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An All-Photonic Molecule-Based Parity Generator/Checker for Error Detection in Data Transmission

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Supporting Information

ABSTRACT: The function of a parity generator/checker, which is an essential operation for detecting errors in data transmission, has been realized with multiphotochromic switches by taking advantage of a neuron-like fluorescence response and reversible light-induced transformations between the implicated isomers.

The use of chemical processes, including electrochemical and photochemical ones, to achieve binary information processing according to Boolean logic, in short molecular logic, continues to receive a great deal of attention.[1−10] In recent years the research efforts have divided into two different, yet complementary directions: (i) the exploitation of relatively simple logic operations, such as AND, OR, INHIBIT, for bioinspired applications (delivery/activation of drugs, diagnostics)[11−23] or the design of smart materials[7,13,14,24−28] and (ii) the challenging task of integrating more and more complex functions into purpose-designed molecular and supramolecular architectures.[28−44] The ultimate goal of the latter task is clearly related to molecular computing, which is also actively pursued in alternative approaches, such as quantum computing[45] and computing with DNA building blocks.[46−50]

Among the various strategies followed for the realization of molecular logic devices, photoswitches have turned out to be very promising.[9,31,36,40,42−44,51] This is related to the possibility of (i) all-photonic operation, i.e., exclusively optical signaling (UV−vis and/or fluorescence) is used to address and read the system, (ii) spatiotemporal control, (iii) remote operation, and (iv) the ease by which many excited state processes (e.g., electron transfer, energy transfer) can be controlled.[31,51,52]

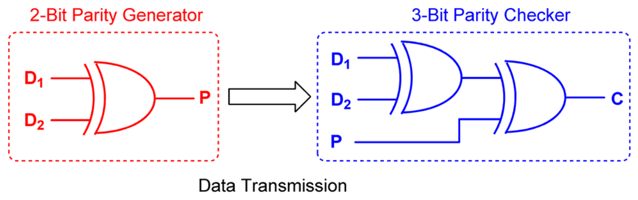
A frequently encountered and essential problem in any type of data transmission is the occurrence of erroneous procedures. These failures can be detected by parity generation and checking.[53] Typically, a parity bit (P) is generated and added to the data bits D_n such that the total number of 1's ($\sum$) in the transmitted string is even. This device is called an even parity generator. For example, if two bits of data are to be transmitted, the parity generator would assign to P the binary value according to the truth table of an exclusive OR (XOR) gate, where D_1 and D_2 are the inputs and P is the output (see Table 1 and Scheme 1). The resulting D_1D_2P string is transmitted to the receiver and subsequently analyzed by a parity checker (see Scheme 1). In the case of an erroneous data transmission of the 3-bit string, the checker device gives an "alert" in form of a binary 1 for the output C (parity error check). This occurs if the number of 1's in the received string is odd (see Table 2). In the case of a correct transmission procedure, the number of 1's in the string is even, and the output is 0.

Table 1. Truth Table of a 2-Bit Parity Generator

entry	inputs		output	$\sum$[a]
	D_1[b]	D_2[b]	P[c]	
1	0	0	0	0, even
2	0	1	1	2, even
3	1	0	1	2, even
4	1	1	0	2, even

[a]Number of 1's in the D_1D_2P string. [b]380 nm light (0.5 mW/cm^2). [c]Fluorescence intensity at 630 nm.

Scheme 1. Representation of a Parity Generator/Checker



Here we report for the first time the molecular implementation of the above-discussed parity generator/checker device. For this purpose the photochromic Triads **1** and **2** shown in Scheme 2a were used. The compounds consist of two different types of photoswitches: a fulgimide (FG) and a dithienylethene (DTE). Triad **1** contains two identical fulgimide units and one DTE unit,[40] whereas Triad **2** contains one FG unit and two identical DTE units (see Supporting Information (SI) for the isomerization scheme, structures, and spectral properties of the individual FG and DTE models).

Given that each switch may exist in an open (o) and a closed (c) form and that only triads with the identical FG or DTE units present in the same form are relevant, four states can be distinguished: FG_o-DTE_o, FG_c-DTE_o, FG_c-DTE_c, and FG_o-DTE_c. However, only the three first isomers are implied in the complete description (see below) of the logic operations of a

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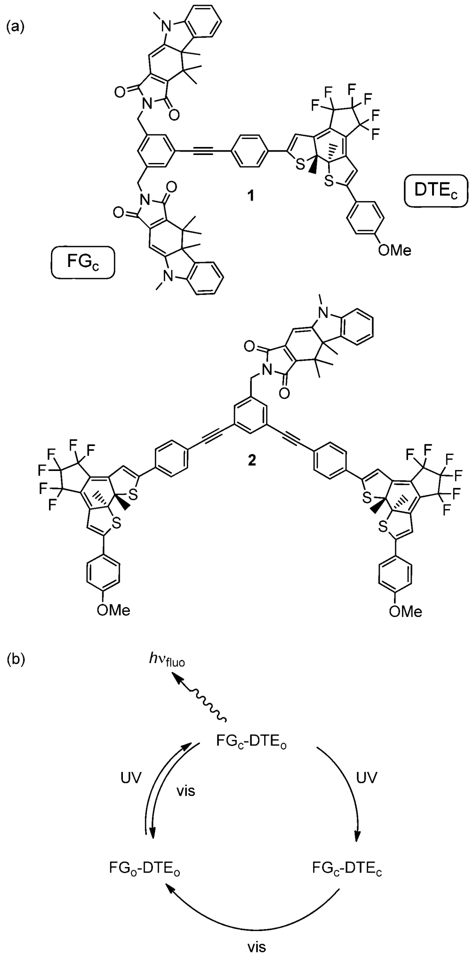
Table 2. Truth Table and Interpretation of a 3-Bit Parity Checker

	inputs			output		
entry	D_1[b]	D_2[c]	P[c]	C[d]	Σ[a]	Interpretation
1	0	0	0	0	0, even	ok
2	0	1	0	1	1, odd	error
3	1	0	0	1	1, odd	error
4	1	1	0	0	2, even	ok
5	0	0	1	1	1, odd	error
6	0	1	1	0	2, even	ok
7	1	0	1	0	2, even	ok
8	1	1	1	1	3, odd	error

[a] Number of 1's in the D_1D_2P string. [b] 380 nm light (0.5 mW/cm^2) for $P = 0$ and visible light ($\lambda > 540$ nm, 30 mW/cm^2) for $P = 1$. [c] 380 nm light (0.5 mW/cm^2). [d] Fluorescence intensity at 630 nm.

Scheme 2. (a) Structures of Triads 1 and 2 in the All-Closed Form and (b) Photoswitching Between the Essential Isomers



molecule-based parity generator/checker. The corresponding photochemical transformations are depicted in Scheme 2b. It is vital to the understanding of the system to realize that only FG_c is fluorescent ($\lambda_{f,max} = 630$ nm, $\tau_f = 135$ ps, $\Phi_f = 0.005$).[40] This emission, however, is quenched by DTE_c in an efficient resonance energy-transfer process.[54] Hence, fluorescence, which herein is defined as output signal, is exclusively observed for FG_c-DTE_o.[40]

The XOR gate required for the 2-bit parity generator can be implemented by defining the FG_c-DTE_o fluorescence at 630 nm as output P. For D_1 and D_2, degenerate 380 nm light inputs are used, a wavelength which can isomerize both open forms FG_o and DTE_o. The input application (one or both active) can be controlled through the time of irradiation. Starting from the nonfluorescent FG_o-DTE_o form ($P = 0$), irradiation with 380 nm light for a defined time (D_1 or D_2 equals binary 1) will enrich the sample in the fluorescent FG_c-DTE_o form ($P = 1$); see Scheme 2b.[55] Upon prolonged irradiation ($D_1 = D_2 = 1$) the prevailing isomer will be the nonfluorescent FG_c-DTE_c form, corresponding to the output $P = 0$.

This notion was confirmed by the experimental observation of a clear off–on–off fluorescence pattern for both triads (see Figure 1) with UV light exposure time, which translates into the desired XOR logic gate.[31] Here, D_1 and D_2 correspond each to 380 nm UV exposure (0.5 mW/cm^2) for 500 and 250 s for Triad **1** and **2**, respectively.[56] The results are presented as bar graphs in Figure 2; the entries 1–4 correspond to the described XOR gate. The fluorescence switching is complemented by the observed changes in the absorption spectra of Triad **1** and **2**; shown in the SI. As a side observation, the prompt rise of the fluorescence signal noted for Triad **2** reflects a more complex kinetic situation than expected from the time constants that were derived from UV–vis measurements (see Table 3 and SI).

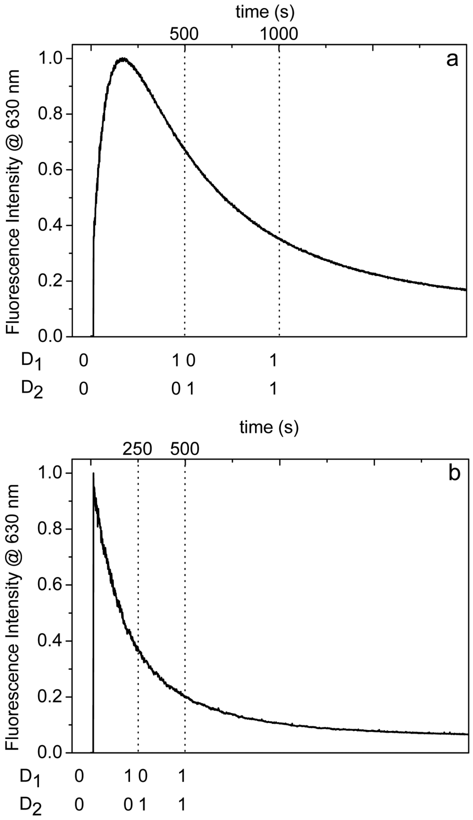


Figure 1. Fluorescence of solutions of Triads (a) **1** and (b) **2** at 630 nm as a function of irradiation time with 380 nm UV light. D_1 and D_2 correspond each to 500 and 250 s irradiation time for Triads **1** and **2**, respectively; see also ref 56.

The observation of the described neuron-like response of Triads **1** and **2** is by no means trivial as a series of conditions must be fulfilled: (i) First of all, only one isomeric form of the triad should be fluorescent. (ii) The fluorescent isomer should be part of a serial photoreaction sequence, being formed from a precursor isomer and subsequently transformed into a final

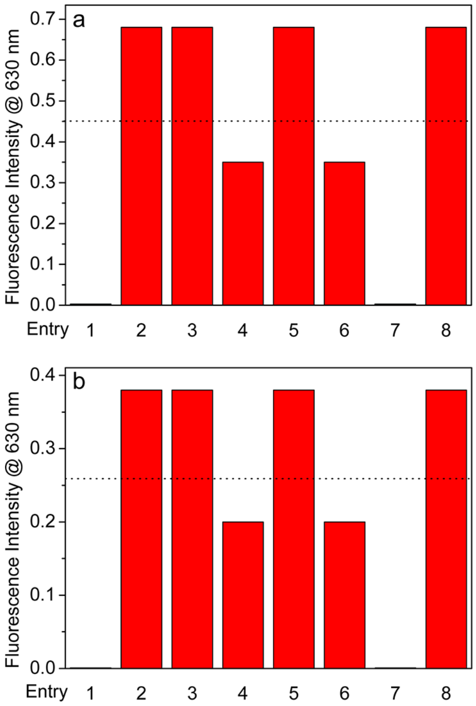


Figure 2. Performance of Triads (a) **1** and (b) **2** as a parity generator/checker under the application of various input entries from Tables 1 and 2. For signal-to-noise ratios and for reproducibility of the data in cycling experiments, see Figure 1 and SI. The dotted line is the threshold used for the assignment of binary 0 (below) and 1 (above).

Table 3. Time Constants and Quantum Yields for Photoisomerization Reactions

compound[a]	photoisomerization	time constant (s)[b]	Φ_r[c]
FG model	$\mathrm{FG_o} \rightarrow \mathrm{FG_c}$[d]	312	0.10
FG model	$\mathrm{FG_c} \rightarrow \mathrm{FG_o}$[e]	40	0.20
DTE model	$\mathrm{DTE_o} \rightarrow \mathrm{DTE_c}$[d]	730	0.34
DTE model	$\mathrm{DTE_c} \rightarrow \mathrm{DTE_o}$[e]	150	0.0077

[a] See structures in SI. [b] 380 nm light (0.5 mW/cm^2) and visible light ($\lambda > 540$ nm, 30 mW/cm^2) used in the closing and the opening reactions, respectively. [c] Photoisomerization quantum yield. [d] Photostationary state distribution: $[\mathrm{FG_c}]/[\mathrm{FG_o}] \sim 100/0$, $[\mathrm{DTE_c}]/[\mathrm{DTE_o}] \sim 80/20$. [e] Photostationary state distribution: $[\mathrm{FG_o}]/[\mathrm{FG_c}] \sim 100/0$, $[\mathrm{DTE_o}]/[\mathrm{DTE_c}] \sim 100/0$.

product isomer, both nonfluorescent. (iii) There is an upper limit for the rate of the closing reaction for the DTE photoswitch. If it occurs too fast, it will suppress the build-up of the fluorescent isomer $\mathrm{FG_c}$-$\mathrm{DTE_o}$. (iv) The photostationary state should contain as much as possible of DTE in its quenching closed form $\mathrm{DTE_c}$, so that the on−off ratio upon prolonged irradiation ($\mathrm{D}_1 = \mathrm{D}_2 = 1$) is maximized. For Triads **1** and **2**, these conditions are clearly fulfilled which is also supported by the kinetic data (see Table 3 and SI).

After demonstrating the molecular implementation of the parity generator, the realization of the corresponding parity checker was attempted. The truth table of this device (Table 2) can be broken down into two parts. The first one refers to the $P = 0$ situations (entries 1−4), which correspond to the XOR logic described before (now the fluorescence output is referred to as C). On the other hand, for $P = 1$ (entries 5−8 of Table 2) the complementary XNOR function with respect to the data inputs D_1 and D_2 is identified. In order to implement this function correctly, D_1 is visible light ($\lambda > 540$ nm, 30 mW/cm^2, 30 min exposure time),[57] whereas P and D_2 are defined as 380 nm UV light (same irradiation conditions as described above for the XOR gate). For the application of P, D_1, and D_2 over the initial form $\mathrm{FG_o}$-$\mathrm{DTE_o}$, the following chemical processes occur: Applying P alone (entry 5; Table 2) yields a high concentration of $\mathrm{FG_c}$-$\mathrm{DTE_o}$, and fluorescence emission is observed ($C = 1$). If this is followed by another dose of UV light irradiation ($P = \mathrm{D}_2 = 1$; entry 6), the nonfluorescent $\mathrm{FG_c}$-$\mathrm{DTE_c}$ is formed ($C = 0$). If instead visible light is applied ($P = \mathrm{D}_1 = 1$; entry 7), back isomerization to the initial form $\mathrm{FG_o}$-$\mathrm{DTE_o}$ is observed; here the fluorescence output is low ($C = 0$). Finally, the additional application of UV light ($P = \mathrm{D}_1 = \mathrm{D}_2 = 1$; entry 8) yields the fluorescent $\mathrm{FG_c}$-$\mathrm{DTE_o}$ state ($C = 1$). Noteworthy, accounting for the well-known memory effects[40,42] that are intrinsic for photochromic switching between thermally stable forms, for $P = 1$ situations the inputs should be applied in the order P, D_1, D_2 (see also SI). The above-described behavior concludes the function described by the truth table of an even 3-bit parity checker (see Table 2 and Figure 2). The system can be quantitatively reset to its initial state ($\mathrm{FG_o}$-$\mathrm{DTE_o}$) by visible light irradiation at any point of operation.

The robustness of the switching and reading processes has been tested as well. Several switching cycles for the alternate application of UV and visible light (reversible switching between $\mathrm{FG_o}$-$\mathrm{DTE_o}$ and $\mathrm{FG_c}$-$\mathrm{DTE_o}$ isomers) and reading of the $\mathrm{FG_c}$ fluorescence output were performed, and the operation can be repeated for at least 10 cycles without loss of performance (see SI). The high thermal stability of all species (<10% variation in the absorption spectra of $\mathrm{FG_c}$-$\mathrm{DTE_c}$ after standing for a week in the dark) makes it possible to read the output state conveniently after input application.

In conclusion, a new molecule-based logic operation in form of parity generation/checking was functionally integrated in the photoswitchable Triads **1** and **2**. The fulfillment of a series of molecular design criteria, including photokinetic considerations, is vital to the successful realization of the molecular device. In a proof-of-principle approach it was shown that the switching and reading of the device can be performed all-photonically, very robust, and in a reversible manner. This underlines the potential of all-photonic devices in molecular information processing and may open new paths for the application of multiphotochromic switches in molecular logic.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis of Triad **2**, additional photophysical and kinetic data, recycling experiments, data for input application by using a neutral density filter, discussion of memory effect. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(54) Singlet−singlet energy-transfer quenching of FG$_c$ fluorescence by DTE$_c$ is seminal for the function of the parity generator/checker. For this purpose the chromophores must be spatially very near one another. Achieving efficient quenching by intermolecular energy transfer in a solution with unlinked components ("cocktail" approach) would require very high concentrations of DTE$_c$ and consequently very high optical densities, which would not be practical.

(55) Note that also FG$_o$-DTE$_c$ will be formed, which however has no relevance as this form lacks fluorescence.

(56) Alternatively, both inputs can be applied at the same time while keeping the irradiation time constant (see data in SI).

(57) In practice this redefinition (from UV to visible light) of D$_1$ could be achieved by frequency down conversion using a strong and long-lived visible light emitter with an appropriate UV absorption (e.g., terbium-containing phosphors).