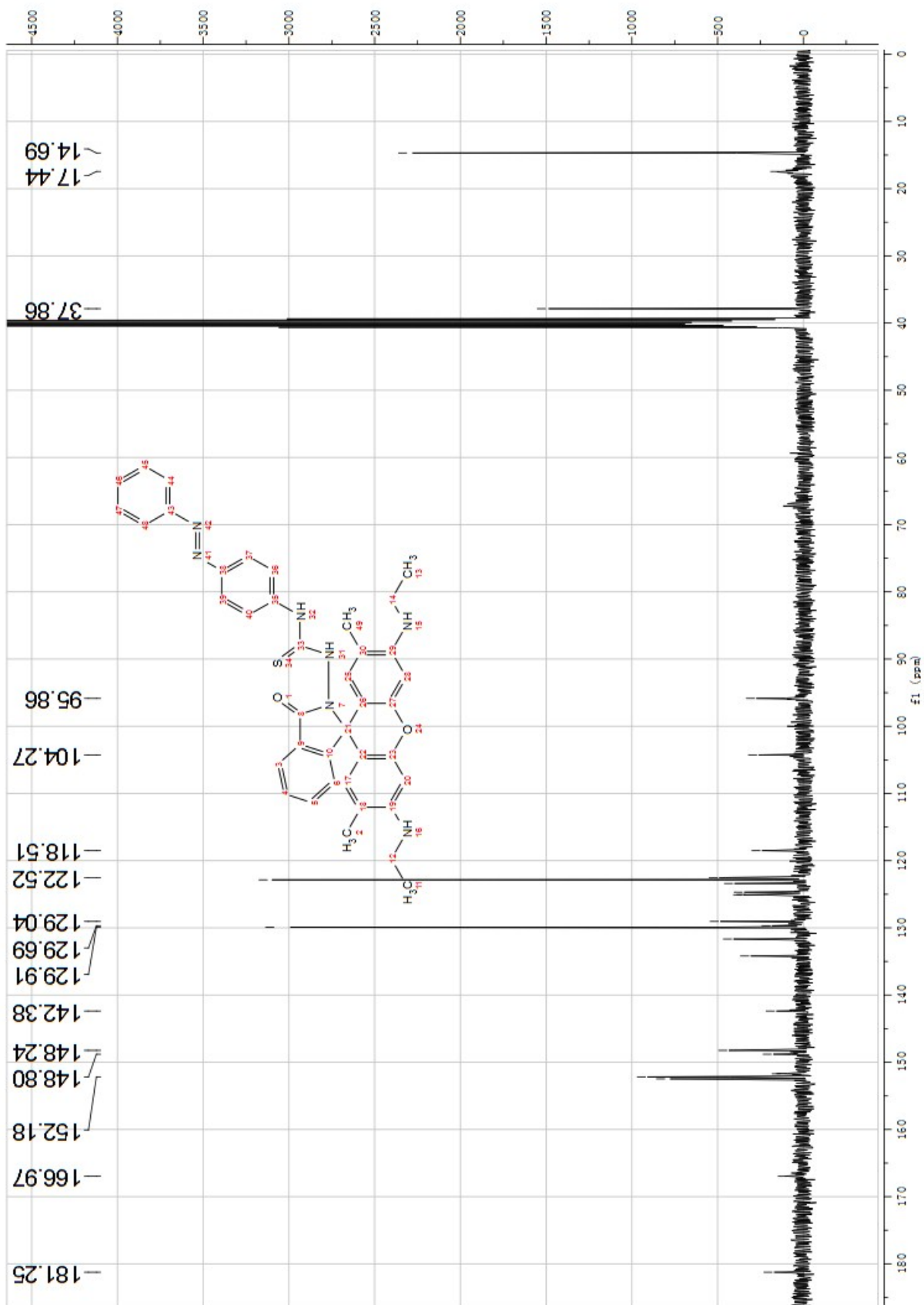


Fig S2. ^{13}C NMR spectrum of ITCRh6G-Azo in $\text{DMSO-}d_6$.