Electronic Supplementary Information (ESI)

Photomodulation of the electrode potential of the photochromic spiropyran-modified Au-electrode in the presence of Zn^{2+}: a new molecular switch based on the electronic transduction of the optical signals

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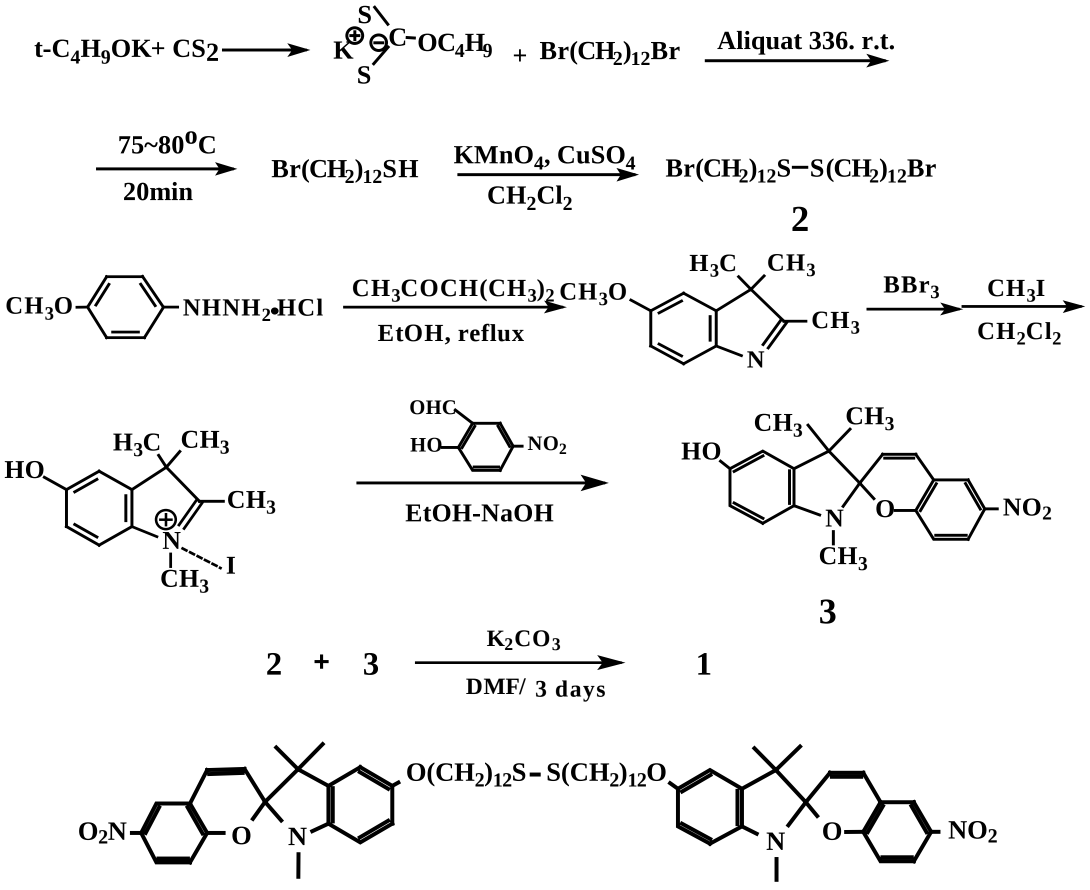
Contents

1. Synthesis of compound 1

Compound **1** was synthesized according to the following Scheme:



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Materials and methods: All reagents were purchased from commercial sources, and used without further purification unless other noted. Solvents were distilled according to standard procedures when necessary. Compound **2** and **3** were synthesized according to the early reported procedures.[1, 2] All reactions were monitored by thin layer chromatography. NMR spectra were recorded with a Bruker Avance 400 spectrometer. The mass spectra were recorded with AEI-MS50 spectrometer and HRMS was measured on Bruker ApEXII. The IR spectrum was recorded using Perkin-Elmer 2000 spectrophotometer in the form of KBr. The membrane potentials were measured with CHI660A instrument. The UV-Vis spectra were recorded with a Hirachi U-3010 spectrophotometer.

Synthesis of 1: To a solution of compound **3** (0.24 g, 0.71 mmol) in dimethylformamide (DMF, 20 mL) was added compound **2** (0.10 g, 0.18 mmol) and anhydrous K_2CO_3 (0.98 g, 7.12 mmol). Then the mixture was stirred at room temperature for 3 days before 300 mL of H_2O was added. The aqueous solution was extracted with dichloromethane (3×100 mL) and the combined extracts were washed with H_2O (2×50 mL) and saturated aqueous NaCl (40 mL), dried with anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified with column chromatography on silica gel, using ethyl acetate/petroleum ether (60-90°C, 1:10, v/v) as eluant, compound **1** was obtained as slight yellow viscous liquid (0.06g) in 31.2% yield. FT-IR (KBr, cm^{-1}): ν = 2976, 2926, 2854, 1620, 1402, 1338, 1274; ^{1}HNMR (400MHz, $CDCl_3$, TMS, ppm). δ = 1.18 (s, 6H), 1.25-1.38 (m, 38H), 1.66-1.69 (m, 4H), 1.76-1.79 (m, 4H), 2.67-2.71(m, 10H), 3.90-3.94 (t, 4H, *J* = 6.54 Hz), 5.84-5.86 (d, 2H, *J* = 10.28 Hz), 6.44-6.46 (d, 2H, *J* = 8.64 Hz), 6.71-6.73 (m, 4H), 6.76-6.78 (d, 2H, *J* = 8.64 Hz), 6.90-6.92 (d, 2H, *J* = 10.28 Hz), 8.00-8.03 (m, 4H); ^{13}CNMR (100MHz, $CDCl_3$) δ = 19.9, 25.8, 26.1, 28.5, 29.0, 29.2, 29.3, 29.4, 29.5, 29.6, 39.6, 52.4, 68.8, 106.9, 107.2, 110.3, 112.1, 115.5, 118.7, 121.7, 122.7, 125.9, 128.2, 137.7, 140.9, 141.8, 153.7, 159.9. HRMS: Anal. calcd. for $C_{62}H_{82}N_4O_8S_2$ [MH^+]: 1075.5646; Found 1075.5623.

References

1. I. Degani, R. Fochi, M. Santi, *Synthesis*. **1977**, 873-874.
2. X. Guo, D. Zhang, Y. Zhou, D. Zhu, *J. Org. Chem*. **2003**, *68*, 5681-5687.

2. Absorption spectra of 1 under light irradiation in the presence of K^+

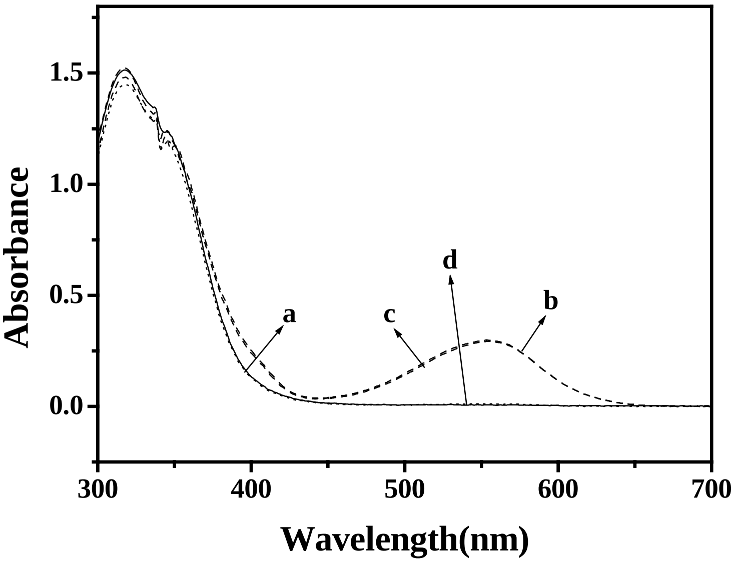

Figure S1 The absorption spectra of **1** (1.0×10^{-4} M) in THF/H_2O (9:1 v/v): (a) before and (b) after irradiation with UV light (365 nm) for 3.0 min., (c) together with that upon addition 50 equiv. of KCl immediately after irradiation with ultraviolet (365 nm) and (d) further irradiation with visible light in the presence of KCl.

3. The absorption spectra of 1 in the MC state in the presence of Zn^{2+} after UV light irradiation and determination of the association constants of 1 in the MC state with Zn^{2+}

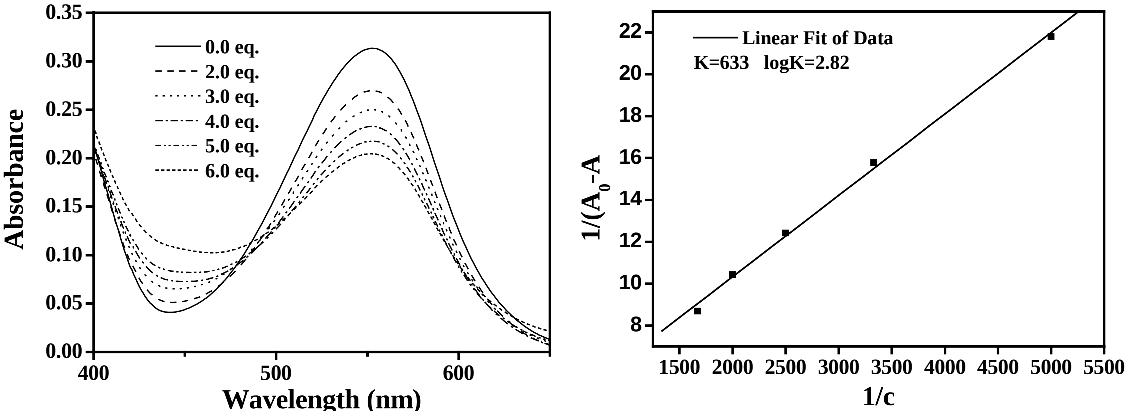

Figure S2 (left) Part of the absorption spectra of **1** (1.0×10^{-4} M) in THF/H_2O (9:1, v/v) in presence of different amounts of Zn^{2+} added to the solution immediately after irradiation with UV light (365 nm) for 3.0 min.

(right) The plot of $1/(A_0\text{-}A)$ vs. 1/c for determining association constant of **1** in the MC state with Zn^{2+}; A_0 was the initial absorbance after UV light irradiation without addition of Zn^{2+}, and A was the absorbance of **1** in presence of Zn^{2+}; c was the concentration of Zn^{2+}. The red line represents the fitting to Benesi-Hildebrand equation, and the association constant was determined to be K = 633.

4. Electrode preparation and modification

Au electrodes (0.18 cm in diameter) were polished with alumina powder (0.3 and 0.05 μm) and sonicated in acetone and doubly distilled water (each for 5 min). The electrodes were then electrochemically cleaned by consecutively cycling the potential between -0.2 and +1.8 V (*vs.* Ag/AgCl) at 0.2 V/s in 0.5 M H_2SO_4 solution until a cyclic voltammogram characteristic for a clean Au electrode was obtained. The surface roughness factor of Au electrodes was calculated to be about 3.0 ($f = Q/Q_{ref.}$, Q is the electric charge for the Au surface oxide determined by integrating reduction peak of the surface oxide in a cathodic scan in 0.5 M H_2SO_4, and $Q_{ref.}$, is the reference electric charge of 400 C/cm^2 for polycrystalline Au [1]).

Self-assembled monolayer (SAM) of compound **1** on the Au electrode surface was prepared by immersing the cleaned Au electrode into ethanol solution containing compound **1** (1.0×10^{-3} M) for 6 days. The SAM-modified Au electrode was then rinsed with ethanol and doubly distilled water and dried in air before electrochemical measurements.

The surface coverage of the SAM was determined with an electroreductive desorption method by cycling the SAM-modified Au electrode from 0 V to -1.2 V (*vs.* Ag/AgCl) at a scan rate of 50 mV/s in 0.5 M KOH solution. Under this condition, the NO2- groups of **1** could not be reduced. The area of reductive peak was attributed to the charge associated with the reduction of the SAM.[2] The surface coverage of the SAM of compound **1** on the Au electrode surface was estimated to be 1.57×10^{-10} mol/cm^2 after self-assembly for 6 days at room temperature (19-20^{o}C).

References

1. J. C. Hoogvliet, M. Dijksma, B. Kamp, W. P. V. Bennekom, *Anal. Chem.* **2000**, *72*, 2016.
2. A. Dalmia, C. C. Liu, R. F. Savinell, *J. Electroanal. Chem.* **1997**, *430*, 205.

5. The electrode potential recorded with the spiropyran-modified electrode under light irradiation in pure water

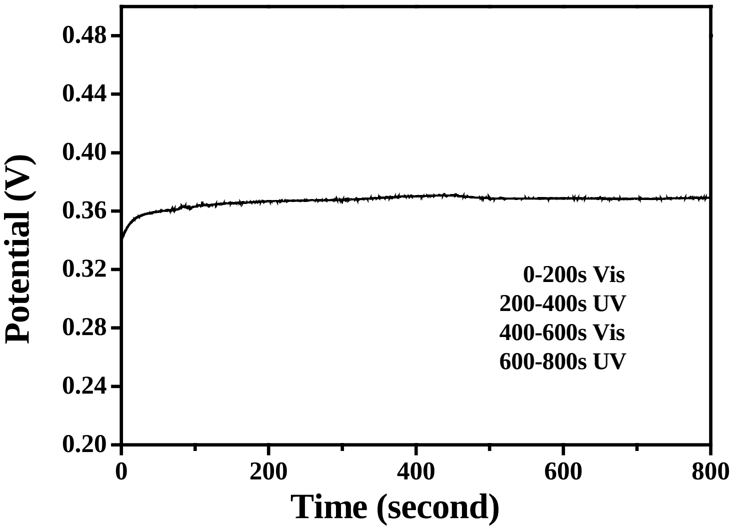

Figure S3 The electrode potential (vs. Ag/AgCl) of the spiropyran-modified Au electrode in pure water under UV/visible light irradiation.