Molecular Computers

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Data Processing on a Unimolecular Platform**

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In living systems, information is processed, transported, stored, and retrieved by molecules or ionic substrates[1] at the molecular and supramolecular levels. Information processing on the molecular level can potentially be used to develop molecular computers that are much smaller and much more powerful than the present computers.[2] These molecule-based "bottom-up" strategies for information processing[2,3] have inspired scientists to design and construct molecular systems[4–10] that mimic the logic functions performed by solid-state semiconductor circuits. Up until now common Boolean functions have been implemented with molecular systems.[4–10] However, to develop information processing and to increase computing complexity on the molecular level, it is necessary to combine the common molecular logic elements and to create complex circuits on a unimolecular platform.[4–19] This can be achieved by the rational design of new molecular systems[11,17] or by applying new concepts to established molecules.[16,18]

An important function in information technology is signal encoding/decoding. In computers, encoding is the process of converting a sequence of characters into a specialized format for efficient transmission or storage. Decoding is the opposite process—the conversion of an encoded format back into the original sequence of characters. Encoding and decoding are used in data communication, networking, and storage, functions that are particularly applicable to wireless communication systems. The importance of encoding/decoding has boosted research on chemical systems that mimic multiplexing/demultiplexing functions,[15,16] which can also be used in encoding/decoding operations. Recent reports on the molecular versions of the 4-to-2 encoder and the 2-to-4 decoder,[17,18] which have potential applications in sensing and labeling as well as data manipulation, have taken molecular logic one step further towards data processing on the molecular level. In data processing, a 4-to-2 encoder converts four input bits of data to two output bits. A 2-to-4 decoder converts two coded inputs to four readable outputs. Truth tables for a 4-to-2 encoder and 2-to-4 decoder are shown in Figure 1.

a)

In_0	In_1	In_2	In_3	Out_0	Out_1
1	0	0	0	0	0
0	1	0	0	0	1
0	0	1	0	1	0
0	0	0	1	1	1

b)

In_0	In_1	Out_0	Out_1	Out_2	Out_3
0	0	1	0	0	0
1	0	0	1	0	0
0	1	0	0	1	0
1	1	0	0	0	1

Figure 1. a) Truth table for a 4-to-2 encoder. b) Truth table for a 2-to-4 decoder.

One can imagine, in data transmission and information processing, the importance of combining the functions of the encoder and decoder on a unimolecular functional platform. Unimolecular logic circuits have been constructed in a straightforward fashion by rational structural design as an alternative to the time-consuming and difficult physical connection of several simple gates.[2,8] In addition, molecules can also be easily immobilized on electrodes and incorporated into a circuit.

In 2008, Gust and co-workers[17] demonstrated that the molecular triad **1** (Figure 2), which comprises a photochromic dithienylethene (DTE) unit covalently linked to two fulgimide (FG) photochromic moieties, can function as a molecular 4-to-2 encoder and 2-to-4 decoder. Key to the design is the fact that the two types of photochromes in triad **1** can be isomerized independently and reversibly by irradiation with

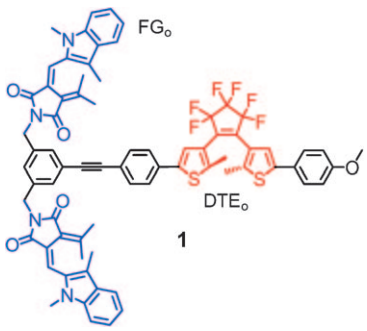

Figure 2. The chemical structure of triad **1** with its all photochromes in the open-ring form. The fulgimide (FG) and dithienylethene (DTE) moieties are in blue and red, respectively.

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light of different wavelengths between their closed-ring and open-ring forms, which exhibit absorption maxima at different wavelengths for each state.

Irradiation of a solution of triad **1** in 2-methyltetrahydrofuran with green light ($\lambda = 460$–590 nm) generates the triad with all three of its photochromes in their open forms, namely, FG_o-DTE_o, with absorption maxima at 286, 331, 387 nm. Irradiation of the solution at $\lambda = 302$ nm selectively isomerizes the DTE moiety and yields a solution enriched predominantly in FG_o-DTE_c (open-ring form of FG and the closed-ring form of DTE), which exhibits absorption maxima at 362 and 604 nm. Irradiation of FG_o-DTE_o at $\lambda = 397$ nm generates FG_c-DTE_o; the mixture has absorption maxima at 270, 324, and 511 nm and emission at 630 nm, which is attributed to the closed form of the FG moiety. Irradiation of FG_o-DTE_o with both $\lambda = 302$ nm and $\lambda = 397$ nm (or alternatively single-wavelength irradiation at $\lambda = 366$ nm) generates predominantly the FG_c-DTE_c species, in which both the FG and DTE moieties are in their closed-ring forms. FG_c-DTE_c has absorption maxima at 266, 357, 535, and 598 nm and no emission at 630 nm, as a result of the intramolecular fluorescence-quenching processes between the closed-ring FG moiety and the closed-ring DTE moiety.

The 4-to-2 encoder function performed by triad **1** has four inputs and two outputs. The four photonic inputs, In_0 to In_3, correspond to irradiation at the following wavelengths: 460–590 nm, 397 nm, 302 nm, and 366 nm, respectively. The two photonic outputs, Out_0 and Out_1, are absorptions at 475 nm and 625 nm, respectively. The 2-to-4 decoder employs two photonic inputs, In_0 and In_1, which correspond to irradiation at 397 nm and 302 nm, respectively, and four photonic outputs, Out_0 to Out_3, corresponding to transmittance at 535 nm, emission at 624 nm, absorption at 393 nm, and absorption at 535 nm, respectively. By a suitable choice of experimental conditions, this molecule follows the truth tables in Figure 1 characteristic of a molecular 4-to-2 encoder and 2-to-4 decoder.

The unique feature of this system is that all inputs and outputs are photonic; this means that no material access to the logic element is necessary, and monolithic three-dimensional arrays of molecular devices based on this system are possible.[17] As we know from related research, when photochromic compounds exhibiting memory effects are employed in complicated logic systems, these memory effects must be removed to reset the system.[9] For this reason application of a photochromic system as the molecular logic element still remains a challenge because the efficiency of the logic functions mainly depends on the efficiency of photoisomerization or other photo-induced processes.[9]

More recently, Balzani and co-workers[18] showed that a very simple and well-known metal complex, $[Ru(bpy)_3]^{2+}$ (bpy = bipyridine; structure in Figure 3), can perform very important and complex functions as both a molecular 4-to-2 encoder and a 2-to-4 decoder by the appropriate combination of electronic and photonic inputs and outputs. This design depends on the outstanding spectroscopic properties of $[Ru(bpy)_3]^{2+}$ generated by a combination of chemical, photochemical, and electronic stimuli.

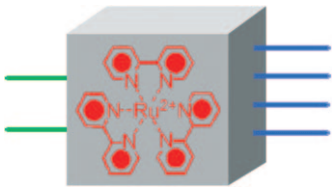

Figure 3. The chemical structure of $[Ru(bpy)_3]^{2+}$ and a schematic representation of a molecular encoder and decoder.

The 4-to-2 encoder function performed by a solution of $[Ru(bpy)_3]^{2+}$ in acetonitrile has four inputs and two outputs. The three electronic and a photonic inputs, In_0 to In_3, involve oxidation at $+1.4$ V, excitation at $\lambda = 450$ nm, reduction at -1.4 V, oxidation and subsequent reduction at alternating potentials of $+1.4$ V and -1.4 V, respectively. The two outputs, Out_0 and Out_1, are absorption at $\lambda = 530$ nm and emission at $\lambda = 620$ nm, respectively. One-electron oxidation ($In_0 = 1$) of $[Ru(bpy)_3]^{2+}$ forms $[Ru(bpy)_3]^{3+}$, which displays neither absorption at $\lambda = 530$ nm ($Out_0 = 0$) nor emission at $\lambda = 620$ nm ($Out_1 = 0$). Excitation of $[Ru(bpy)_3]^{2+}$ at $\lambda = 450$ nm ($In_1 = 1$) forms a spin-allowed excited state, $^{**}[Ru(bpy)_3]^{2+}$, which undergoes fast and efficient radiationless deactivation to form the spin-forbidden, long-lived $^{*}[Ru(bpy)_3]^{2+}$ excited state, which is luminescent at $\lambda = 620$ nm ($Out_1 = 1$). One-electron reduction ($In_2 = 1$) of $[Ru(bpy)_3]^{2+}$ generates reduced $[Ru(bpy)_3]^{+}$, which has an absorption at $\lambda = 530$ nm ($Out_0 = 1$). The reaction between the oxidized $[Ru(bpy)_3]^{3+}$ and reduced $[Ru(bpy)_3]^{+}$ can result in the formation of a ground-state $[Ru(bpy)_3]^{2+}$ species and an excited-state $^{*}[Ru(bpy)_3]^{2+}$ species. Through the choice of appropriate experimental conditions, the four-component mixture generated by oxidation and subsequent reduction of $[Ru(bpy)_3]^{2+}$ by alternating potentials $+1.4$ V and -1.4 V ($In_3 = 1$), has an absorption at $\lambda = 530$ nm higher than the established threshold ($Out_0 = 1$) and emission at $\lambda = 620$ nm ($Out_1 = 1$). As a result, it yields a truth table like that in Figure 1 a characteristic of a molecular 4-to-2 encoder.

The 2-to-4 decoder employs two electronic inputs, In_0 and In_1, corresponding to oxidation at $+1.4$ V and reduction at -1.4 V, respectively. The four outputs are absorptions at $\lambda = 450$ nm (Out_0), $\lambda = 310$ nm (Out_1), and $\lambda = 530$ nm (Out_2), and emission at $\lambda = 620$ nm (Out_3). The initial state, before application of any input ($In_0 = 0$, $In_1 = 0$), is $[Ru(bpy)_3]^{2+}$, which exhibits an absorption band at $\lambda = 450$ nm ($Out_0 = 1$). When $In_0 = 1$ and $In_1 = 0$, the system is in the oxidized $[Ru(bpy)_3]^{3+}$ state, which has an absorption band at $\lambda = 310$ nm higher than established threshold ($Out_1 = 1$). When $In_0 = 0$ and $In_1 = 1$, the system is in the reduced $[Ru(bpy)_3]^{+}$ state, which has an absorption band at $\lambda = 530$ nm higher than the threshold ($Out_2 = 1$). When $In_0 = 1$ and $In_1 = 1$, the system is in the electrostationary state, which has four species as mentioned previously. By a suitable choice of experimental conditions, the system has an emission at $\lambda = 620$ nm ($Out_3 = 1$), and the absorptions at $\lambda = 450$ nm, 310 nm, and 530 nm of the electrostationary state can be controlled below the thresholds of the three outputs. The two electronic inputs, In_0 and In_1, are converted into four photonic outputs, Out_0 to Out_3, characteristic of the function of a 2-to-4 decoder.

When all the processes are combined, $[Ru(bpy)_3]^{2+}$ can function as both a 4-to-2 encoder and a 2-to-4 decoder through the combination of electronic and photonic inputs and outputs. The system is reset to the original state prior to each input operation. Because both the oxidation and reduction processes are reversible and highly efficient, the operation of the molecular 4-to-2 encoder and 2-to-4 decoder has very good reversibility and efficiency. It should be emphasized that the elegance of this approach lies in its chemical simplicity and creativity as well as the unambiguous interpretation of the logic behavior.

It should be pointed out that no chemical reagents were involved in the operation of the molecular logic devices mentioned above;[17,18] thus they are true unimolecular logic elements. This research gives very important examples in the framework of decision-making molecules and has great potential in future applications for more complex molecular computing on a unimolecular functional platform. Although the construction of a molecular-based computer is currently unrealistic and is extremely ambitious even in the long term, simple and dedicated computing tasks may in fact be performed by molecular systems. Some specific problems that traditional electronic circuits cannot address include, for example, labeling and tracking nano- and micrometric objects[20] and monitoring and controlling biological processes.[21] The potential of molecular logic for other applications may be realized in a molecular keypad lock system.[13,14] Potential applications of molecular encoders and decoders for labeling and sensing nano- and microsacle objects as well as data processing can also be envisioned.

Although many barriers must be overcome in the field of molecular logic before real molecular computing and computational devices based on chemical systems can compete with traditional semiconductor-based processors, the concept of "molecular computers" and research in this field are very important. In principle there are two different approaches for the construction of "molecular computers".[2] The first is to use molecules as nanoscale components to create miniaturized electric circuits, which mainly rely on the circuit architecture. When this succeeds, ultrahigh-density molecular circuitry is possible which would have tremendous impact on information processing and computer science.[22] The second approach, inspired by information processing in living organisms, is based on the inherent "smart" behavior of designed molecular systems that function in solution by the combination of chemical, photochemical and electronic input and output signals; this is the strategy behind the research described in this Highlight. At this stage, it is difficult to say which approach is the most promising. The second strategy is more along the line of chemists, who have demonstrated that, at present, the integration of complex logic functions can be realized in a unimolecular functional platform. An important message indicated by all the excellent work in this field is that classical chemistry can stimulate ingenuity among researchers engaged in the "bottom-up" approach to information science and nanotechnology.[2,18]

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