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Molecular AND Logic Gate Based on Electric Dichroism of a Photochromic Dihydroindolizine**

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Molecular switches that perform Boolean logic operations are scientifically interesting and may have technological potential.[1–4] A variety of molecule-based logic switches (AND gates, OR gates, etc.) have been reported.[5–9] In the vast majority of cases, at least one of the gate inputs requires physical addition of a chemical species. We have reported several molecular switches that employ photochromes, and function with only optical or thermal inputs.[9–12] Orientation of molecules by electric fields can lead to optically detectable electric linear dichroic phenomena.[13] The ability to control solution absorbance by using either photochromism or electric fields suggests that molecular logic gates switched by these two inputs might be realizable. Here, we report a molecular AND gate based on photochromic dihydroindolizine **1** (Scheme 1) whose two inputs are light at 366 nm and an electric field, and whose output is the electric linear dichroism (ELD) of **1**.

The dihydroindolizine[14] photochrome **1** exists in two isomeric forms. The closed, thermally stable spiro form **1c** does not absorb light significantly in the visible region (Figure 1); its longest-wavelength absorption band is at 415 nm. Irradiation of **1c** with ultraviolet light causes isomerization to the open, zwitterionic form **1o**, which absorbs in the visible region ($\lambda_{max} = 585$ nm). Compound **1o** is isomerized back to **1c** by heat or visible light. Irradiation (≈ 1.5 mW cm^{-2}) of a solution of **1c** in 2-methyltetrahydrofuran at 366 nm at 20.5 °C, produces a photostationary state greatly enriched in **1o** with a time constant of 10.6 s. This

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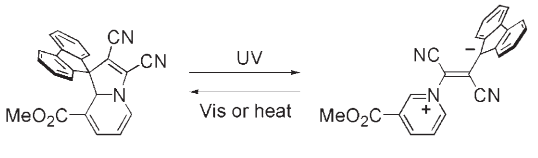

1c **1o**

Scheme 1. Structures of the closed (**1c**) and open (**1o**) isomers of the dihydroindolizine. The thermally stable **1c** may be photoisomerized to **1o** with UV light of wavelength 366 nm and **1o** may be isomerized to **1c** with visible light or heat.

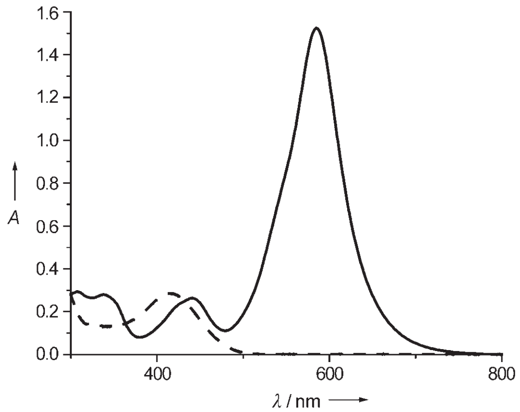

Figure 1. Absorption spectra of solutions in 2-methyltetrahydrofuran of the open (**1o** ——) and closed (**1c** -----) forms of the photochrome.

sample thermally isomerizes slowly back to **1c** ($\tau = 580$ min) in the dark. Irradiation of a sample in the **1o** state with visible light ($580\,\text{nm} < \lambda < 900\,\text{nm}$, $\approx 50\,\text{mW}\,\text{cm}^{-2}$) leads to photoisomerization back to **1c** ($\tau = 9.8$ min).

ELD is the change in absorbance of plane-polarized light by a substance caused by an applied electric field. Isotropically oriented achiral molecules in an isotropic solvent have the same absorbance of plane-polarized light, regardless of the polarization. In the presence of an electric field, a molecule with a permanent dipole moment, such as **1o**, will partially align with the field. This causes orientation of the transition moment for absorption, and anisotropic behavior results. The magnitude of the absorbance change observed upon application of a field depends upon, among other things, the dipole moment and the isotropic extinction coefficient. Molecule **1o** is relatively polar, which favors alignment with an external field. It has an absorption maximum at 585 nm and could exhibit a significant ELD effect. Isomer **1c** does not absorb in the visible spectral region and is not expected to have a significant ELD response.

The ELD response for **1** was observed by using the apparatus detailed in the Experimental Section. The sample of **1** was placed in a cuvette containing two parallel, flat-plate metal electrodes separated by 1.6 mm. A beam of monochromatic plane-polarized light was passed through the sample between the electrodes, such that its plane of polarization was parallel to the electric field generated by application of a voltage across the electrodes. The intensity of the transmitted light was monitored with a photomultiplier tube. A voltage was applied across the electrodes to observe the ELD response. A 1.5 kV ac electric field (50 Hz, $940\,\text{kV}\,\text{m}^{-1}$) was used, and the change in light intensity induced by the field was measured by using lock-in detection. An ac signal from the lock-in amplifier reflects the change in absorption of the sample caused by the field (ELD response).

Figure 2 shows the ELD response (decrease in the intensity of transmitted light) for a sample of **1** that has been irradiated at 366 nm, and thereby converted into a photostationary state consisting mainly of **1o**. The large band at approximately 583 nm is associated with the absorption of **1o** (Figure 1). The signal-to-noise ratio at 583 nm is very high, and the ELD response is easily observable. The ELD response and the absorption spectra are not expected to match exactly, as the ELD signal has not been corrected for the (wavelength-dependent) incident intensity nor converted into a logarithmic form. However, the lamp output as a function of wavelength is reasonably constant in this spectral region.

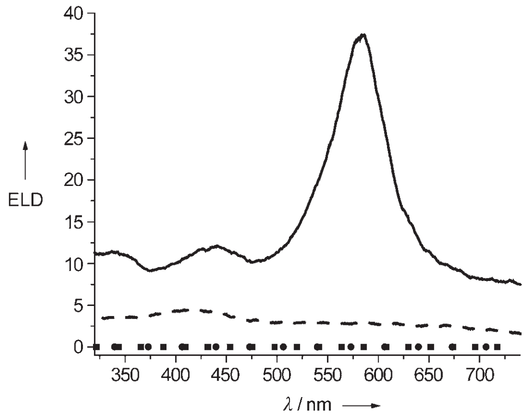

Figure 2. ELD response (arbitrary units) of a solution of **1** in 2-methyltetrahydrofuran: ——: following irradiation at 366 nm and with the application of the electric field; -----: following red light irradiation and with the application of the electric field; ●: following irradiation at 366 nm and in the absence of the electric field; and ■: following irradiation with red light and in the absence of the electric field. Note that the two data sets in the absence of the electric field overlap.

A similar experiment carried out with the closed form **1c** (obtained by irradiation with red light) yields a small electric-field response at the absorption maximum of approximately 416 nm (Figure 2). The response of **1c** is much smaller than that of **1o** because of differences in the dipole moment, extinction coefficient and orientation of the transition dipole. The small response in regions where **1** does not absorb is ascribed to the solvent, and it was observed even in the absence of molecule **1**. Figure 2 also shows the ELD response for **1o** and **1c** in the absence of the electric field. The response is essentially zero in both cases.

A Boolean AND logic gate requires two inputs, A and B, and an output. In the initial state with no inputs, the gate does not generate an output. No output is produced when either input A or input B is switched on. However, if both inputs are on, then the gate produces an output. On the basis of the ELD effects noted above, a solution of **1** can function as a molecule-based AND gate. Inputs A and B are UV irradiation at 366 nm and the application of an electric field, as discussed above. The output of the gate is the ELD signal, monitored at 583 nm.

In the initial state of the AND gate, the molecule is set in the thermally stable **1c** form. This solution does not generate an ELD response in the absence of an electric field, and the output of the gate is off (Figure 3a). Irradiation of this solution at 366 nm (input A on) generates a photostationary state containing mainly **1o**. However, in the absence of an electric field (input B off), no ELD response is observed, and the gate remains off. If, on the other hand, the original solution of **1c** is subjected to the 50 Hz electric field (input B on), only a small ELD response caused by the solvent is obtained. If a suitable threshold level is chosen, the gate in this case remains off. Alternatively, when the solution of **1c** is subjected to both irradiation at 366 nm and the electric field, photoisomerization to **1o** occurs, and **1o** gives a strong ELD response at 583 nm. The gate is switched on. Thus, the conditions for the AND function are met. After applying any combination of inputs, the gate may be reset to **1c** by irradiation with red light.

Although the purpose of this research has been to investigate a new approach to molecular gates rather than to make practical devices, the stability of **1** is important for any future applications. Figure 4a shows the ELD response of **1o** during application of 10 on–off cycles of the electric field. There is no degradation of the signal. Figure 4b reports the absorption between 500 and 700 nm (absorption from **1o**) after each of ten 40-s exposures to light at 366 nm alternated with nine 40-min exposures to red light. Only a small amount of photodegradation occurred after these cycles. The sample was degassed prior to the experiment with six freeze–pump–thaw cycles to a final pressure of approximately 1×10^{-4} Torr to reduce photodegradation.[15]

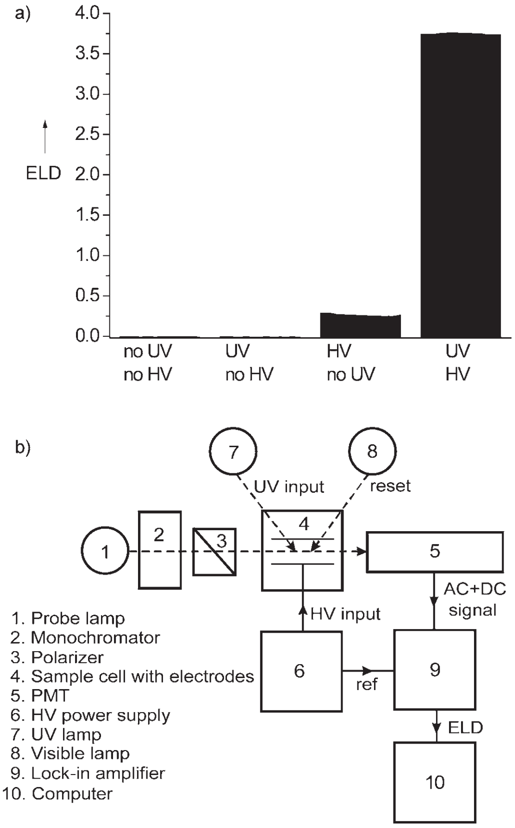

Figure 3. a) ELD response (arbitrary units) at 583 nm of **1** in 2-methyltetrahydrofuran following combinations of light (UV) and electric field (HV) inputs for the AND logic gate. Prior to the indicated inputs, the sample was in the **1c** state. The signal-to-noise ratio (variation of the ELD signal with time during a 4 s collection period, 20 data points) is shown by the small height variations within each bar. b) Schematic diagram of the experimental apparatus.

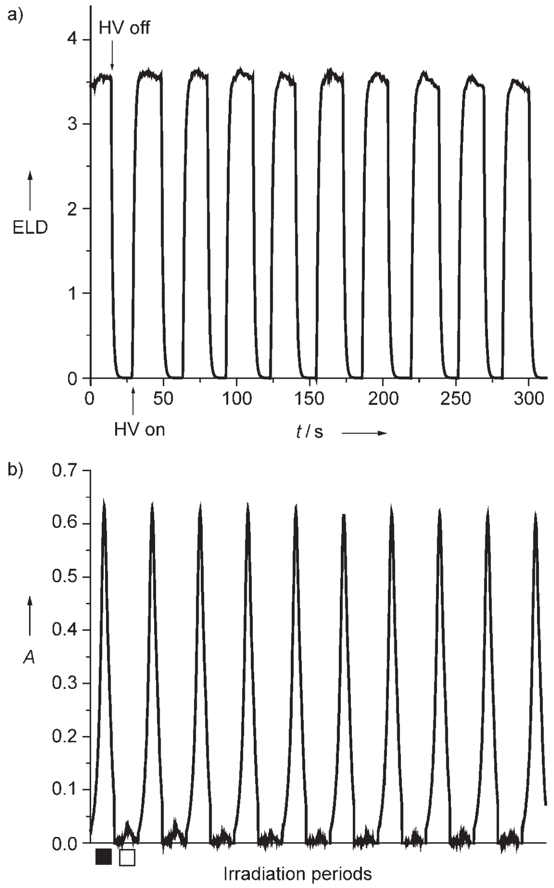

Figure 4. Cycling of the AND gate switching operations. a) The ELD signal at 583 nm from **1** in 2-methyltetrahydrofuran, measured for ca. 15 s after each switching operation, as a function of cycling of the applied voltage (HV) between 1.5 kV (HV on) and 0 V (HV off). b) Variation of the absorbance of **1**, recorded between 500 and 700 nm (where the zwitterionic isomer **1o** absorbs): after UV irradiation (■), and after red-light irradiation (□), as described in the text.

This molecular AND gate does not require the addition of chemicals or translational diffusion of molecules. The times required for the photoisomerizations involved in one input and in the resetting operation are determined by the light-flux applied. The light intensities used here were chosen for convenience, rather than switching speed. The photoisomerization reactions themselves occur in ns or less. The time required for readout is ultimately limited by the time required to align the molecular dipoles sufficiently, and will be on the order of rotational diffusion times. If ac detection is employed, the frequency of the applied ac field and time constant of the cell circuit will determine the time required for detection.

The UV photonic input to the AND gate may be applied at any time prior to readout and the system will "remember" that this input was turned on because of the photoisomerization. The gate will persist in the **1o** state until thermal reversion eventually occurs. However, the second input, the ac high voltage, must be on during readout or no ELD will be detected. This behavior differs from that of photonic gates in which both inputs are photoisomerization reactions and the final state of the gate may be read out at any convenient time after the inputs have been applied and turned off.[9,12]

In summary, a solution of photochrome **1** functions as a molecule-based AND Boolean logic gate with inputs of light of 366 nm and an ac electric field. The output is the electric linear dichroism response. Resetting the gate to the initial state is accomplished by irradiation with red light. The signal-to-noise ratio is more than ample for observation of gate switching, and the sample can be cycled many times before photodegradation interferes. The apparatus is relatively simple, requiring only UV, visible, and plane-polarized light, a light-sensitive detector, an ac voltage source, and, for high sensitivity, lock-in detection.

Experimental Section

Dihydroindolizine **1** was synthesized as reported.[14] The solvent for all measurements was freshly distilled 2-methyltetrahydrofuran. Photoisomerizations of **1** were achieved by using a UVP UV lamp UVGL-25 (366 nm, ca. 1.5 $\mathrm{mW\,cm^{-2}}$) or a 1000 W Xe/Hg-lamp at 450 W. The light from the Xe/Hg-lamp was filtered with two hot mirrors (each having $A = 1.8$ at 900 nm) to reduce the IR intensity and a long pass filter (> 580) nm. The power density at the sample was approximately 50 $\mathrm{mW\,cm^{-2}}$.

The electric linear dichroism (ELD) measurements (Figure 3b) were performed on a JASCO J-500 A CD spectropolarimeter with the photoelastic modulator disconnected, so that the incident light was linearly polarized parallel to the applied electric field. The silica cuvette (10 × 10 mm) was equipped with two planar stainless-steel electrodes (9.5 mm×22 mm) connected to a 50-Hz ac high-voltage power supply. The gap between the electrodes was 1.6 mm, and the voltage was 1.5 kV, which gave a maximal field strength of 940 $\mathrm{kV\,m^{-1}}$. The light passing between the electrodes was detected with a photomultiplier tube (PMT) connected to a lock-in amplifier (LIA; EG&G Model 124A) equipped with a differential preamplifier (EG&G Princeton Applied Research Model 116). The LIA received a 50 Hz reference signal from the high voltage power supply. The LIA detects only the ac component of the PMT response in phase with the high voltage. The output of the LIA, which represents the raw ELD response, is shown in the Figures.

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