Organic Optical Transistors

DOI: 10.1002/ange.201104193

An Organic Optical Transistor Operated under Ambient Conditions**

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Transistors are one of the most important inventions of the last century and have paved the road for the triumphal procession of electronic technologies into everyday life.[1] However, driven by the continuous pressure for miniaturization, transistor technology has arrived at a point at which further increasing the speed of data processing has become increasingly difficult to accomplish. Consequently, the demand for faster control and trigger elements has stimulated the search for devices that operate with photons instead of electrons as signal carriers. The first steps towards this direction have been taken already by the demonstration of transistor functionalities that exploit nonlinear light–matter interactions.[2,3] However, these systems featured either a low gain, and/or had to be operated at cryogenic temperatures. Herein we demonstrate that a molecular triad that consists of fluorophores covalently linked to a photochromic molecule can be operated as an optical transistor under ambient conditions.

A promising class of organic materials for data processing are photochromic systems, that is, molecules that can be interconverted between two bistable forms by light. In the past photochromic systems based on *cis–trans* isomerization or photocyclization reactions have been studied[4–7] and apart from fascinating results also severe problems that concern insufficient discrimination between read-out and switching, low fatigue resistance, and/or weak contrast between the signals registered from the two states have been reported.[8–14] Herein we present a photochromic system that consists of two perylene bisimide (PBI) units that are covalently linked to a dithienylcyclopentene (DCP; for details of the chemical synthesis see the Supporting Information). The DCP unit undergoes a photoinduced cyclization reaction from the open to the closed form upon irradiation with light in the UV spectral range (280–310 nm) and vice versa a photoinduced ring-opening reaction upon irradiation with light in the visible spectral range (500–650 nm; Figure 1a). The design strategy of this triad facilitates the combination of the superior fatigue resistance of the diarylethene derivatives[15] with the superior fluorescence properties of the perylene derivatives.[16–19] The absorption spectrum of the triad is shown in Figure 1b. For the open state of the DCP unit (Figure 1b, red line), the triad features a strong absorption band around 300 nm and three bands at 460 nm, 492 nm, and 529 nm, respectively. By comparison with the absorption spectrum from a solution of pure PBI, (Figure 1b, dashed line), the three bands can be assigned to characteristic vibronic bands of the $S_1 \leftarrow S_0$ transition of the PBI units. For the closed form of the DCP unit, (Figure 1b, blue line), the absorption spectrum of the triad features, in addition to the identical bands from the perylene units, broad absorption bands between 300–400 nm and between 500–700 nm.

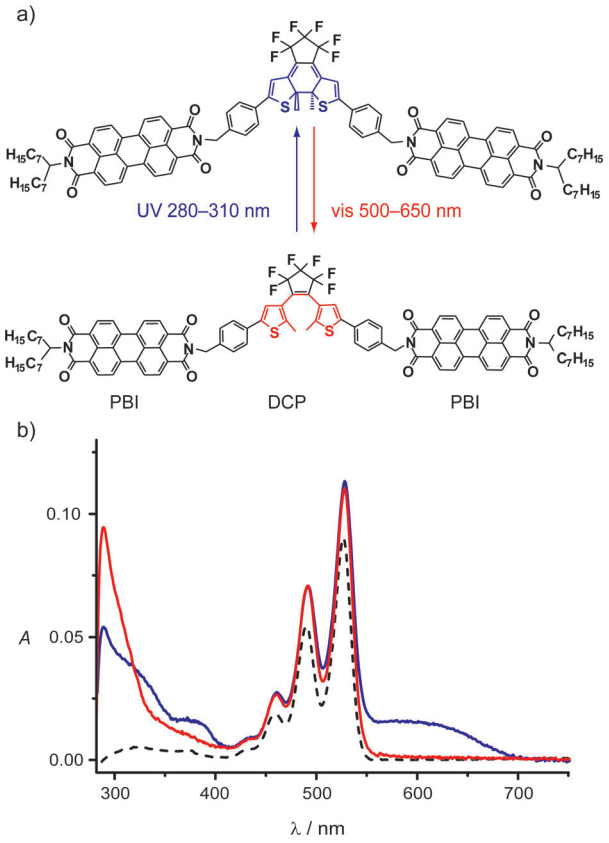

Figure 1. a) Schematic sketch of the molecular triad consisting of two perylene bisimide (PBI) units that are covalently linked to a dithienylcyclopentene (DCP). Top: Closed form, bottom: open form. b) Absorption spectra of the PBI–DCP–PBI triad dissolved in toluene at a concentration of 1.5×10^{-6} mol L^{-1} for the open (red) and the closed (blue) form of the DCP unit. For comparison the dashed line shows the absorption spectrum of pure PBI in the same solvent at a concentration of 1.5×10^{-6} mol L^{-1}.

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[**] We thank S. Frank and Prof. Dr. S. Kümmel for fruitful discussions and gratefully acknowledge financial support from the German Science Foundation (DFG; GRK-1640).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201104193.

For the exploitation of PBI–DCP–PBI as an optical gate, the triads are immobilized in a low-molecular-weight polystyrene matrix and are studied by fluorescence microscopy. In order to convert the DCP to the closed state, the sample was illuminated at 300 nm with an intensity of 30 mW cm^{-2} (exposure time 500 ms) and the fluorescence was probed by illumination at 514 nm with an intensity of 23 mW cm^{-2} (300 ms). This conversion/probe sequence was repeated m times (here $m = 50$). Subsequently, the sample was exposed to an analogous illumination sequence (300 nm: 130 mW cm^{-2}, 250 ms; 514 nm: 96 mW cm^2, 250 ms) to convert the DCP back to the open state. In the following such a full cycle of $2m$ conversion/probe sequences will be referred to as one switching cycle. This illumination scheme allows us to modulate the fluorescence intensity from the PBI units. This process is illustrated in the inset of Figure 2 top left that shows the relative change of the observed fluorescence intensity for converting the DCP unit from closed→open→closed conformations. For brevity, in the following we will refer to the intensity levels as ON and OFF (corresponding to the open and closed conformation of DCP), being aware that OFF means low intensity rather than no intensity. For further quantification we determine the relative change of the fluorescence intensity before and after switching, that is, $(I_{final}-I_{initial})/I_{ON} = \Delta I/I_{ON}$ where $I_{final/initial}$ refer to $I_{ON}/_{OFF}$ depending on the chronological order of the switching process. Obviously the magnitude of this ratio corresponds to the contrast of the modulation of the fluorescence intensity, which amounts to 0.73 for the example shown in the inset of Figure 2. The large contrast can be understood as a modulation of the energy transfer efficiency between the PBI and the DCP subunits as a function of the conformation of the DCP (Figure 2, inset bottom right). In the closed conformation, the lowest excited singlet state of the DCP is lower in energy than the lowest excited singlet state of PBI allowing for efficient PBI→DCP energy transfer and subsequent radiationless decay.[12] In the open conformation the ordering of the DCP and PBI singlet energies is reversed and energy transfer from PBI to DCP becomes impossible. Hence the DCP acts as externally controlled trap for the PBI excitation energy.

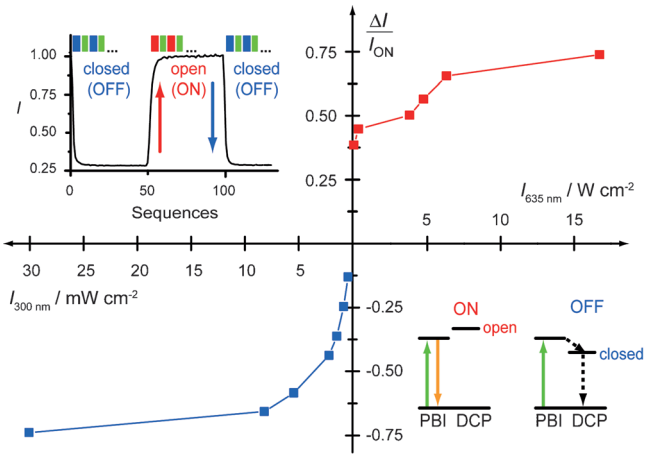

Figure 2. Fluorescence response of the sample as a function of the conversion of the DCP unit. Main panel: change of the fluorescence with respect to the ON state signal as a function of the intensities of the conversion beams; left hand side (blue data points): variation of the intensity of the 300 nm beam; right hand side (red data points): variation of the intensity of the 635 nm beam. For more details see text. Inset top: Example for the change of the normalized fluorescence intensity for a closed→open→closed switching cycle. The bars on top indicate the timing of the illumination periods in the various spectral ranges. The changes from OFF→ON and ON→OFF, respectively, as indicated by the arrows, correspond to the outermost data points of the main panel. Inset bottom: Schematic representation of the modulation of the fluorescence from the PBI units caused by energy transfer from PBI to DCP unit in the closed conformation.

Subsequently we investigated the achievable contrast as a function of the intensities of the conversion beams. In order to do so, the parameters of the 635 nm illumination were kept fixed as given above and the intensity of the 300 nm radiation was varied between 0.4 mW cm^{-2} and 30 mW cm^{-2}. The result of this experiment reveals that the ON–OFF contrast of the modulation of the fluorescence intensity increases for increasing UV intensity and is shown by the blue data points in Figure 2. Next the experiment was reversed and the parameters for the 300 nm illumination were fixed to the initial values, while the intensity of the 635 nm beam was varied between 0 and 16.7 W cm^{-2} (Figure 2, red data points). Also the OFF–ON contrast for the change of the fluorescence intensity increases for an increase of the intensity of the 635 nm beam. Yet this experiment reveals as well that an ON–OFF contrast of about 0.38 is achieved already without any radiation at 635 nm. This observation reflects that also the probing beam at 514 nm induces the ring-opening reaction in the DCP units and converts the sample partly to the ON state.

Further we investigated the fatigue resistance of the triads. For that experiment, the sample was illuminated at 635 nm with an intensity of 43 W cm^{-2} (exposure time 250 ms) and the fluorescence was probed by illumination at 514 nm with an intensity of 96 mW cm^{-2} (250 ms). This conversion/probe sequence was repeated 5 times for one switching cycle. Subsequently, the sample was exposed to an analogous illumination sequence (300 nm: 130 mW cm^{-2}; 250 ms/514 nm: 96 mW cm^{-2}; 250 ms) to convert the DCP back to the closed state. The result of an experiment, in which the triads have been irradiated for more than 3000 cycles is shown in Figure 3. The main figure shows the contrast of the fluorescence as a function of the number of switching cycles. From its initial value of 0.83 it drops to about 0.38 after 3000 cycles. The two insets at the bottom of Figure 3 show the modulation of the fluorescence intensity at the beginning and at the end of the experiment reflecting a telegraph-like alternation between a high- and a low-intensity level.

For these traces the abscissa has been converted to real time, thus demonstrating the reversible conversion of the triad for more than five hours. Analysis of the intensity of the fluorescence in the ON and OFF state revealed a decrease of the ON intensity as a function of time, indicating a slight photobleaching of the PBI chromophores. Nevertheless, we note that the end of the experiment was determined by the experimentalist and not by the photo(in)stability of the sample. Identifying the S_1 and S_0 states of the PBI units as "source" and "drain" for the flow of fluorescence photons and

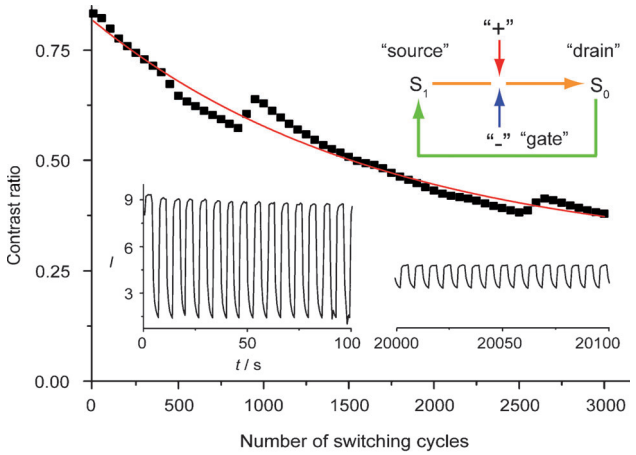

Figure 3. Contrast of the modulation of the fluorescence intensity as a function of the number of switching cycles that each consist of 2×5 conversion/probe sequences. Each data point corresponds to the average over 50 switching cycles. The illumination intensities (exposure times) were 96 mW cm^{-2} (250 ms) at 514 nm, 130 mW cm^{-2} (250 ms) at 300 nm, and 43 W cm^{-2} (250 ms) at 635 nm. The kinks after about 1000 and 2500 switching cycles reflect slight readjustments of the fourth-harmonic generation due to drifts during the long-term experiment. The line serves as a guide for the eye. Insets bottom: Modulation of the fluorescence intensity at the beginning and the end of the experiment. Inset top: Transistor analogy identifying the S_1 and S_0 state of PBI as source and drain, the conversion beams as gate voltage of different polarity, and the optical pumping as external circuit, respectively.

the conversion beams as "gate", the triads can be associated with an optical transistor or an optical gate (see inset Figure 3, top right). In this analogy the type of conversion beam, 300 nm or 635 nm, corresponds to the polarity of the gate voltage of a conventional transistor, which commonly controls the flow of electrons between source and drain. Here it controls the flow of photons emitted from the PBI units and thereby the contrast ratio of the fluorescence. In order to obtain the efficiency of the photoconversion processes in terms of the number of photons per molecule required to induce a conversion process it would be desirable to measure the change of the absorption of the sample in real time. Unfortunately this is impossible in our setup and therefore we have to rely on the change of the fluorescence signal allowing us at least to obtain an order of magnitude estimate for these numbers. This approach is based on several approximations (details are given in the Supporting Information). From these calculations we find that the photocyclization reaction (open→close) requires only about 10 photons per triad at 300 nm, whereas the ring-opening reaction (close→open) needs about 100 photons at 514 nm and about 5000 photons at 635 nm per triad, respectively. These numbers should be read as rough estimates, because of the approximations made in the calculations. Nevertheless, the accuracy is sufficient to testify that the flow of fluorescence photons from the PBI units, which are emitted at a rate of 10^7–10^8 photons s^{-1} per molecule,[18] can be controlled by relatively few photons that trigger the conversion processes. In terms of a logical gate we can distinguish unambiguously between ON and OFF, which is a basic requirement for encoding information. In the ON state, the flow of fluorescence photons can be significantly reduced by illumination with UV light. Reading out the system, that is, detecting the fluorescence intensity under continuous illumination at 514 nm, restores (in part) the ON state because the ring-opening reaction of the DCP units can also be induced at this wavelength which offers an interesting option for nondestructive read-out. For possible applications it will be challenging to develop triads with reduced crosstalk between the read-out and switching channels. Another field that might benefit from these findings is superresolution imaging. At low temperatures the classical diffraction limit of optical microscopy can be circumvented by taking advantage of the slight spectral variations in the absorption spectra of single molecules.[20–23] Under ambient conditions, newly developed techniques take advantage of chromophores that can be converted either stochastically (STORM)[24] or by photoactivation (PALM)[25] to nonfluorescing states, which has led to a growing demand for (photo)switchable chromophores.[26,27]

We have demonstrated the key functionalities of an optical transistor, gating and amplification, exploiting the photophysical properties of a molecular triad. This is a crucial step towards the realization of future devices that can be operated with photons instead of electrons. It is shown that the triad can be operated under ambient conditions for several hours. Our next challenges are to extend these experiments to individual triads thereby reducing the amount of material that is required for storing one bit of information to a single molecule, and to speed up the gating process, which is limited in principle only by the fluorescence lifetime of the PBI units (5 ns).

Experimental Section

Two 100 μL solutions of toluene, one containing 3×10^{-6} mol L^{-1} of the triads, and one containing polystyrene/toluene in a mass ratio of 1:3 were prepared. Equal volume fractions of these two solutions were mixed. From the mixture we dropped 30 μL on a microscope cover slip and let the solvent evaporate for about 5 min. Subsequently, a second cover slip was put on top of the sample resulting in polystyrene films with a thickness of about 10 μm and a triad concentration of about 1.4×10^{-5} mol l^{-1}. Then the samples were mounted in a home-built inverted microscope. The optical setup provides light beams with wavelengths of 300 nm and 635 nm for the photoconversion of the DCP between its bistable forms, and a probe beam of 514 nm to excite the fluorescence of the PBI. The Supporting Information gives more details about the synthesis, sample preparation and the optical setup.

Received: June 17, 2011
Published online: October 5, 2011

Keywords: chromophores · fluorescence · optical transistors · photoswitches

[1] I. M. Ross, *Proc. IEEE* **1998**, *86*, 7–28.
[2] J. Hwang, M. Pototschnig, R. Lettow, G. Zumofen, A. Renn, S. Götzinger, V. Sandoghdar, *Nature* **2009**, *460*, 76–80.

[3] D. E. Chang, A. S. Sørensen, E. A. Demler, M. D. Lukin, *Nat. Phys.* **2007**, *3*, 807 – 812.
[4] H. Dürr, *Angew. Chem.* **1989**, *101*, 427 – 445; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 413 – 431.
[5] H. Bouas-Laurent, H. Dürr, *Pure Appl. Chem.* **2001**, *73*, 639 – 665.
[6] *Molecular Switches* (Ed.: B. L. Feringa), Wiley-VCH, Weinheim, **2001**.
[7] Y. Yokoyama, *Chem. Rev.* **2000**, *100*, 1717 – 1739.
[8] N. P. M. Huck, W. F. Jager, B. de Lange, B. L. Feringa, *Science* **1996**, *273*, 1686 – 1688.
[9] B. L. Feringa, W. F. Jager, B. de Lange, *Tetrahedron* **1993**, *49*, 8267 – 8310.
[10] T. Fukaminato et al., *Photochem. Photobiol. Sci.* **2010**, *9*, 181 – 187.
[11] M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Nature* **2002**, *420*, 759 – 760.
[12] T. Fukaminato et al., *J. Am. Chem. Soc.* **2007**, *129*, 5932 – 5938.
[13] A. Fernaíndez-Acebes, J.-M. Lehn, *Chem. Eur. J.* **1999**, *5*, 3285 – 3292.
[14] H. Hu et al., *J. Photochem. Photobiol. A* **2007**, *189*, 307 – 313.
[15] M. Irie, *Chem. Rev.* **2000**, *100*, 1685 – 1716.
[16] T. Weil, T. Vosch, J. Hofkens, K. Peneva, K. Müllen, *Angew. Chem.* **2010**, *122*, 9252 – 9278; *Angew. Chem. Int. Ed.* **2010**, *49*, 9068 – 9093.
[17] E. Lang, F. Würthner, J. Köhler, *ChemPhysChem* **2005**, *6*, 935 – 941.
[18] E. Lang et al., *ChemPhysChem* **2007**, *8*, 1487 – 1496.
[19] F. Würthner, *Chem. Commun.* **2004**, 1564 – 1579.
[20] A. M. van Oijen, J. Köhler, J. Schmidt, M. Müller, G. J. Brakenhoff, *Chem. Phys. Lett.* **1998**, *292*, 183 – 187.
[21] A. M. van Oijen, J. Köhler, J. Schmidt, M. Müller, G. J. Brakenhoff, *J. Opt. Soc. Am. A* **1999**, *16*, 909 – 915.
[22] A. V. Naumov, A. A. Gorhelev, Y. G. Vainer, L. Kador, J. Köhler, *Angew. Chem.* **2009**, *121*, 9930 – 9934; *Angew. Chem. Int. Ed.* **2009**, *48*, 9747 – 9750.
[23] A. V. Naumov, A. A. Gorshelev, Y. G. Vainer, L. Kador, J. Köhler, *Phys. Chem. Chem. Phys.* **2011**, *13*, 1734 – 1742.
[24] B. Huang, W. Wang, M. Bates, X. Zhuang, *Science* **2008**, *319*, 810 – 813.
[25] E. Betzig et al., *Science* **2006**, *313*, 1642 – 1645.
[26] M. Heilemann, P. Dedecker, J. Hofkens, M. Sauer, *Laser Photonics Rev.* **2009**, *3*, 180 – 202.
[27] J. Vogelsang, T. Cordes, C. Forthmann, C. Steinauer, P. Tinnefeld, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 8107 – 8112.

