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 computing45 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, such that the total number of 1’s (∑s) 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 D1 and D2 are the inputs and P is the output (see Table 1 and Scheme 1). The resulting D1D2P 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.

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 and DTE units present in the same form are relevant, four states can be distinguished: FG−DTEo, FG−DTEc, FGc−DTEo, and FGc−DTEc. However, only the three first isomers are implied in the complete description (see below) of the logic operations of a

| Table 1. Truth Table of a 2-Bit Parity Generator |
|---|---|---|---|
| entry | D1 | D2 | P |
| 1 | 0 | 0 | 0 |
| 2 | 0 | 1 | 1 |
| 3 | 1 | 0 | 1 |
| 4 | 1 | 1 | 0 |
| ∑s | even | even | even |

*Number of 1’s in the D1D2P string. bFluorescence intensity at 380 nm light (0.5 mW/cm²).

Scheme 1. Representation of a Parity Generator/Checker

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.

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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 FGc is fluorescent (λf,max = 630 nm, τf = 135 ps, Φf = 0.005).40 This emission, however, is quenched by DTEc in an efficient resonance energy-transfer process.54 Hence, fluorescence, which herein is defined as output signal, is exclusively observed for FGc-DTEc.40

The XOR gate required for the 2-bit parity generator can be implemented by defining the FGc-DTEc fluorescence at 630 nm as output P. For D1 and D2, degenerate 380 nm light inputs are used, a wavelength which can isomerize both open forms FGo and DTEo. The input application (one or both active) can be controlled through the time of irradiation. Starting from the nonfluorescent FGo-DTEo form (P = 0), irradiation with 380 nm light for a defined time (D1 or D2 equals binary 1) will enrich the sample in the fluorescent FGc-DTEc form (P = 1); see Scheme 2b.55 Upon prolonged irradiation (D1 = D2 = 1) the prevailing isomer will be the nonfluorescent FGc-DTEc form, corresponding to the output P = 0.

This notion was confirmed by the experimental observation of a clear 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, D1 and D2 correspond each to 380 nm UV exposure (0.5 mW/cm²) for P = 0 and visible light (λ > 540 nm, 30 mW/cm²) for P = 1.380 nm light (0.5 mW/cm²).40 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](image)

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

| entry | D1 | D2 | P | C | Σ | 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     | 0  | 0  | 1 | 0 | 2 | even ok       |
| 5     | 0  | 1  | 1 | 0 | 2 | even ok       |
| 6     | 1  | 0  | 0 | 2 | 3 | odd error     |
| 7     | 0  | 0  | 1 | 3 | 3 | odd error     |
| 8     | 1  | 1  | 1 | 3 | 3 | odd error     |

Number of 1’s in the D1D2P string.380 nm light (0.5 mW/cm²) for P = 0 and visible light (λ > 540 nm, 30 mW/cm²) for P = 1.380 nm light (0.5 mW/cm²).40 Fluorescence intensity at 630 nm.

![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. D1 and D2 correspond each to 500 and 250 s irradiation time for Triads 1 and 2, respectively; see also ref 56.](image)
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 FGc-DTEc. (iv) The photostationary state should contain as much as possible of DTE in its 
photoswitch. If it occurs too fast, it will suppress the build-up of the fluorescent isomer FGc-DTEc. If this is followed by another dose of UV light irradiation \((P = D_1 = 1; \text{entry } 7)\), back isomerization to the initial form \(FG_r\) is observed; here the fluorescence output is low \((C = 0)\). Finally, the additional application of UV light \((P = D_1 = D_2 = 1; \text{entry } 8)\) yields the fluorescent \(FG_r\) 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 \((FG_r-DTE_o)\) 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 \(FG_r-DTE_o\) and \(FG_r-DTE_c\) isomers) and reading of the \(FG_r\) 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 \(FG_r-DTE_c\) 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 multiphotonic switches in molecular logic.

### Table 3. Time Constants and Quantum Yields for Photoisomerization Reactions

| compound\(^{a}\) | photoisomerization | time constant \((s)\)\(^{b}\) | \(\Phi^d\) |
|-----------------|-------------------|---------------------|--------|
| FG model        | \(FG_c \rightarrow FG_o\) | 312                  | 0.10   |
| FG model        | \(FG_c \rightarrow FG_o\) | 40                   | 0.20   |
| DTE model       | \(DTE_c \rightarrow DTE_o\) | 730                  | 0.34   |
| DTE model       | \(DTE_o \rightarrow DTE_c\) | 150                  | 0.0077 |

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

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**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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