Molecular 2:1 Digital Multiplexer[**]

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Binary devices require inputs and outputs that can assume either of two values (0 or 1). Photochromic molecules, which can be isomerized between two metastable forms using light, are natural candidates for components of molecule-based logic systems. We have been investigating how energy and electron transfer between covalently linked photochromes and other chromophores may be used to perform binary switching and Boolean logic operations using light as an input and light or electrical potential as outputs. We have reported[1] various simple switches, a double-throw switch, molecular AND,[2] INHIBIT, XOR[3] and NOR[3] Boolean logic gates, and two molecule-based half-adders.[4,5] A variety of other logic devices based on molecular phenomena have been reported.[6-16] Although some employ photochromes, in the vast majority at least one of the inputs requires physical addition of a chemical species that diffuses to a molecule and carries out a reaction, changing molecular structure.

Digital multiplexers are analogous to mechanical rotary switches that connect any one of several possible inputs to the output. Here, we report the realization of a molecular 2:1 multiplexer. The molecule, **1**, comprises two photochromes linked to a central porphyrin (Figure 1). As explained below, the molecule reacts to two inputs: red light or heat. A third photonic input switches the molecule so that the output (porphyrin fluorescence) reports on the binary state of either one of these inputs, or the other.

The truth table of a 2:1 digital multiplexer is shown in Table 1. The two inputs, A and B, as well as the control input S may be *off* (0) or *on* (1), as may be the output. When S is in the *off* state, the output reports on the state of input B, ignoring the state of input A. After switching S to the *on* state, the output reports the state of input A, rather than B.

The synthesis and structure of triad **1** have been reported.[17] The triad consists of a tetraarylporphyrin (P) linked to both a substituted dihydropyrene photochrome and a photochrome of the dihydroindolizine family based on pyrrolo[1,2-b]pyridazine. Because each photochrome may exist in two metastable forms, the triad may assume any of four isomeric structures (Figure 1). Although the three chromophores of **1** interact photochemically (*vide infra*), photoisomerization of the two photochromes still occurs,

Input *A* (heat)	Input *B* (red light)	Input *S* (green light)	Output (Fluorescence)
0	0	0	0
1	0	0	0
0	1	0	1
1	1	0	1
0	0	1	0
1	0	1	1
0	1	1	0
1	1	1	1

Table 1. Truth table for a 2:1 multiplexer

and it is possible to prepare photostationary distributions greatly enriched in each of the four isomers.[17] For the multiplexer, only three isomers are required: CPD-P-DHI, DHP-P-DHI, and CPD-P-BT. Isomer CPD-P-DHI features the dihydropyrene in the colorless cyclophanediene (CPD) form and the dihydroindolizine in the colorless spiro form (DHI). The absorption spectrum of CPD-P-DHI in 2-methyltetrahydrofuran is nearly identical with that of a model porphyrin in the visible region (λ_{max} = 428, 513, 547, 592 and 648

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nm) and features absorbance characteristic of the photochromes mainly in the ultraviolet (Figure 2).[17] The CPD and DHI chromophores have no significant effect on the photophysics of the porphyrin excited singlet state, and normal porphyrin fluorescence from CPD-P-DHI is observed (Figure 3). The lifetime of the porphyrin first excited singlet state is 11 ns, which is essentially identical to that of model porphyrins.[17]

By using various combinations of light and heat, it is possible to prepare photostationary states enriched in any of the three relevant isomers (Figure 4). Irradiation with ultraviolet light (254 nm) followed by heat converts CPD-P-DHI to a photostationary distribution containing mainly DHP-P-DHI, where the cyclophanediene has been converted to the dihydropyrene form. This isomer displays DHP absorbance centered at about 513 nm underlying the porphyrin absorption (Figure 2). In DHP-P-DHI porphyrin fluorescence is quenched due to photoinduced electron transfer to the porphyrin first excited singlet state from the dihydropyrene moiety (Figure 3). Time resolved emission experiments show that the lifetime of the porphyrin first excited singlet state has been reduced to 1.55 ns.[17]

Irradiating DHP-P-DHI with red light (580 nm $< \lambda <$ 900 nm) converts it back to CPD-P-DHI. Alternatively, irradiation in the green at 530 nm results in photoisomerization to a distribution containing mainly CPD-P-BT, where the spiro form of the dihydroindolizine has opened to the betaine (BT). The betaine demonstrates strong absorption with a maximum at ~560 nm (Figure 2) superimposed on the porphyrin Q-bands. The CPD-P-BT form of the triad is only weakly emissive (Figure 3) due to quenching of the porphyrin excited singlet state by photoinduced electron transfer to the betaine, producing a charge-separated state; the lifetime of CPD-^{1}P-BT is only 43 ps.[17] As indicated in

Figure 4, CPD-P-BT may be converted back to DHP-P-DHI by UV light and heat, or to CPD-P-DHI by heat alone. These various interconversions are possible in part because thermal conversion of BT to DHI is facile, thermal interconversion of CPD and DHP is extremely slow, and the quantum yield of photoisomerization of BT to DHI is relatively low.

The function of triad **1** as a digital multiplexer was evaluated using a solution (~1.5×10^{-5} M) in 2-methyltetrahydrofuran. The initial state was the thermally stable DHP-P-DHI. Input A was heat (*on* state, 55º C for 30 min), and input B was red light (*on* state, 580 nm < λ < 900 nm, ~50 mW/cm^2 for 3.5 min). An *on* state for the switching input S was green light (530 nm, 20 mW average power, provided by a pulsed laser operating at 10 Hz for 18 min). The multiplexer output was porphyrin fluorescence excited at 590 nm and measured at 653 nm.

When the control input was not applied ($S = 0$), and both A and B were *off*, the molecule remained in the thermally stable DHP-P-DHI form. Because porphyrin fluorescence in this isomer is quenched by DHP, porphyrin fluorescence is below a threshold level, resulting in an output of *0* (Figure 5a, "reset"). Switching on input A by heating the sample has no effect, as the molecule is already in its thermally stable form, and the output remains *0* (Figure 5a, "heat"). Alternatively, turning on input B results in absorption of the red light by DHP and photoisomerization to yield CPD-P-DHI. The porphyrin excited singlet state is no longer quenched, strong fluorescence is observed, and the output of the multiplexer turns *on* (Figure 5a, "red light"). Finally, applying both inputs A and B to DHP-P-DHI also leads to net isomerization to a distribution containing mainly CPD-P-DHI (as heat has no effect), and the output of the multiplexer again turns

on. Examination of Table 1 shows that this behavior is exactly that required of the multiplexer with $S = 0$. The output of the multiplexer reports the state of input *B*, without regard to that of input *A*.

Next, an identical solution of DHP-P-DHI was subjected to green light (530 nm laser irradiation, as described above), switching control input *S* to the *on* state. This irradiation converts the sample to a photostationary distribution consisting mainly of CPD-P-BT. If inputs *A* and *B* are both *off*, then porphyrin emission is quenched by the BT moiety, and the output is also *off* (Figure 5b, "green light"). However, if heat is then applied (input *A on*), the sample is converted to CPD-P-DHI, strong porphyrin fluorescence is observed, and the output is *on* (Figure 5b, "heat"). If instead, input *B* is turned *on* (red light for 3.5 min), the molecule remains in the CPD-P-BT form, as photoisomerization of BT to DHI with light of these wavelengths is slow. The output remains *off*. Finally, if both inputs are applied, isomerization to CPD-P-DHI occurs, and porphyrin fluorescence is again observed (output *on*). In the context of Table 1, after control input *S* has been applied the output now tracks the state of input *A*, and is insensitive to input *B*. Thus, the triad solution performs as a 2:1 digital multiplexer. The porphyrin fluorescence intensity reports on either the state of input *A* or input *B*, depending on the state of control input *S*.

In actual operation, the molecular multiplexer must be reset to the initial DHP-P-DHI state after each application of inputs. This may be accomplished most efficiently by irradiation at 254 nm (photoisomerizing all isomers present to DHP-P-BT) followed by heating (thermally isomerizing DHP-P-BT to DHP-P-DHI) as described above. However, the 254 nm radiation leads to undesirably rapid photodegradation of the DHI/BT moiety, degrading performance of the multiplexer over many cycles. In order to permit extensive

cycling, the reset operation was conducted by irradiating at 366 nm (~2 mW/cm^2 for 40 s) followed by heating at 55º C for 90 min. In the cycling experiments, input S was also modified slightly by reducing the exposure time to 280 s. These changes somewhat decreased the dynamic range of the emission amplitude changes, but permitted extensive cycling. The results appear in Figure 6. The sample was initially reset ($A = B = S = 0$), and the porphyrin fluorescence intensity measured. Prior to setting $S = 1$, the fluorescence output tracks input B. After applying the control input S, the output tracks input A. It is evident from the Figure that no significant decomposition was observed over several cycles.

Triad **1** fulfills the requirements of a 2:1 digital multiplexer in that the output (porphyrin fluorescence above a threshold value) reports the value (0 or 1) of either input A or input B, depending on the prior setting of control input S. Although this study was not performed in order to produce a practical device, it is interesting to speculate on some factors that would come into play should actual devices based on this or related molecules be desired. Many applications would require extensive cycling. Although no significant decomposition was noted in the few cycles shown in Figure 6, the stability of this and other organic molecules through repeated cycling in suitable matrices (e.g. polymer) remains to be determined. In part for reasons of convenience, the switching time for the inputs was rather slow. The actual photochemical isomerization reactions occur on the ns time scale or shorter, and the rate of isomerization of an ensemble of molecules depends on the light flux. The red light input (B) was of low intensity, and minutes of irradiation were necessary. The pulsed green laser light was much more intense, and only 17 μs of actual irradiation time was used for the switching of input S.

The thermal reaction (input *A*) required the most time in these experiments, but the necessary time is a function of the temperature, which is ultimately limited by the stability of the molecule. Note that infrared light can be used instead of heat to trigger the isomerization if all-photonic inputs are desired.[17] The use of optical inputs does not require physical access by chemicals or wires to the volume element containing the molecules, and in principle this allows 3-dimensional architectures for arrays of devices. Any practical device would necessarily be based on an ensemble of molecules. Although fluorescence switching in a photochrome has been observed at the single molecule level,[18] practical application of single photochrome-based molecules for switching and logic operations will be limited because quantum yields for photochemical and photophysical process are not precisely unity, and at many irradiation wavelengths photostationary distributions exist. Therefore, it is not possible to predict with certainty the outcome of a particular excitation event in a given molecule.

Experimental Section

The synthesis and characterization of triad **1** have been reported.[17] The spectroscopic solvent was distilled 2-methyltetrahydrofuran. The samples were degassed by 6 freeze-pump-thaw cycles to a final pressure of ~10^{-5} Torr. For the emission measurements, a SPEX Fluorolog τ2 was used. The 530 nm light was generated by an OPO (Continuum Surelight) pumped by a Nd:YAG laser (Continuum Surelite II-10, fwhm = 6 ns). The red light was generated by a 1000 W Xe/Hg-lamp running at 450 W. The Xe/Hg-lamp light was filtered by two hot mirrors (each having A = 1.8 at 900 nm) to reduce the IR intensity, and a long pass filter (>580 nm) to remove light of shorter wavelengths. The

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resulting light power density on the sample was ~ 50 mW/cm^2. The 366 nm UV light

source was a UVP UV lamp Model UVGL-25 (~ 2 mW/cm^2).

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Figure Captions

Figure 1. Isomeric forms of triad **1**.

Figure 2. Absorption spectra in 2-methyltetrahydrofuran of solutions of model porphyrin 5,15-bis(4-methoxycarbonylphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (   ), CPD-P-DHI (•   •), DHP-P-DHI (   ), and CPD-P-BT (••   ••). In some cases, the spectra represent photostationary distributions containing more than one isomer, as explained in the text.

Figure 3. Emission spectra of photostationary distributions enriched in the different states of triad **1** in 2-methyltetrahydrofuran following excitation at 590 nm: model porphyrin (   ), CPD-P-DHI (•   •), DHP-P-DHI (   ), and CPD-P-BT (•• ••). The three triad spectra were obtained from the same sample, and the model porphyrin spectrum is shown at an arbitrary amplitude.

Figure 4. Interconversion pathways of triad **1** that are relevant for multiplexer performance.

Figure 5. Performance of triad **1** as a 2:1 multiplexer. The bars show the porphyrin fluorescence emission intensity at 653 nm with excitation at 590 nm. (a) Response to inputs with control input S in the *off* position. (b) Response to inputs with control input S in the *on* position. The dashed line signifies a threshold level for the fluorescence output. Heat = input A, red light = input B, green light = input S (control input), reset sets $A = B = S = 0$ (see text). The reproducibility of the emission intensities is ±2%.

Figure 6. Cycling of the multiplexer. R = emission intensity after reset, A = emission intensity after input A (heat), B = emission intensity after input B (red light), S = emission

intensity after input S (green light). Excitation was at 590 nm, and emission was
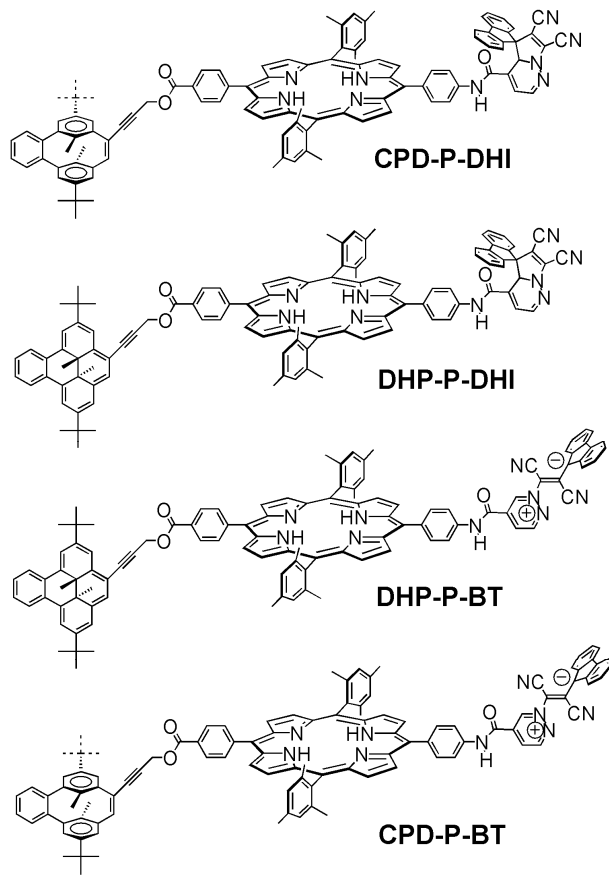
monitored at 653 nm for 5 s.

Figure 1
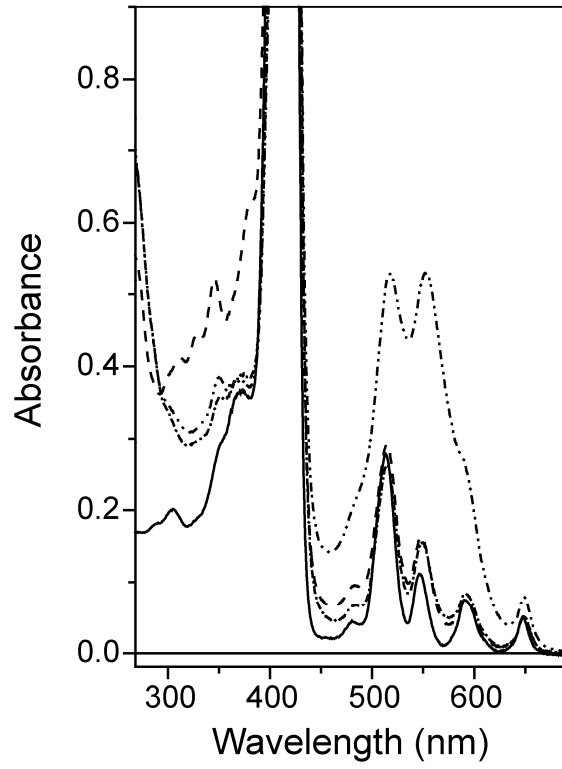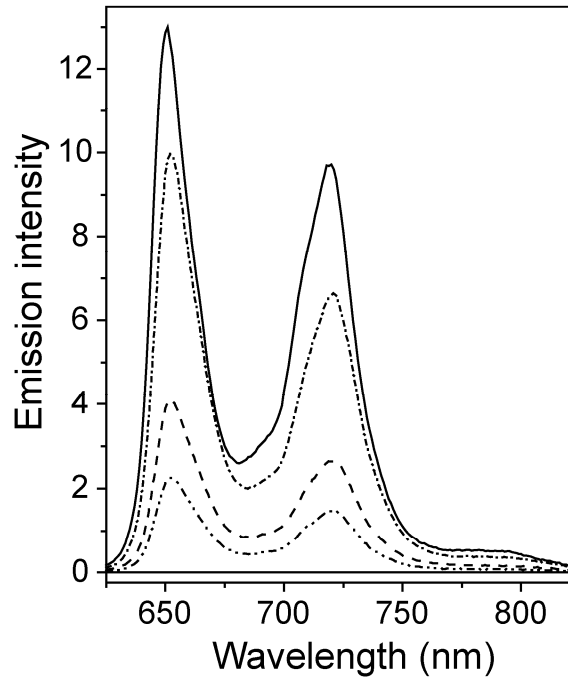

CPD-P-DHI

DHP-P-DHI

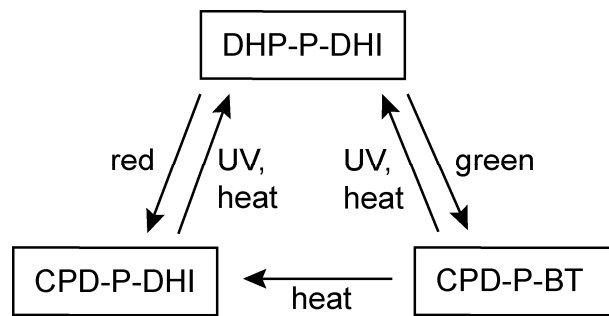DHP-P-BT

CPD-P-BT

Figure 2
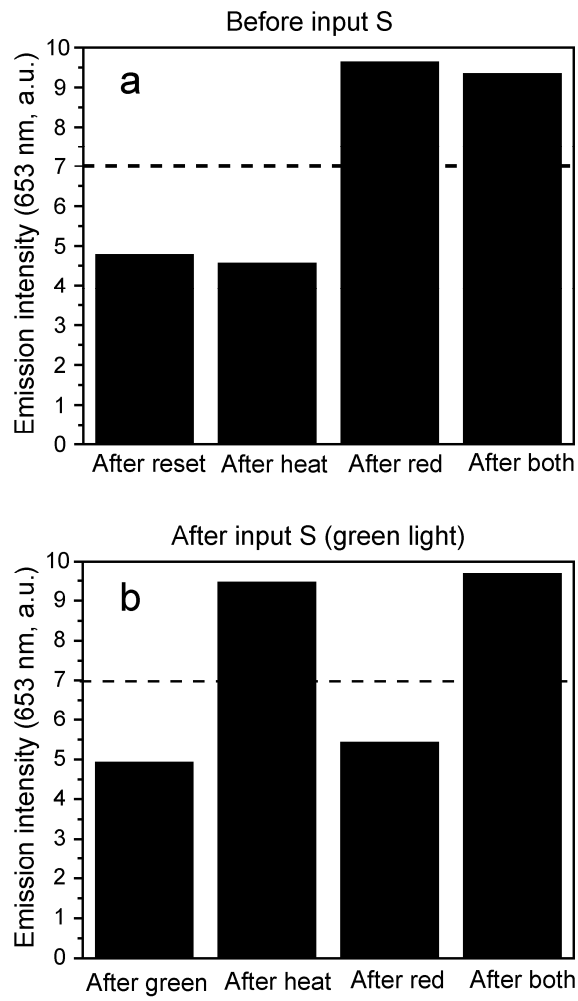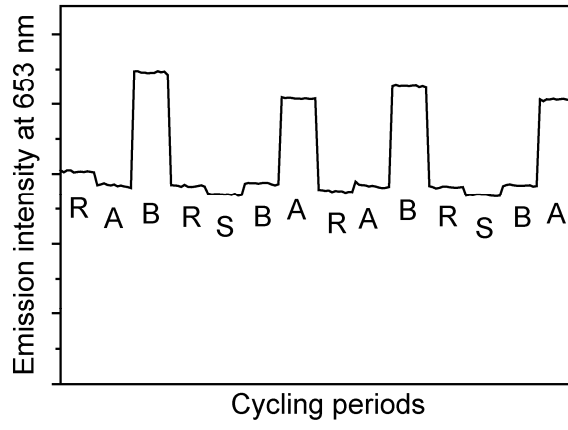
Figure 3

Figure 4

Figure 5

Figure 6

Text for Table of Contents

A porphyrin covalently linked to two photochromes performs as a 2:1 digital multiplexer. Either of the two inputs, heat (*A*) and red light (*B*), may be turned *on* or *off*. The output is porphyrin fluorescence. A third switchable input, green light, selects whether the output reports the state of input *A* or input *B*. The multiplexer function is based on the ability to independently photoisomerize each photochrome and thereby access isomers that quench porphyrin fluorescence through photoinduced electron transfer.

TOC Graphic
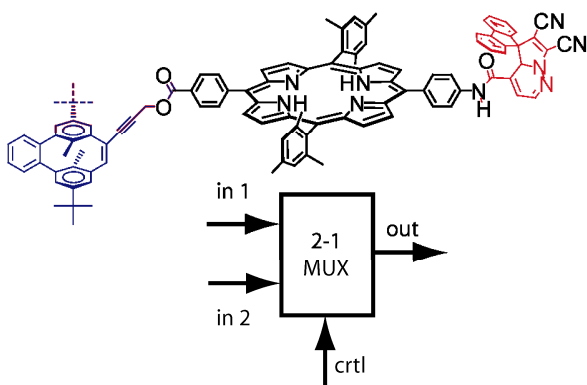
Keywords

Photochromism

Molecular switches

Electron transfer

Chromophores

Photochem. react.

Porphyrins