A multistate ensemble of molecular switches

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The four distinct states associated with a mixture of an electrochromic complex and a photochromic compound can be interconverted by operating the two molecular switches in parallel under the influence of electrical and optical inputs.

Molecular switches can be interconverted between two stable states under the influence of chemical, electrical and optical stimulation.[1–4] These processes are often reversible and can be exploited to reproduce logic operations at the molecular level.[5–11] Indeed, diverse and clever operating principles have already been identified to implement NOT, OR and AND functions, as well as complex combinations of these three basic operations, with collections of identical molecular switches operating in solution. Although several examples of molecular logic gates with chemical and electrical outputs are known, most commonly the state of these fascinating systems is read optically relying on either absorption or emission spectroscopy. These analytical methods offer fast and sensitive responses, convenient and reliable experimental setups and, perhaps more importantly, the opportunity to probe a chemical system at different wavelengths simultaneously.[12,13] In fact, the ability of photons with distinct wavelengths to travel through the same region of space without interfering can be exploited, in principle at least, to monitor the state of multiple molecular switches confined within the same environment. In order to illustrate the potential of this protocol for data processing with molecules, we have identified an electrochromic complex and a photochromic compound, which respond to electrical and optical stimulation respectively with pronounced absorbance changes at distinct wavelengths. Here, we demonstrate that (1) this particular pair of molecular switches can be operated within the same solution without interference and (2) four optically-distinct states can be interconverted with this ensemble of molecules.

The absorption spectrum (Fig. 1a) of the ruthenium complex **1** shows a metal-to-ligand charge-transfer (MLCT) band at *ca.* 590 nm. The electrolysis of this solution at +0.2 V, relative to a platinum pseudo-reference electrode, results in the monoelectronic oxidation of the ruthenium center with the disappearance of the MLCT band (Fig. 1b). The process is fully reversible. The back reduction of the ruthenium center restores the initial absorption spectrum after electrolysis for 35 min at −0.2 V. Thus, the absorbance at 590 nm can effectively be modulated by operating this particular electrochromic switch with oxidative and reductive voltage stimulations.

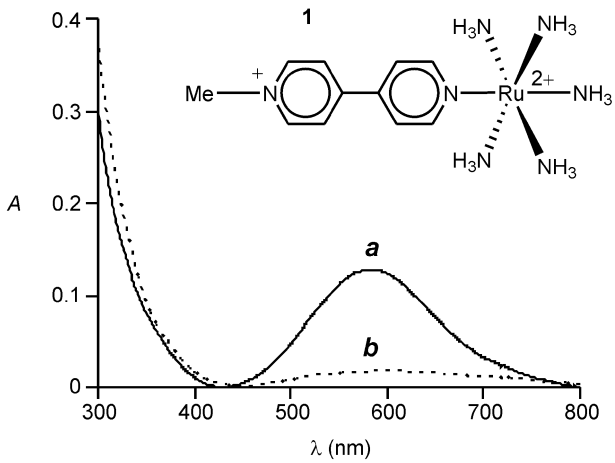

Fig. 1 Absorption spectra of **1** (0.05 mM, sodium phosphate buffer, pH = 7, 20 °C) before (***a***) and after (***b***) electrolysis for 35 min at +0.2 V, relative to a platinum pseudo-reference electrode.

The absorption spectrum (Fig. 2a) of the *trans*-azobenzene **2** shows a band at *ca.* 320 nm corresponding to a $\pi \rightarrow \pi^*$ transition. The irradiation of this solution at 341 nm induces a *trans* → *cis* isomerization. Consistently, the absorbance for the $\pi \rightarrow \pi^*$ transition of the *trans* isomer decreases (Fig. 2b). Once again, the process is fully reversible. Upon irradiation at 413 nm, the *cis* isomer reverts to the original *trans* form restoring the initial absorption spectrum. Thus, the absorbance at 320 nm can effectively be modulated by operating this photochromic switch with ultraviolet and visible stimulations.

The electrochromic complex **1** and the photochromic compound **2** can be co-dissolved in aqueous solution and operated in parallel without interference.† Indeed, the moderate potentials sufficient to switch **1** do not alter the redox state of **2**. Similarly, **2** can be irradiated at wavelengths where the

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† The lack of covalent connections between the electrochromic and photochromic components prevents deleterious photoinduced electron and energy transfer processes that would otherwise quench the photoisomerization of the azobenzene unit and, presumably, sensitize the decomposition of the ruthenium complex.

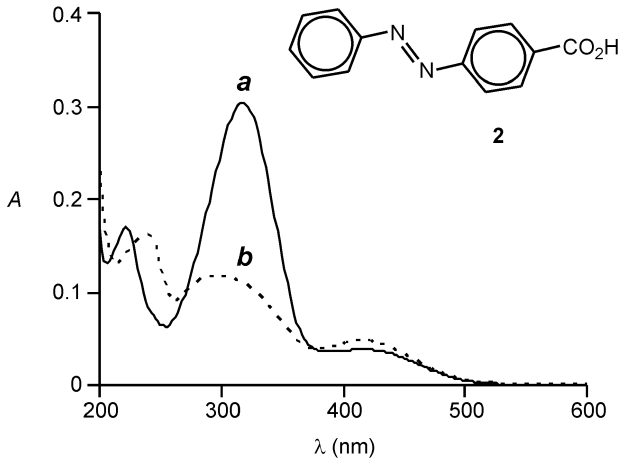

Fig. 2 Absorption spectra of **2** (0.01 mM, sodium phosphate buffer, pH = 7, 20 °C) before (***a***) and after (***b***) irradiation for 10 min at 341 nm.

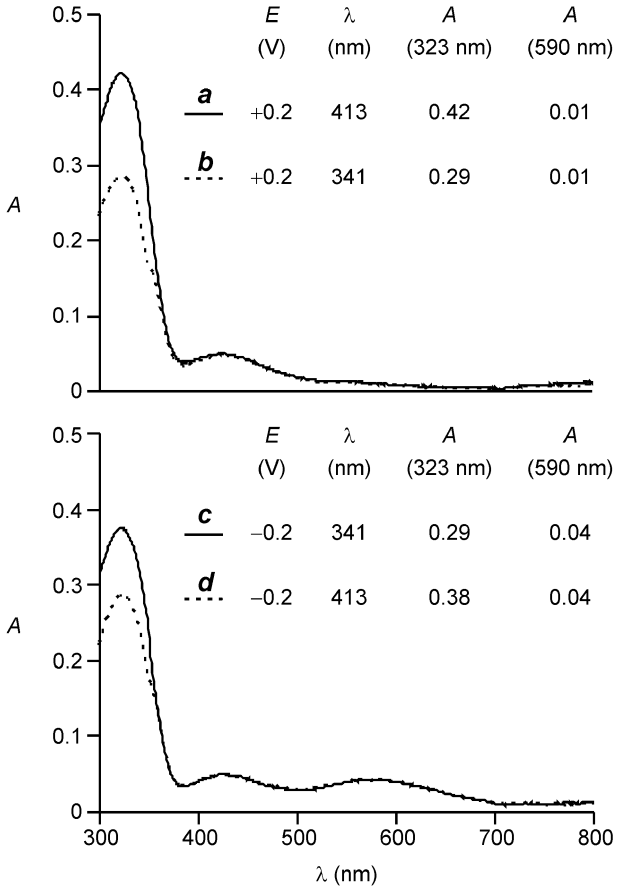

Fig. 3 Absorption spectra of **1** (0.02 mM) and **2** (0.08 mM) in sodium phosphate buffer (pH = 7, 20 °C) after electrolysis for 10 min at the potential E, relative to a platinum pseudo-reference electrode, and irradiation for 10 min at the wavelength λ and the corresponding absorbance (A) values at 323 and 590 nm.

absorbance of **1** is negligible.‡ Under these conditions, four spectroscopically-distinct states can be interconverted by addressing the pair of molecular switches with their respective electrical and optical inputs. For example, the absorption spectrum (Fig. 3a) recorded after electrolysis at +0.2 V and irradiation at 413 nm shows the band for the *trans*-azobenzene at 323 nm, but not the MLCT absorption for the ruthenium complex at 590 nm. After switching the irradiation wavelength to 341 nm, the absorbance at 323 nm drops from 0.42 to 0.29 (Fig. 3b), while that at 590 nm is unaffected. If the potential is changed to −0.2 V, the absorbance at 590 nm increases from 0.01 to 0.04 (Fig. 3c), but the one at 323 nm remains at 0.29. When the irradiation wavelength is reverted to 413 nm, the absorbance at 323 nm increases to 0.38 (Fig. 3d) and that at 590 nm stays at 0.04.

A glance at the tables in Fig. 3 indicates that the electrical and optical inputs are both switched between low and high values (E = −0.2 or +0.2 V, λ = 341 or 413 nm). Similarly, the two absorbance outputs at 323 and 590 nm also switch between low and high values. Under a positive logic convention (low = 0, high = 1), binary digits can be encoded in the two inputs and in the two outputs. The resulting truth table (Table 1) shows that each of the four states associated with the pair of molecular switches is described by a distinct two-digit output string. A further analysis of the input–output correlations also demonstrates that (1) the electrical input has no influence on the absorbance at 323 nm and (2) the optical input does not affect the absorbance at 590 nm. Thus, the two molecular switches do not interfere with each other even although they are operated in parallel within the same region of space.

In summary, we have demonstrated that molecular switches with complementary inputs and distinct optical outputs can be operated in parallel within the same environment without cross-talk. Furthermore, four stable states with discrete optical signatures can be accessed by addressing the pair of molecular switches with their respective input stimulations. In principle, this general mechanism can be extended to molecular ensembles containing more than two molecular switches in order to implement interconvertible chemical systems with multiple stable states.

‡ The complex **1** is known to be photolabile.[15] In order to minimize the amount of light absorbed directly by **1** at the irradiation wavelengths, we have employed a fourfold excess of **2**.

Experimental

Materials

All chemicals were purchased from commercial sources and used as received with the exception of **1**, which was synthesized

Table 1 Correlation between the electrical (E) and optical (λ) inputs of **1** and **2** and their absorbance (A) outputs[a]

E	λ	A (323 nm)	A (590 nm)
0	0	0	1
0	1	1	1
1	0	0	0
1	1	1	0

[a] Binary 0 and 1 are assigned to E, λ and A by applying a positive logic convention (low = 0, high = 1) to the values in Fig. 3.

following a literature procedure.[14] Specifically, the hexafluorophosphate salt of **1** was prepared from 4,4′-bipyridine, methyl iodide, $[Ru^{III}(NH_3)_5Cl]Cl_2$ and NH_4PF_6 in two synthetic steps with an overall yield of 24%. ESI-MS: m/z = 647 $[M - PF_6]^+$; ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 8.95 (2H, d, 6 Hz), 8.89 (2H, d, 6 Hz), 8.68 (2H, d, 6 Hz), 7.77 (2H, d, 6 Hz), 4.16 (3H, s), 3.46 (3H, s), 2.39 (12 H, s).

Methods

The electrospray ionization mass spectrum (ESI-MS) was recorded with an Agilent 1100 Series spectrometer. The ^{1}H nuclear magnetic resonance spectrum (^{1}H-NMR) was recorded with a Varian Inova 500 spectrometer. The spectroelectrochemical measurements were performed in aqueous solutions with a CH Instruments 140 cell (path length = 1.54 mm) incorporating an indium–tin oxide working electrode, a platinum counter electrode and a platinum pseudo-reference electrode. The water (resistivity = 18.2 MΩ cm) was purified with a Barnstead International NANOpure DIamond Analytical system. The cell was operated with a CH Instruments 660 electrochemical workstation and the absorption spectra were recorded with a Varian Cary 100 Bio spectrometer. The samples were irradiated with a Thermo Oriel liquid light guide coupled to a Spectral Energy LH 150/1 light source, a Spectral Energy 150 W xenon arc lamp and Thermo Oriel interference filters (341 or 413 ± 10 nm).

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