

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

Guoyong Wen,<sup>ab</sup> Jie Yan,<sup>b</sup> Yucheng Zhou,<sup>ab</sup> Deqing Zhang,<sup>\*a</sup> Lanqun Mao<sup>\*a</sup> and Daoben Zhu<sup>\*a</sup>

Received (in Cambridge, UK) 2nd May 2006, Accepted 25th May 2006

First published as an Advance Article on the web 14th June 2006

DOI: 10.1039/b606141a

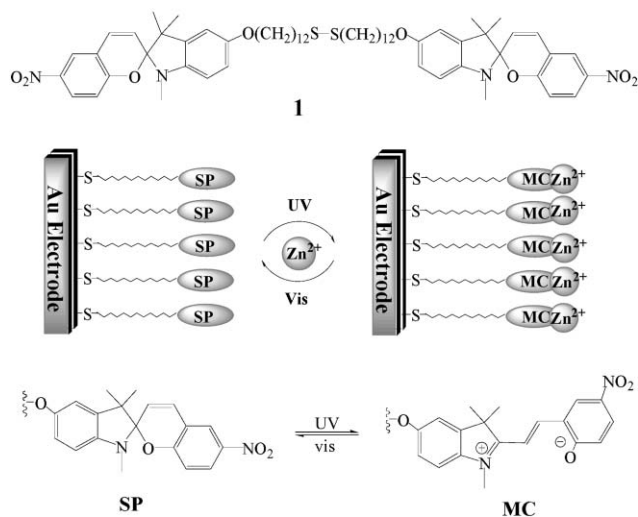
The electrode potential of a photochromic spiropyran-modified Au electrode could be reversibly modulated by UV/visible light irradiation in the presence of  $Zn^{2+}$ , and a new molecular switch and an “AND” logic gate based on this electronic transduction of the optical signals were established.

It is well known that signal transduction is one of the important steps for processing information. More and more results indicate that signal transduction is involved in some biological functions.<sup>1</sup> In fact, a molecular switch can be regarded as the device performing the signal transduction at the molecular level. Willner *et al.* described several unique examples of electronic transduction of optical signals by taking advantage of photochromic compounds.<sup>2</sup> For instance, they immobilized photochromic compounds on surfaces through self-assembly approach to construct “photo-command surfaces”; the electron-transfer processes taking place on the surfaces were tuned by light irradiation, and as a result the optical signals were successfully converted into electronic ones.<sup>2b,c</sup> Signal transduction with other types of combinations of input and output signals was also reported.<sup>3</sup>

In this communication, we report a new example of the electronic transduction of optical signals based on an Au electrode modified with molecules containing photochromic spiropyran units. The design rationale is schematically demonstrated in Scheme 1. It is well known that the closed form of spiropyran (SP) can be transformed into the corresponding open form (merocyanine form, MC) by UV light irradiation, and the MC form can be converted back to the original SP form by visible light irradiation.<sup>4</sup> By making use of the reversible transformation between SP and MC forms, molecular switches and logic gates were described.<sup>5</sup> The unique feature of the photochromic spiropyran is that the MC form is able to coordinate with metal ions,<sup>6</sup> and that the SP form does not show such a property. Therefore, molecules with the spiropyran unit can function

as photo-responsive ligands.<sup>7</sup> Molecules with spiropyran and –SH/–S–S– units are able to self-assemble on the Au surface<sup>8</sup> to generate a self-assembled monolayer-modified Au electrode, which can be regarded as a membrane electrode as shown in Scheme 1. When this electrode is immersed into an electrolyte solution, a membrane potential is generated.<sup>9</sup> Upon UV light irradiation, the spiropyran unit will be transformed into the corresponding MC form, which can coordinate with metal ions present in the solution. As a result, the concentration of ions in the membrane will be altered, leading to variation of the membrane potential of the modified electrode after UV light irradiation.<sup>9</sup> On the other hand, further visible light irradiation will cause the conversion of the MC form into the SP form. Concomitantly, the coordinated metal ions will be released, leading to the restoration of the membrane potential. Therefore, the electrode potential recorded with this spiropyran-modified Au electrode can be reversibly modulated by UV/visible light irradiation of the electrode.

Compound **1** (Scheme 1) with two spiropyran units and one –S–S– group was synthesized and characterized.<sup>10</sup> As expected, compound **1** shows typical photochromism: a new absorption spectrum around 556 nm emerged upon UV light irradiation (365 nm), which gradually disappeared after further visible light irradiation (Fig. 1). This is clearly due to the reversible

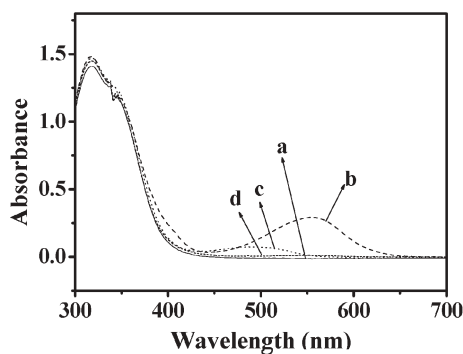


**Scheme 1** The chemical structure of compound **1** and illustration of the reversible structural transformations of SP units into MC units as well as coordination with metal ions on the surfaces of an Au electrode.

<sup>a</sup>Beijing National Laboratory for Molecular Sciences, Organic Solids Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080, China. E-mail: dqzhang@iccas.ac.cn; Fax: +86 1062569564

<sup>b</sup>Graduate School of the Chinese Academy of Sciences, Beijing, 100080, China

† Electronic supplementary information (ESI) available: Synthesis and characterization details, UV-vis spectra of **1**, electrode potential data for **1** as well as the preparation of the modified Au electrode. See DOI: 10.1039/b606141a

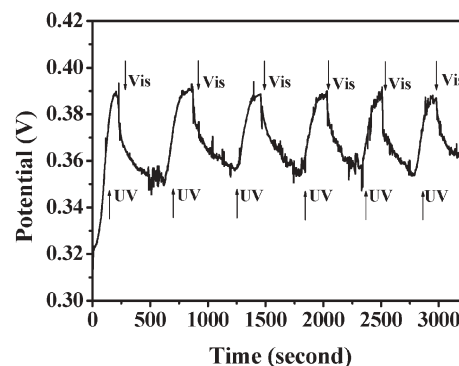


**Fig. 1** The absorption spectra of **1** ( $1.0 \times 10^{-4}$  M) in THF–H<sub>2</sub>O (9 : 1, v/v) before (a) and after (b) irradiation with ultraviolet light (365 nm) for 3.0 min, together with (c) that upon addition of 50 equiv. of ZnCl<sub>2</sub> immediately after irradiation with ultraviolet light (365 nm) and (d) further irradiation with visible light in the presence of ZnCl<sub>2</sub>.

transformation of closed forms of the SP units and the corresponding MC forms. When Zn<sup>2+</sup> was present in the solution of **1**, the corresponding absorption band of MC form became weak and a new absorption appeared at around 486 nm after exposure to UV light (see Fig. 1), because of the coordination of Zn<sup>2+</sup> with the MC form as reported previously.<sup>6</sup> The association constant of **1** in the MC state with Zn<sup>2+</sup> was determined to be  $K = 633$  (see Fig. S2 of ESI†). Similarly, further visible light irradiation led to the original absorption spectrum of **1** as displayed in Fig. 1, implying the simultaneous occurrence of the release of Zn<sup>2+</sup> from the MC–Zn<sup>2+</sup> complex and the transformation of the MC form into the SP form. Such absorption spectral variation of **1** in the presence of Zn<sup>2+</sup> can be repeated under light irradiation. But, addition of alkali metal ions such as K<sup>+</sup> could not induce any absorption spectral change for the solution of **1** under the same conditions (see Fig. S1 of ESI†).

The spiropyran-modified Au electrode was prepared by soaking the electrode in a solution of **1** ( $1.0 \times 10^{-4}$  M in ethanol) for 6 days at room temperature.† The surface coverage of the SAM of compound **1** on the Au electrode surface was estimated to be  $1.57 \times 10^{-10}$  mol cm<sup>-2</sup> after self-assembly for 6 days at room temperature.<sup>11</sup> After that, the modified electrode was air-dried and put into an aqueous solution of ZnCl<sub>2</sub> ( $1.0 \times 10^{-2}$  M). The electrode potential vs. Ag/AgCl was measured. As anticipated, the electrode potential increased after UV light (365 nm) irradiation of the spiropyran-modified electrode, and the maximum enhancement (ca. 35 mV) in the potential was achieved after continuous UV light irradiation of the modified electrode for 200 s. Further visible light irradiation led to reduction of the potential, and the initial potential was restored after visible light irradiation for 300 s as shown in Fig. 2. Such electrode potential variation recorded with the spiropyran-modified Au electrode can be reversibly performed at least for five cycles. The preliminary results also indicated that the potential enhancement was dependent on the concentration of Zn<sup>2+</sup>.

However, the electrode potential of the spiropyran-modified Au electrode was unchanged after either UV or visible light irradiation when the electrode was immersed in a solution containing alkali metal ions, such as K<sup>+</sup> (Fig. 3) or in pure water (see Fig. S3 of ESI†). To summarize, the electrode potential of the spiropyran-modified Au electrode can be reversibly modulated after

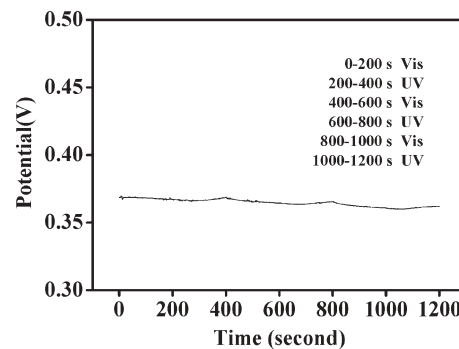


**Fig. 2** The reversible variation of the electrode potential (vs. Ag/AgCl) recorded with the spiropyran-modified Au electrode in the presence of ZnCl<sub>2</sub> ( $1.0 \times 10^{-2}$  M in H<sub>2</sub>O) under alternating UV/visible light irradiation.

alternating UV and visible light irradiation in the presence of Zn<sup>2+</sup>, but there was no potential variation in the presence of alkali metal ions, such as K<sup>+</sup>. This is in agreement with the absorption spectral changes observed for the solution of **1** in the presence of different metal ions (see Fig. 1 and Fig. S1†). Thus, it can be assumed that the electrode potential variation recorded with the spiropyran-modified Au electrode under light irradiation is due to the transformation of the SP form into the corresponding MC form and its sequential coordination with metal ions as schematically demonstrated in Scheme 1.

Consequently, the electronic transduction of optical signals was realized with compound **1**, and a new molecular switch was established with UV/visible light and the electronic potential as the input and output signals, respectively. Since the electrode potential variation recorded with the modified Au electrode needs both UV light irradiation and the presence of Zn<sup>2+</sup>, this signal transduction mimics the performance of an “AND” logic gate,<sup>12</sup> with UV light and Zn<sup>2+</sup> as the input signals and the electronic potential as the output signal; visible light can be used to reset the electrode potential to its initial value.

In summary, by making use of the features of photochromic spiropyran, compound **1** with two spiropyran units linked by one –S–S– group was designed and synthesized for studies of the electronic transduction of optical signals. Assembly of compound **1** on the surface of an Au electrode led to a photochromic



**Fig. 3** The electrode potential (vs. Ag/AgCl) of the spiropyran-modified Au electrode in an aqueous solution of KCl ( $1.0 \times 10^{-2}$  M in H<sub>2</sub>O) under UV/visible light irradiation.

spiropyran-modified Au electrode. The results show that the electrode potential of the modified Au electrode can be reversibly modulated by UV/visible light irradiation in the presence of  $Zn^{2+}$ .<sup>13</sup> The variation of the electrode potential was assumed to be due to the membrane potential change of the modified electrode, as a result of the reversible transformation of the SP and MC forms of spiropyran units and the coordination of metal ions by the MC form upon alternating UV and visible light irradiation. Accordingly, the electronic transduction of optical signals was successfully achieved with compound **1**, and a new molecular switch based on this signal transduction was established. Moreover, such electronic transduction of optical signals also mimics the performance of an “AND” logic gate.

The present research was financially supported by NSFC, Chinese Academy of Sciences and State Key Basic Research Program. D.-Q. Zhang thanks the National Science Fund for Distinguished Young Scholars.

## Notes and references

‡ Electrode preparation and modification was carried out as follows: Au electrodes (0.18 cm in diameter) were polished with alumina powder (0.3 and 0.05  $\mu\text{m}$ ) 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  $\text{s}^{-1}$  in  $0.5$  M  $\text{H}_2\text{SO}_4$  solution until a cyclic voltammogram characteristic for a clean Au electrode was obtained. The self-assembled monolayer (SAM) of compound **1** on the Au electrode surface was prepared by immersing the cleaned Au electrode into an ethanol solution containing compound **1** ( $1.0 \times 10^{-4}$  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.

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  - 10 The synthesis details are provided in ESI.† The characterization data for compound **1**: FT-IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 2976, 2926, 2854, 1620, 1402, 1338, 1274$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS, ppm):  $\delta = 1.18$  (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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 19.9, 25.8, 26.1, 28.5, 29.0, 29.2, 29.3, 29.4, 29.5, 29.6, 39.6, 52.4, 68.8, 106.9, 107.2, 110.3, 112.1, 115.5, 118.7, 121.7, 122.7, 125.9, 128.2, 137.7, 140.9, 141.8, 153.7, 159.9$ . HRMS: Anal. calcd. for  $\text{C}_{62}\text{H}_{82}\text{N}_4\text{O}_8\text{S}_2$  [ $\text{MH}^+$ ]: 1075.5646; found 1075.5623.
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