Molecular Electronics

DOI: 10.1002/anie.200603856

Molecular 2:1 Digital Multiplexer**

Joakim Andréasson, Stephen D. Straight, Subhajit Bandyopadhyay, Reginald H. Mitchell, Thomas A. Moore,* Ana L. Moore,* and Devens Gust**

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 by using light, are natural candidates for components of molecule-based logic systems. We have been investigating how energy and electron transfer between covalently linked photochromic units and other chromophores may be used to perform binary switching and Boolean logic operations with 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.[6–19] Although some employ photochromic materials, the vast majority require for at least one of the inputs the physical addition of a chemical species that diffuses to a molecule and reacts to change the molecular structure.

Digital multiplexers are analogous to mechanical rotary switches that connect any one of several possible inputs to an output. Herein, we report a molecular 2:1 multiplexer (**1**) that comprises two photochromic moieties linked to a central porphyrin (Figure 1). As explained below, the molecule reacts to two inputs: red light and heat. A third photonic input switches the molecule so that the output (porphyrin fluorescence) reports 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 the state of input *B* and ignores the state of input *A*. After input *S* is switched to the on state, the output reports only the state of input *A*.

The synthesis and structure of triad **1** have been reported.[20] The triad consists of a tetraarylporphyrin (P) linked to both a substituted dihydropyrene photochromic unit and a photochromic unit of the dihydroindolizine family

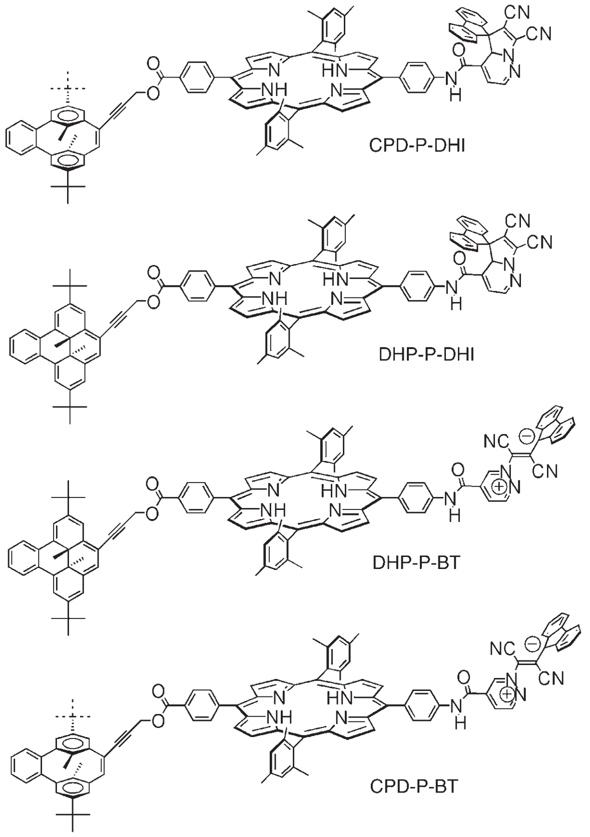


Figure 1. Isomeric forms of triad **1**.

Table 1: Truth table for a 2:1 multiplexer.

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

---

[*] Prof. Dr. J. Andréasson
Department of Chemical and Biological Engineering
Chalmers University of Technology
41296 Göteborg (Sweden)
Fax: (+46) 31-772-3858
E-mail: a-son@chalmers.se

S. D. Straight, Prof. Dr. T. A. Moore, Prof. Dr. A. L. Moore,
Prof. Dr. D. Gust
Center for the Study of Early Events in Photosynthesis
Department of Chemistry and Biochemistry
Arizona State University
Tempe, AZ 85287 (USA)
Fax: (+1) 480-965-2747
E-mail: tmoore@asu.edu
amoore@asu.edu
gust@asu.edu

Dr. S. Bandyopadhyay, Prof. Dr. R. H. Mitchell
Department of Chemistry
University of Victoria
P. O. Box 3065, Victoria, BC, V8W 3V6 (Canada)

[**] This work was supported by the Swedish Research Council (VR) and the U.S. National Science Foundation (CHE-0352599).

based on pyrrolo[1,2-*b*]pyridazine. Because each photochromic unit 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 (see below), photoisomerization of the two photochromic units still occurs, and it is possible to prepare photostationary distributions that are greatly enriched in each of the four isomers.[20] 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 to that of a model porphyrin in the visible region ($\lambda_{max} = 418$, 515, 549, 592, and 649 nm) and features absorbance bands characteristic of the photochromic units mainly in the ultraviolet (Figure 2).[20] 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 first excited singlet state of the porphyrin is 11 ns, which is essentially identical to that of model porphyrins.[20]

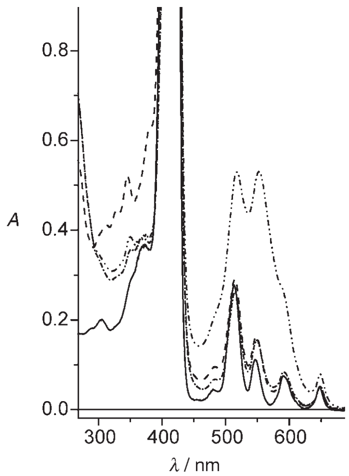


Figure 2. Absorption spectra in 2-methyltetrahydrofuran of solutions of model porphyrin 5,15-bis(4-methoxycarbonylphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (——), CPD-P-DHI (–•–•), DHP-P-DHI (-----), and CPD-P-BT (—··—··). In some cases, the spectra represent photostationary distributions containing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

By using various combinations of light and heat, it is possible to prepare photostationary states that are enriched in any of the three relevant isomers (Scheme 1). Irradiation with ultraviolet light (254 nm) and subsequent heating converts CPD-P-DHI into a photostationary distribution containing mainly DHP-P-DHI, whereby the cyclophanediene has been converted into the dihydropyrene form. The absorbance of the DHP unit of this isomer centered at about 513 nm is covered by the absorption of the porphyrin (Figure 2). The fluorescence of the porphyrin in DHP-P-DHI is quenched as a result of photoinduced electron transfer from the dihydropyrene moiety to the first excited singlet state of the porphyrin (Figure 3). Time-resolved emission experiments show that the lifetime of the first excited singlet state of the porphyrin is decreased to 1.55 ns.[20]

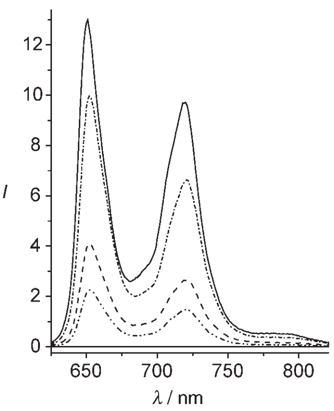
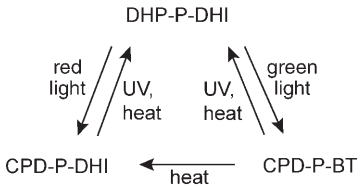


Figure 3. Emission spectra of photostationary distributions enriched in the different states of triad **1** in 2-methyltetrahydrofuran following excitation at 590 nm: model porphyrin (——), CPD-P-DHI (–•–•), DHP-P-DHI (-----), and CPD-P-BT (—··—··). The three triad spectra were obtained from the same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



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

Irradiating DHP-P-DHI with red light ($580\ \text{nm} < \lambda < 900\ \text{nm}$) converts it back into CPD-P-DHI. Alternatively, irradiation with green light ($\lambda = 530$ nm) results in photoisomerization to a distribution containing mainly CPD-P-BT, in which the spiro form of the dihydroindolizine is opened to the betaine (BT) form. The betaine form demonstrates strong absorption whereby a maximum at around 560 nm (Figure 2) is superimposed on the Q bands of the porphyrin. The CPD-P-BT form of the triad is only weakly emissive (Figure 3) owing to quenching of the excited singlet state of the porphyrin by photoinduced electron transfer to the betaine, which produces a charge-separated state; the lifetime of CPD-^{1}P-BT is only 43 ps.[20] As indicated in Scheme 1, CPD-P-BT may be converted back into DHP-P-DHI by irradiation with UV light along with heating or into CPD-P-DHI by heat alone. These various interconversions are possible in part because thermal conversion of BT into 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 by using a solution (ca. 1.5×10^{-5} M) in 2-methyltetrahydrofuran. The initial state was the thermally stable

DHP-P-DHI. Input A was heat (on state, 55 °C for 30 min), and input B was red light (on state, $580\,\text{nm} < \lambda < 900\,\text{nm}$, ca. $50\,\text{mW}\,\text{cm}^{-2}$ for 3.5 min). The on state for the control 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 the fluorescence of the porphyrin 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 the fluorescence of the porphyrin in this isomer is quenched by DHP, it is below a threshold level, so the output is 0 (Figure 4a, "Reset"). Switching on input A by heating the sample has no effect, as the molecule is already in its thermally stable form; thus the output remains 0 (Figure 4a). Alternatively, turning on input B results in absorption of the red light by the DHP unit and photoisomerization to yield CPD-P-DHI. The excited singlet state of the porphyrin is no longer quenched, thus strong fluorescence is observed and the output of the multiplexer turns on. 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.

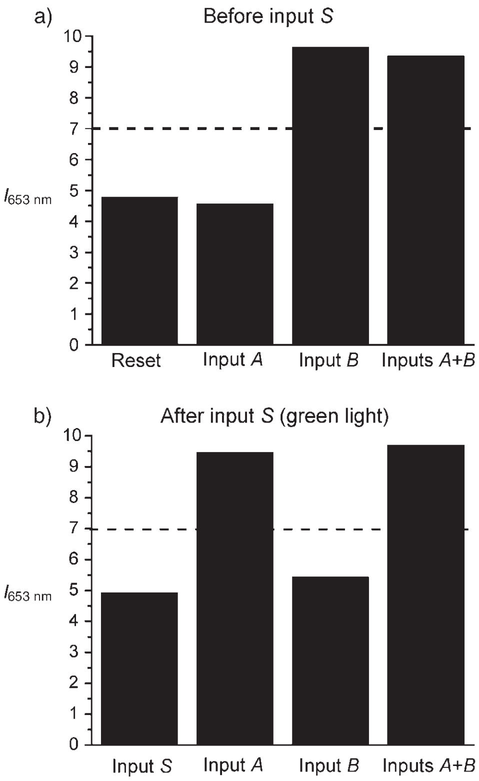


Figure 4. Performance of triad **1** as a 2:1 multiplexer. The bars show the fluorescence emission intensity of the porphyrin at 653 nm with excitation at 590 nm. The reproducibility of the emission intensities is within ±2%. Input A = heat, Input B = red light, Input S = green light (control input), Reset sets $A = B = S = 0$ (see text). a) Response to inputs with control input S off. The photostationary distributions estimated from the absorbance data after each input were: A: 100% DHP and DHI; B: 100% CPD, >95% DHI; Reset: 100% DHP and DHI. b) Response to inputs with control input S on. The photostationary distributions after each input were: S: 100% CPD and approximately 60% BT; $S + A$: approximately 90% CPD and 100% DHI; $S + B$: 100% CPD and approximately 60% BT. The dashed line signifies the threshold level for an on response of the fluorescence output.

Next, an identical solution of DHP-P-DHI was subjected to green light (530 nm laser irradiation, as described above), thereby switching control input S to the on state. This irradiation converts the sample into a photostationary distribution consisting mainly of CPD-P-BT. If inputs A and B are both off, then the porphyrin emission is quenched by the BT moiety, and the output is also off (Figure 4b, "Input S"). However, if heat is then applied (input A on), then the sample is converted into CPD-P-DHI, strong porphyrin fluorescence is observed, and the output is on. If, instead, input B is turned on (irradiation with 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 is applied the output 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 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 (which photoisomerizes the isomers present to DHP-P-BT) followed by heating (which thermally isomerizes DHP-P-BT to DHP-P-DHI) as described above. However, the irradiation at 254 nm leads to undesirably rapid photodegradation of the DHI/BT moiety, which degrades the performance of the multiplexer over many cycles. To permit extensive cycling, the reset operation was conducted by irradiation at 366 nm (ca. $2\,\text{mW}\,\text{cm}^{-2}$ for 40 s) followed by heating at 55 °C for 90 min. In the cycling experiments, input S was also modified slightly by decreasing 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 5. The sample was initially reset ($A = B = S = 0$), and the porphyrin fluorescence

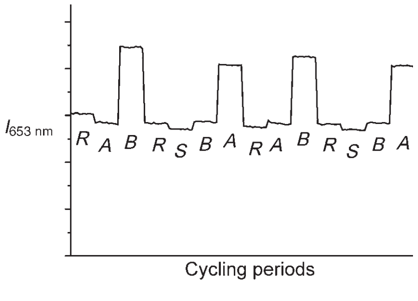


Figure 5. Cycling of the multiplexer. R: after reset, A: after input A (heat), B: after input B (red light), S: after input S (green light). Excitation at 590 nm; emission monitored at 653 nm for 5 s.

intensity measured. Prior to setting $S=1$, the fluorescence output tracks input *B*. After the control input *S* is applied, the output tracks input *A*. 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 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 5, 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 timescale 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 irradiation for a period of minutes was necessary. The pulsed green laser light was much more intense, and an actual irradiation time of only 17 μs 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.[20] 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 three-dimensional architectures for arrays of devices. Any practical device would necessarily be based on an ensemble of molecules. Although fluorescence switching in a photochromic material has been observed at the single molecule level,[21] the practical application of single photochrome-based molecules for switching and logic operations will be limited because the quantum yields for photochemical and photophysical processes 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.[20] Distilled 2-methyltetrahydrofuran was used as the solvent for spectroscopic measurements. The samples were degassed by six freeze–pump–thaw cycles to a final pressure of approximately 10^{-5} Torr. A SPEX Fluorolog $\tau2$ was used for the emission measurements. The 530-nm light was generated by an optical parametric oscillator (OPO, Continuum Surelite) pumped by a Nd:YAG laser (Continuum Surelite II-10, full width at half maximum = 6 ns). The light from the OPO was passed through a lens (focal length (fl) = 3 cm) and focused on to the sample with a spot size of approximately 1 cm^2. The red light was generated by a 1000-W Xe/Hg lamp running at 450 W. The light from the Xe/Hg lamp was filtered by two hot mirrors (each with $A=1.8$ at 900 nm) to reduce the IR intensity, and a long-pass filter (> 580 nm) to remove light of shorter wavelengths. A lens (fl = 10 cm) was used to focus the light on to the sample with a spot size of about 1 cm^2. The total distance between the light source and the sample was 50 cm, and the resulting light power density on the sample was approximately 50 mW cm^{-2}. A UVP UV lamp (Model UVGL-25, ca. 2 mW cm^{-2}) was used to provide the UV light at 366 nm. The sample was held about 1 cm from the UV-light source during irradiation. All samples were stirred continuously during all irradiation processes.

Received: September 19, 2006

Keywords: chromophores · molecular devices · photochemistry · photochromism · porphyrinoids

[1] D. Gust, T. A. Moore, A. L. Moore, *Chem. Commun.* **2006**, *2006*, 1169–1178.

[2] J. Andréasson, Y. Terazono, B. Albinsson, T. A. Moore, A. L. Moore, D. Gust, *Angew. Chem.* **2005**, *117*, 7763–7766; *Angew. Chem. Int. Ed.* **2005**, *44*, 7591–7594.

[3] S. D. Straight, P. A. Liddell, Y. Terazono, T. A. Moore, A. L. Moore, D. Gust, *Adv. Funct. Mater.*, in press.

[4] J. Andréasson, G. Kodis, Y. Terazono, P. A. Liddell, S. Bandyopadhyay, R. H. Mitchell, T. A. Moore, A. L. Moore, D. Gust, *J. Am. Chem. Soc.* **2004**, *126*, 15926–15927.

[5] J. Andréasson, S. D. Straight, G. Kodis, C.-D. Park, M. Hambourger, M. Gervaldo, B. Albinsson, T. A. Moore, A. L. Moore, D. Gust, *J. Am. Chem. Soc.*, DOI: 10.1021/ja0654579.

[6] D. Kuciauskas, P. A. Liddell, A. L. Moore, T. A. Moore, D. Gust, *J. Am. Chem. Soc.* **1998**, *120*, 10880–10886.

[7] F. Pina, M. J. Melo, M. Maestri, P. Passaniti, V. Balzani, *J. Am. Chem. Soc.* **2000**, *122*, 4496–4498.

[8] S. J. Langford, T. Yann, *J. Am. Chem. Soc.* **2003**, *125*, 11198–11199.

[9] T. Gunnlaugsson, D. A. Mac Donaill, D. Parker, *J. Am. Chem. Soc.* **2001**, *123*, 12866–12876.

[10] P. Ghosh, P. K. Bharadwaj, *J. Am. Chem. Soc.* **1996**, *118*, 1553–1554.

[11] A. P. de Silva, N. D. McClenaghan, *Chem. Eur. J.* **2002**, *8*, 4935–4945.

[12] H. Xu, X. Xu, R. Dabestani, G. M. Brown, L. Fan, S. Patton, H. F. Ji, *J. Chem. Soc. Perkin Trans. 2* **2002**, 636–643.

[13] F. M. Raymo, S. Giordani, *J. Am. Chem. Soc.* **2002**, *124*, 2004–2007.

[14] A. Saghatelian, N. H. Volcker, K. M. Guckian, V. S. Y. Lin, M. R. Ghadiri, *J. Am. Chem. Soc.* **2003**, *125*, 346–347.

[15] K. L. Kompa, R. D. Levine, *Proc. Natl. Acad. Sci. USA* **2001**, *98*, 410–414.

[16] X. Guo, D. Zhang, G. Zhang, D. Zhu, *J. Phys. Chem. B* **2004**, *108*, 11942–11945.

[17] D. Margulies, G. Melman, A. Shanzer, *Nat. Mater.* **2005**, *4*, 768–771.

[18] D. Margulies, G. Melman, C. E. Felder, R. Arad-Yellin, A. Shanzer, *J. Am. Chem. Soc.* **2004**, *126*, 15400–15401.

[19] Y. Zhou, H. Wu, L. Qu, D. Zhang, D. Zhu, *J. Phys. Chem. B* **2006**, *110*, 15676–15679.

[20] S. D. Straight, J. Andréasson, G. Kodis, S. Bandyopadhyay, R. H. Mitchell, T. A. Moore, A. L. Moore, D. Gust, *J. Am. Chem. Soc.* **2005**, *127*, 9403–9409.

[21] T. Fukaminato, T. Sasaki, T. Kawai, N. Tamai, M. Irie, *J. Am. Chem. Soc.* **2004**, *126*, 14843–14849.