

## ARTICLES

## A New Redox-Resettable Molecule-Based Half-Adder with Tetrathiafulvalene

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A new redox molecule-based half-adder with tetrathiafulvalene (TTF) was reported for the first time. This half-adder employs electrochemical and chemical oxidations (NOPF<sub>6</sub>) as input signals and absorbances at 350 and 435 nm as output signals. It is interesting to note that this new molecule-based half-adder shows reset capability by making use of the unique redox behaviors of TTF.

## 1. Introduction

Investigation of signal processing at the molecular level has received more and more attention in recent years and become one of the frontiers in modern chemistry.<sup>1</sup> This is mainly due to the urge for the miniaturization of electronic devices on one hand and the significance of understanding the signal elaboration mechanism of some biological process on the other hand.<sup>2</sup> These studies have led to the emergence and development of molecular logic gates.<sup>3</sup> Since the first report of molecular AND logic gate by de Silva et al.,<sup>4</sup> many individual logic gates have been described on the basis of the spectral variations of molecular systems in response to external stimulations.<sup>3</sup> Integration of simple logic gates into combinational circuits is an important step for the realization of complex information processing. For instance, the combination of an AND gate and an XOR gate leads to a half-adder that can carry out elementary addition by using the XOR gate to generate the sum digit and the AND gate to generate the carry digit. Several examples of half-adders have been demonstrated<sup>5</sup> since de Silva and co-workers reported the molecular half-adder based on two molecules with chemicals as the input signals in 2000.<sup>5a</sup> Molecular half-adders based on photoisomerization processes with light as the only input signals have been recently described.<sup>5b,c,e,h</sup> We have also recently reported a molecule-based half-adder, by making use of the multistate photochromic spiropyran in the presence of Fe<sup>3+</sup> under light irradiation.<sup>5i</sup> Nevertheless, study of the molecular half-adder is still at its early stage. Rational design and development of new molecular half-adders with resettable character based on rather simple and easily accessible molecules still remain challenging. Herein, we report a new redox-resettable molecule-based half-adder with tetrathiafulvalene (TTF), a rather simple, commercially available, and easily derivable molecule in terms of chemical structure but possessing unique electronic properties, with electric energy (electrochemical oxidation) and chemical oxidant as input signals and

absorbance as output signals. To the best of our knowledge, this is the first time employing tetrathiafulvalene to mimic the performance of a molecule-based half-adder showing reset capability.

TTF and its derivatives have been intensively studied as organic conducting materials.<sup>6</sup> The unique feature of TTF (and its derivatives) is that it can be reversibly transformed into the radical cation TTF<sup>•+</sup> and dication TTF<sup>2+</sup> through either chemical or electrochemical oxidations at easily accessible potentials (Figure 1). By making use of this feature, functional molecules and supramolecules containing TTF units were studied for molecular switches,<sup>7</sup> logic gates,<sup>8</sup> sensors,<sup>9</sup> and machines.<sup>10</sup> Another notable feature of TTF is that each species of the three states of TTF, TTF<sup>•+</sup>, and TTF<sup>2+</sup> shows a distinct absorption spectrum (Figure 2). As will be discussed below, the manner of the absorption spectral changes in association with the interconversion among TTF, TTF<sup>•+</sup>, and TTF<sup>2+</sup> mimics the function of a half-adder. Because both TTF<sup>•+</sup> and TTF<sup>2+</sup> can be reduced to the neutral state of TTF, this new molecule-based half-adder shows reset capability.

## 2. Experimental Section

TTF was purchased from Aldrich and NOPF<sub>6</sub> from Alfa and used directly without further purification. CH<sub>3</sub>CN (HPLC grade) was used as the solvent, which was distilled over CaH<sub>2</sub> prior to use. Absorption spectra were recorded using a Jasco V-570 spectrophotometer. Cyclic voltammetry (CV) and electrochemical experiments were performed with an EG&G 283 electrochemical working station.

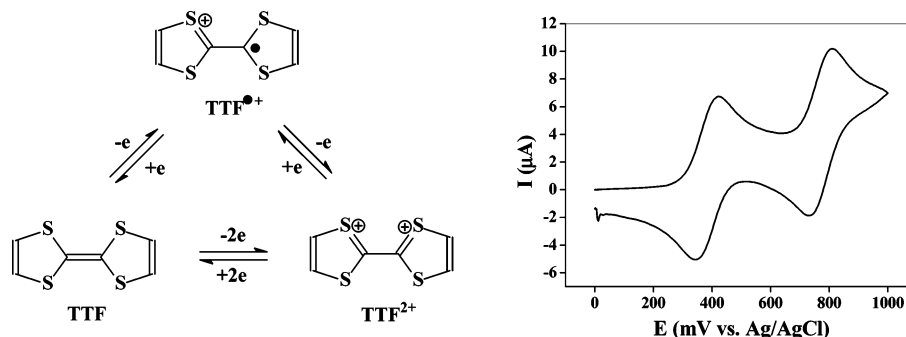
Electrochemical experiments were carried out in a standard three-electrode cell, containing Pt working and counter electrodes and Ag/AgCl reference electrode with *n*-Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) as supporting electrolyte. For recording the CV data, the scan rate was 50 mV/S, and the concentration of the solution was 5.0 × 10<sup>-4</sup> M in CH<sub>3</sub>CN. Electrochemical oxidation (with Pt plate as the working electrode) lasted for 5.0 min, and reduction was carried out for 15.0 min.

Absorption spectra were recorded immediately after electrochemical and/or chemical oxidations. After addition of NOPF<sub>6</sub>,

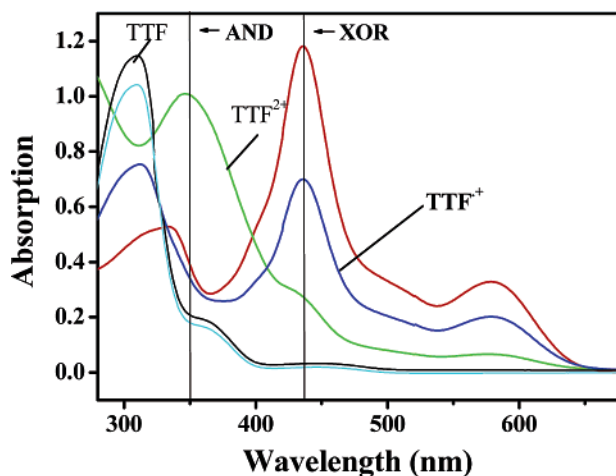
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**Figure 1.** Illustration of the three states of TTF before and after oxidation/reduction (left) and cyclic voltammogram of TTF (right).



**Figure 2.** Absorption spectra ( $1.0 \times 10^{-4}$  M in dry  $\text{CH}_3\text{CN}$ , 298 K) of TTF (black), after addition of 1.2 equiv of  $\text{NOPF}_6$  (red), after electrochemical oxidation at +0.65 V (vs Ag/AgCl) for 5.0 min (blue), after electrochemical oxidation at +0.65 V (vs Ag/AgCl) for 5.0 min, followed by addition of 1.2 equiv of  $\text{NOPF}_6$  (green), and after electrochemical reduction at -0.1 V (vs Ag/AgCl) for 15.0 min following the above operation (cyan).

a subtle nitrogen gas was bubbled through the solution for 1.0 min to remove the generated gas.

### 3. Results and Discussion

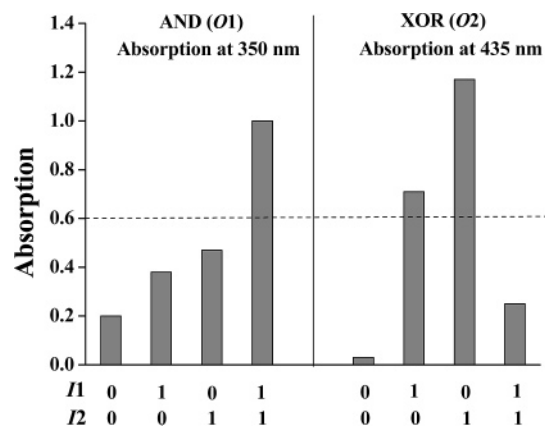
TTF exhibits two reversible one-electron oxidation processes, corresponding to  $\text{TTF}/\text{TTF}^{\bullet+}$  (at +0.42 V vs Ag/AgCl) and  $\text{TTF}^{\bullet+}/\text{TTF}^{2+}$  (at +0.81 V vs Ag/AgCl) redox reactions, respectively (Figure 1, right). Thus, the transformation of TTF into  $\text{TTF}^{\bullet+}$  and  $\text{TTF}^{2+}$  can be achieved by electrochemical oxidations. Alternatively, the reaction of TTF with stoichiometric amounts of suitable oxidants can also lead to the formation of  $\text{TTF}^{\bullet+}$  and  $\text{TTF}^{2+}$ . In experiments, TTF can be transformed into  $\text{TTF}^{\bullet+}$  by either application of an oxidation potential at +0.65 V (vs Ag/AgCl) or reaction with the stoichiometric amount of oxidants such as  $\text{NOPF}_6$ , and the formation of  $\text{TTF}^{2+}$  can be realized by sequential oxidation of TTF through the application of an oxidation potential and then reaction with the stoichiometric amount of oxidant.  $\text{NOPF}_6$  is chosen as the oxidant, because the gaseous product generated after its reaction with TTF can be easily removed from the solution.<sup>11</sup> Furthermore, both  $\text{TTF}^{\bullet+}$  and  $\text{TTF}^{2+}$  can be reduced to the neutral TTF after applying a reduction potential (at -0.10 V vs Ag/AgCl). This will prevent the accumulation of chemical wastes, leading to a resettable molecule-based half-adder as will be discussed below.<sup>12</sup>

TTF shows a strong absorption band at 305 nm and a small shoulder around 365 nm, as shown in Figure 2, where the

absorption spectrum of TTF ( $1.0 \times 10^{-4}$  M in dry  $\text{CH}_3\text{CN}$ ) and those after chemical/electrochemical oxidations were displayed. After oxidation, either by applying an oxidation potential at +0.65 V (vs Ag/AgCl) or by 1.2 equiv of  $\text{NOPF}_6$ , new absorption bands at about 435 and 585 nm appeared, and the absorption at 305 nm (due to neutral TTF) decreased, indicating the transformation of TTF into  $\text{TTF}^{\bullet+}$  according to previous studies.<sup>13</sup> The solution generated by electrochemical oxidation shows relatively weak absorptions compared to that produced by oxidation with  $\text{NOPF}_6$ . This is likely due to the incomplete oxidation of TTF molecules by electrochemical way under this condition.<sup>14</sup> However, this will not affect the interpretation of the absorption spectral changes of TTF upon electrochemical oxidation and reaction with  $\text{NOPF}_6$  by applying the Boolean logic convention as will be discussed below. Addition of 1.2 equiv of  $\text{NOPF}_6$  to the TTF solution that had been electrochemically oxidized for 5.0 min led to the emergence of the typical absorption of  $\text{TTF}^{2+}$  centered at 350 nm, and concomitantly, almost complete disappearance of the absorption bands attributed to  $\text{TTF}^{\bullet+}$ . This is consistent with the formation of  $\text{TTF}^{2+}$  from neutral TTF by first electrochemical oxidation followed by chemical oxidation with  $\text{NOPF}_6$ . The absorption spectrum of the solution was almost overlapped with that of the original TTF solution by the application of a reduction potential at -0.1 V (vs Ag/AgCl) to the oxidized solution for 15.0 min, indicating the reduction of  $\text{TTF}^{2+}$  to the neutral TTF (see Figure 2). Further oxidation resulted in almost the same absorption spectral variations. The interconversion among TTF,  $\text{TTF}^{\bullet+}$ , and  $\text{TTF}^{2+}$  upon electrochemical and chemical oxidations followed by electrochemical reduction can be repeated for at least four cycles.

The corresponding absorption spectra of TTF at different concentrations were also measured. As shown in Supporting Information Figure S1 ( $[\text{TTF}] = 5.0 \times 10^{-5}$  M) and Figure S3 ( $[\text{TTF}] = 2.5 \times 10^{-4}$  M), similar absorption spectral changes occurred, indicating the transformation of TTF into  $\text{TTF}^{\bullet+}$  and  $\text{TTF}^{2+}$  under similar chemical and electrochemical oxidations. As expected, the intensities for the absorption bands were dependent on the TTF concentrations.

The interconversion among TTF,  $\text{TTF}^{\bullet+}$ , and  $\text{TTF}^{2+}$  in response to electrochemical oxidation (at +0.65 V vs Ag/AgCl) and chemical oxidation with  $\text{NOPF}_6$  can be represented by binary logic (Figure 3). The application of an oxidation potential (at +0.65 V vs Ag/AgCl) and addition of 1.2 equiv of  $\text{NOPF}_6$  can be regarded as two input signals,  $I_1$  and  $I_2$ , respectively. The presence of TTF,  $\text{TTF}^{\bullet+}$ , and  $\text{TTF}^{2+}$  in the solution can be characterized by the corresponding typical absorption bands. The absorptions at 350 nm (due to  $\text{TTF}^{2+}$ ) and 435 nm (due to  $\text{TTF}^{\bullet+}$ ) can be considered as two outputs,  $O_1$  and  $O_2$ , respectively:  $O_1 = 0$  when the absorbance at 350 nm is low ( $<0.6$ );  $O_1 = 1$  when the absorbance at 350 nm is high ( $>0.6$ );



**Figure 3.** Illustration of the construction of the AND ( $O1$ ) and XOR ( $O2$ ) gates by detecting the absorption at 350 nm ( $O1$ ) and 435 nm ( $O2$ ) under the actions of two input signals:  $I1$ , electrochemical oxidation at +0.65 V (vs Ag/AgCl) for 5.0 min.;  $I2$ , addition of 1.2 equiv of NOPF<sub>6</sub>. The following convention is followed: If the absorbances at 350 nm ( $O1$ ) and 435 nm ( $O2$ ) are higher than 0.6 (represented by the dashed line), the output signals ( $O1$  or  $O2$ ) are 1; otherwise, they are 0 for both “AND” and “XOR” gates.

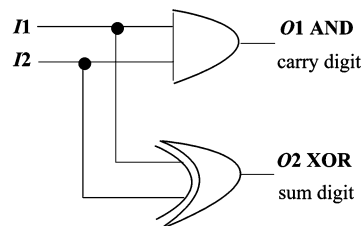
$O2 = 0$  when the absorbance at 435 nm is low ( $<0.6$ );  $O2 = 1$  when the absorbance at 435 nm is high ( $>0.6$ ). As mentioned above, only under the combined actions of electrochemical and chemical oxidations, namely,  $I1 = 1$  and  $I2 = 1$ , is the output signal  $O1$  equal to 1. Otherwise,  $O1$  is 0.<sup>15</sup> Therefore, the absorption change at 350 nm upon external inputs,  $I1$  and  $I2$ , can be interpreted as an “AND” logic gate.

On the other hand, electrochemical or chemical oxidations alone led to the generation of TTF<sup>•+</sup> showing strong absorption at 435 nm. Namely, if either  $I1 = 1$  and  $I2 = 0$  or  $I1 = 0$  and  $I2 = 1$ ,  $O2 = 1$  in the binary logic convention. The original TTF solution (without electrochemical and chemical oxidations, namely,  $I1 = 0$  and  $I2 = 0$ ) does not show absorption at 435 nm, and thus,  $O2 = 0$ . Interestingly, under the combined electrochemical oxidation at +0.65 V (vs Ag/AgCl) and chemical oxidation with NOPF<sub>6</sub>, TTF was converted to TTF<sup>2+</sup>, which shows weak absorption at 435 nm ( $O2 = 0$ ). Consequently, the manner of the absorption changes at 435 nm in response to electrochemical oxidation ( $I1$ ) and chemical oxidation ( $I2$ ) mimics the performance of an “XOR” gate.

As discussed above, similar absorption spectral changes were also observed for TTF solutions of different concentrations (see Supporting Information Figures S1 and S3). Therefore, the variation of the absorbances at 350 nm ( $O1$ ) and 435 nm ( $O2$ ) upon electrochemical oxidation ( $I1$ ) at +0.65 V (vs Ag/AgCl) and chemical oxidation ( $I2$ ) with NOPF<sub>6</sub> will also mimic the performance of “AND” and “XOR” gates, respectively (see Supporting Information Figures S2 and S4). However, the threshold values for absorbances at 350 nm ( $O1$ ) and 435 nm ( $O2$ ) were dependent on the TTF concentration; for instance, they were defined as 0.4 and 1.5 for TTF solutions with concentrations of  $5.0 \times 10^{-5}$  M and  $2.5 \times 10^{-4}$  M, respectively (see Figures S2 and S4).

The “AND” and “XOR” gates mentioned above were based on the entity of a single molecule of TTF under the same inputs (electrochemical oxidation,  $I1$ ; chemical oxidation,  $I2$ ), and thus, the “AND” and “XOR” gates can be “operated” in parallel. Therefore, the absorption spectral changes observed for the solution of TTF, due to the interconversion among TTF, TTF<sup>•+</sup>, and TTF<sup>2+</sup> upon electrochemical and chemical oxidations (see above), mimic the function of a half-adder represented by conventional electronic symbols in Figure 4. As illustrated in

$I1$ (+0.65 V)	$I2$ (NOPF <sub>6</sub> )	$O1$ (AND) (carry digit)	$O2$ (XOR) (sum digit)	Half-adder (added number)
0	0	0 (low, $<0.6$ )	0 (low, $<0.6$ )	00
1	0	0 (low, $<0.6$ )	1 (high, $>0.6$ )	01
0	1	0 (low, $<0.6$ )	1 (high, $>0.6$ )	01
1	1	1 (high, $>0.6$ )	0 (low, $<0.6$ )	10



**Figure 4.** Truth table (top) and schematic representation (bottom) of the 2-input logic half-adder circuit.

the truth table, the first binary number is coded for by the presence (1) or absence (0) of electrochemical oxidation input signals ( $I1$ ), and the second binary number is coded for by the presence (1) or absence (0) of chemical oxidation ( $I2$ ). The sum digit is coded for by the absorption variation at 435 nm ( $O2$ ) when high (1) or low (0). The carry digit is coded for by the absorbance at 350 nm ( $O1$ ) when high (1) or low (0). The table demonstrates the binary additions:  $0 + 0 = 00$ ,  $0 + 1 = 01$ ,  $1 + 0 = 01$ , and  $1 + 1 = 10$ .

It is anticipated that the molecule-based half-adder can also be established with TTF derivatives in a similar manner. According to previous studies,<sup>6,7e,11</sup> the interconversion among TTF derivatives and the corresponding radical cations and dications can be achieved upon electrochemical and chemical oxidations in the same manner as for TTF. Although the radical cations and dications of TTF derivatives show different absorption spectra from those of TTF, similar absorption spectral variations should be observed in response to electrochemical and chemical oxidations. Thus, the molecule-based half-adder can be also established with TTF derivatives.

Finally, it should be noted that this molecule-based half-adder with TTF works in solution, and the input signals are more complicated because of the use of two types of stimulation (chemical and electrochemical oxidations).

#### 4. Conclusions

The corresponding absorption spectral changes in association with the interconversion among TTF, TTF<sup>•+</sup>, and TTF<sup>2+</sup> upon electrochemical and chemical oxidations (Figure 1) mimic the function of a half-adder. Because TTF derivatives show similar absorption spectral variation under similar conditions, the molecule-based half-adder can also be established with TTF derivatives. In comparison with the reported examples of molecular half-adders, this molecule-based half-adder has at least the following distinct features: (1) It is based on the electroactive TTF molecule, which has been extensively studied and is easily derivable. Thus, it is possible to link external stimuli-responsive groups to TTF and then integrate more complex logic functions on a single molecule through rational molecular design. (2) It displays reset capability because both the radical cations and dications of TTF and its derivatives can be reduced to neutral TTF by applying a suitable reduction potential to the solution.

For the construction of complex molecular logic gates, finding rather simple, easily available, and derivable molecules is an important step for the future application of this topic. The present



studies not only provide a new example of molecule-based half-adder but also add new merits to the already enriched chemistry of TTF.

**Supporting Information Available:** Absorption spectra of TTF solutions in CH<sub>3</sub>CN with concentrations of  $5.0 \times 10^{-5}$  M and  $2.5 \times 10^{-4}$  M before and after chemical and/or electrochemical oxidation, illustration of the construction of the AND (O1) and XOR (O2) gates based on the absorption spectral changes of TTF solutions with concentrations of  $5.0 \times 10^{-5}$  M and  $2.5 \times 10^{-4}$  M. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) After performing one cycle for the half-adder, 1 equiv of Ag<sup>+</sup> (from Ag electrode) and PF<sub>6</sub><sup>−</sup> (from NOPF<sub>6</sub>) remained in the solution. They could function as the supporting electrolyte and should have little effect on the following cycles, since high concentration (0.1 M) of *n*-Bu<sub>4</sub>NPF<sub>6</sub> was employed as the initial supporting electrolyte in the solution. In fact, the realization of the reset capability of our half-adder is at the price of the gentle wasting of the Ag electrode.
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- (14) This is probably because the electrochemical oxidation was carried out for just 5.0 min, and longer reaction time may be needed for the complete oxidation of TTF molecules in the solution under this condition.
- (15) It should be pointed out that the sequence of imposing input signals is first *I*1 and then *I*2 and cannot be converted for the realization of the “AND” gate.