Molecular Logic

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# Old Molecules, New Concepts: $[Ru(bpy)_3]^{2+}$ as a Molecular Encoder–Decoder**

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Although the most creative act in chemistry is still "the design and creation of new molecules",[1] creativity in chemistry has, in the last few years, often arisen from novel conceptual interpretations of well-known chemical reactions of well-established molecules.[2–5] In particular, the rapid development of signal processing at the molecular level[6] has projected chemistry toward the frontiers of information science and nanotechnology.

The first proposal to execute logic operations at the molecular level was made in 1988,[7] but the field developed only five years later when the analogy between molecular switches and logic gates was experimentally demonstrated.[8] Since then, processing photonic, electronic, and chemionic signals by molecular or supramolecular substrates in solution has been proposed[2–4,6] as an alternative route to solid-state molecular electronics towards the design and construction of the much-sought chemical computer.[9] The field has recently developed from simple switches to produce more complex molecular systems that are capable of performing a variety of classical logic functions,[6] including extensions to switches on surfaces,[10] and examples of half-adder,[11] full-adder,[12] keypad lock,[13] multiplexer,[14] multiplexer–demultiplexer,[15] and, very recently, a multicomponent decoder[16] and an encoder-decoder triad.[17] Herein, we show that a very simple and well-known metal complex, $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine), can perform as both an encoder and a decoder of a combination of electronic and photonic inputs and outputs, thereby increasing the long list of outstanding properties of this complex.[18]

The chemical, photochemical, and electrochemical behavior of $[Ru(bpy)_3]^{2+}$ and of hundreds of its derivatives has been extensively investigated in the past 30 years.[18,19] The ground-state complex (Figure 1) can be excited by visible light with formation of a spin-allowed excited state, $^{**}[Ru(bpy)_3]^{2+}$, which undergoes fast and efficient radiationless deactivation to form the spin-forbidden, long-lived, and luminescent $^{*}[Ru(bpy)_3]^{2+}$ excited state. $[Ru(bpy)_3]^{2+}$ can also undergo reversible one-electron oxidation and reduction processes (e.g., in acetonitrile solution), which become energetically much more favorable starting from $^{*}[Ru(bpy)_3]^{2+}$ because of the extra energy available to the excited state (photoinduced electron transfer, Figure 1).

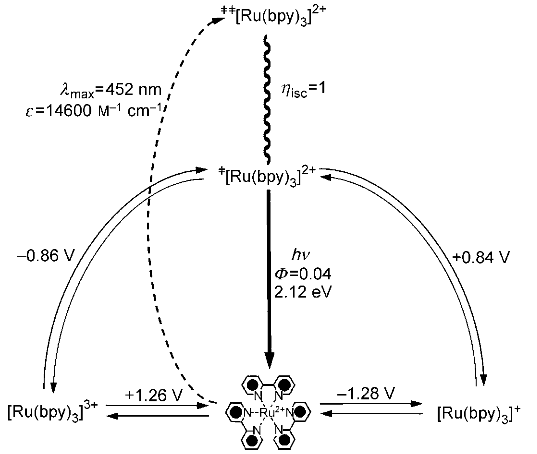

**Figure 1.** One-electron excitation and redox processes for $[Ru(bpy)_3]^{2+}$. See text for details.

Since the pioneering work by Tokel and Bard,[20] it is also well known [Figure 2, Eqs. (1)–(4)] that the comproportiona-

$$[Ru(bpy)_3]^{2+} + e^- \rightarrow [Ru(bpy)_3]^{+} \qquad (1)$$

$$[Ru(bpy)_3]^{2+} - e^- \rightarrow [Ru(bpy)_3]^{3+} \qquad (2)$$

$$[Ru(bpy)_3]^{3+} + [Ru(bpy)_3]^{+} \rightarrow [Ru(bpy)_3]^{2+} + {}^{*}[Ru(bpy)_3]^{2+} \qquad (3)$$

$$^{*}[Ru(bpy)_3]^{2+} \rightarrow [Ru(bpy)_3]^{2+} + h\nu \qquad (4)$$

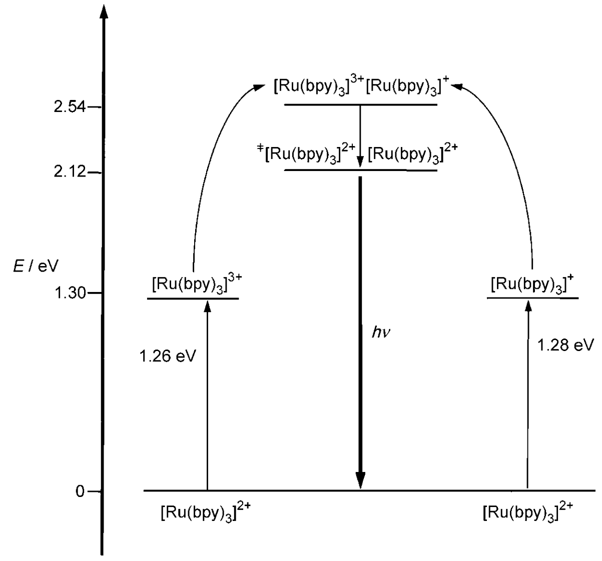

**Figure 2.** Energy diagram showing that the reaction between the oxidized $[Ru(bpy)_3]^{3+}$ and reduced $[Ru(bpy)_3]^{+}$ species is sufficiently exergonic to generate luminescence.

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tion reaction between the oxidized $[Ru(bpy)_3]^{3+}$ and the reduced $[Ru(bpy)_3]^{+}$ species is strongly exergonic and can in fact generate a ground $[Ru(bpy)_3]^{2+}$ and an excited $^*[Ru(bpy)_3]^{2+}$ species, followed by radiative deactivation of the latter (luminescence induced by electron transfer). These results show that $[Ru(bpy)_3]^{2+}$ is able to process, and even interchange, photonic and electronic inputs (Figure 1 and Figure 2).

The absorption spectra of $[Ru(bpy)_3]^{3+}$,[21] $[Ru(bpy)_3]^{2+}$,[18] and $[Ru(bpy)_3]^{+}$ [22] species are displayed in Figure 3 a, 3 b, and 3 c, respectively. These spectra are substantially different and it is not difficult to choose appropriate absorbance thresholds related to the three interconverting species at three different wavelengths (310, 450, and 530 nm; Figure 3). Furthermore, $[Ru(bpy)_3]^{2+}$ exhibits a luminescence band (Figure 3 b), whereas $[Ru(bpy)_3]^{3+}$, and $[Ru(bpy)_3]^{+}$ are not luminescent. By elaborating these spectroscopic properties and electrochemical processes, we have found that a simple molecule such as $[Ru(bpy)_3]^{2+}$ can indeed perform as both an encoder and a decoder.

The function performed by a digital encoder is that of converting data into a code, an operation that is useful to compress information that have to be transmitted or stored. A 4-to-2 encoder compresses 4 input bits into 2 output bits (Figure 4).

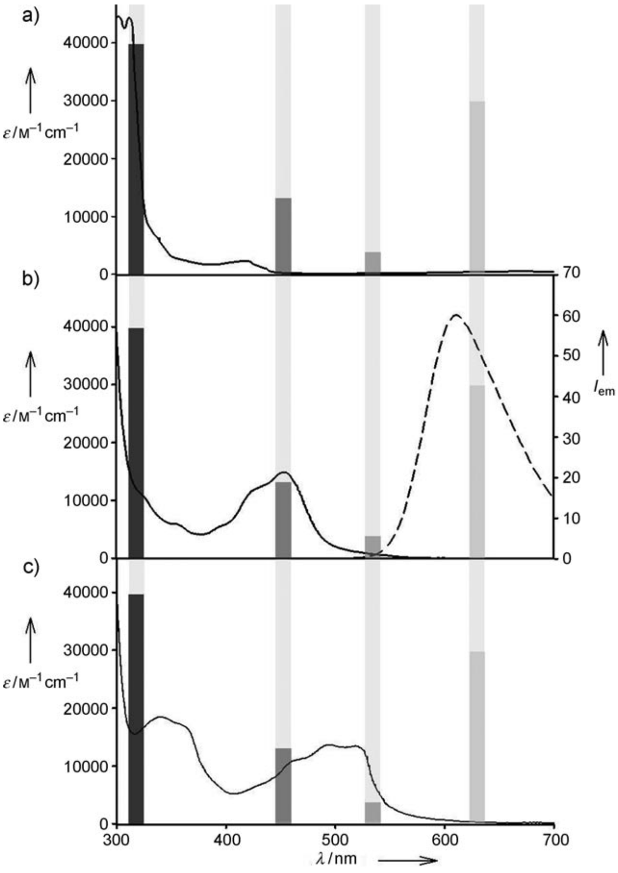

**Figure 3.** Absorption and emission spectra of $[Ru(bpy)_3]^{2+}$ (b), and its oxidized $[Ru(bpy)_3]^{3+}$ (a) and reduced $[Ru(bpy)_3]^{+}$ (c) species. The shaded rectangles indicate the chosen value of the thresholds for encoding/decoding operations.

| $In_0$ | $In_1$ | $In_2$ | $In_3$ | $Out_0$ | $Out_1$ |
|---|---|---|---|---|---|
| +1.4 V | $\lambda_{ex}$ = 450 nm | −1.4 V | +1.4/−1.4 V | Abs 530 nm | Em 620 nm |
| 1 | 0 | 0 | 0 | 0 | 0 |
| 0 | 1 | 0 | 0 | 0 | 1 |
| 0 | 0 | 1 | 0 | 1 | 0 |
| 0 | 0 | 0 | 1 | 1 | 1 |

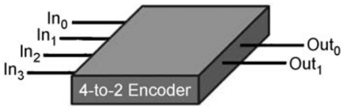

**Figure 4.** Schematic representation and truth table for a 4-to-2 encoder based on $[Ru(bpy)_3]^{2+}$.

The encoder function played by $[Ru(bpy)_3]^{2+}$ is based on the specific electronic and photonic inputs and outputs (Figure 4). As is common in electrochemical and spectroscopic experiments, studies were carried out on a solution of $[Ru(bpy)_3](PF_6)_2$ in acetonitrile. The initial state is $[Ru(bpy)_3]^{2+}$; the system is reset to this state prior to each input operation. Three electronic and a photonic inputs, $In_0$ to $In_3$, are compressed into two photonic outputs, $Out_0$ and $Out_1$, which are absorption at 530 nm and emission at 620 nm, respectively.

$In_0$, which involves oxidation at +1.4 V,[23] converts $[Ru(bpy)_3]^{2+}$ into $[Ru(bpy)_3]^{3+}$ (Figure 1), which exhibits neither absorption at 530 nm ($Out_2 = 0$), nor emission at 620 nm ($Out_1 = 0$; Figure 3 a). Reset of the system is obtained by reduction at 0.0 V. $In_1$, which involves excitation of $[Ru(bpy)_3]^{2+}$ with 450 nm light, causes no change in absorbance ($Out_0 = 0$), and generates emission at 620 nm ($Out_1 = 1$; Figure 3 b). After this input, there is no need to reset the system. $In_2$, which involves reduction at −1.4 V, converts $[Ru(bpy)_3]^{2+}$ into $[Ru(bpy)_3]^{+}$, which exhibits absorption at 530 nm (Figure 3 c; $Out_0 = 1$) and no emission at 620 nm ($Out_1 = 0$). Oxidation at 0.0 V resets the system. $In_3$, which involves subsequent oxidation and reduction of $[Ru(bpy)_3]^{2+}$ by a square wave alternate potential +1.4 and −1.4 V,[20,24] causes the formation of an electrostationary state that contains $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_3]^{3+}$, $[Ru(bpy)_3]^{+}$, and $^*[Ru(bpy)_3]^{2+}$ [Eqs. (1)–(4), Figure 2]. By a suitable choice of experimental conditions, an absorption at 530 nm higher than the established threshold ($Out_0 = 1$) and emission at 620 nm ($Out_1 = 1$) can be obtained.

$[Ru(bpy)_3]^{2+}$ is also able to act as a 2-to-4 decoder (Figure 5), which converts two coded inputs into four readable outputs. As before, the inputs used are reduction and oxidation [Eqs. (1) and (2)], and the outputs are absorption at 450 nm ($Out_0$), 310 nm ($Out_1$), 530 nm ($Out_2$), with thresholds

| $In_0$ | $In_1$ | $Out_0$ | $Out_1$ | $Out_2$ | $Out_3$ |
|---|---|---|---|---|---|
| +1.4 V | −1.4 V | Abs 450 nm | Abs 310 nm | Abs 530 nm | Em 620 nm |
| 0 | 0 | 1 | 0 | 0 | 0 |
| 1 | 0 | 0 | 1 | 0 | 0 |
| 0 | 1 | 0 | 0 | 1 | 0 |
| 1 | 1 | 0 | 0 | 0 | 1 |

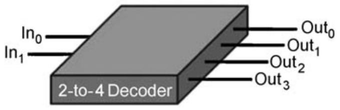

**Figure 5.** Schematic representation and truth table for a 2-to-4 decoder based on $[Ru(bpy)_3]^{2+}$.

indicated in Figure 3 and related to the three $[Ru(bpy)_3]^{n+}$ forms (Figure 3), and emission at 620 nm of $[Ru(bpy)_3]^{2+}$ ($Out_3$). Reset of the system is obtained at 0.0 V.

When neither $In_0$ nor $In_1$ are applied, the system exhibits the absorption band of $[Ru(bpy)_3]^{2+}$ with a maximum at 450 nm. Application of $In_0$ alone (oxidation at +1.4 V) converts $[Ru(bpy)_3]^{2+}$ into $[Ru(bpy)_3]^{3+}$ (Figure 3a), which exhibits an absorption higher than the threshold at 310 nm, but no absorption at 450 and 530 nm, and no emission at 620 nm. $In_1$ (reduction at −1.4 V) converts $[Ru(bpy)_3]^{2+}$ into $[Ru(bpy)_3]^{+}$ (Figure 3c), which exhibits an absorption higher than the threshold at 530 nm, but lower than the threshold at 310 and 450 nm, and no emission at 620 nm. Concomitant oxidation at +1.4 V and reduction at −1.4 V of $[Ru(bpy)_3]^{2+}$ by using a bipotentiostat causes the formation of an electrostationary state that contains $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_3]^{3+}$, $[Ru(bpy)_3]^{+}$, and $^*[Ru(bpy)_3]^{2+}$ [Eqs. (1)–(4)]. By a suitable choice of the experimental conditions, the concentration of the three ground-state species can be controlled. When the three species have approximately equal concentrations, absorbance values below the threshold are obtained at 450, 310, and 530 nm, together with an emission at 620 nm, which is generated by the excited state continuously produced by the reactions in Equations (1)–(4). The function of a decoder is indeed important; 2-to-4 decoders are used in the macroscopic world for a variety of applications, as demonstrated by the fact that a commercial 2-to-4 decoder with the same logic function of the molecular analogue described above (Figure 6) is available from Texas Instruments.[25]

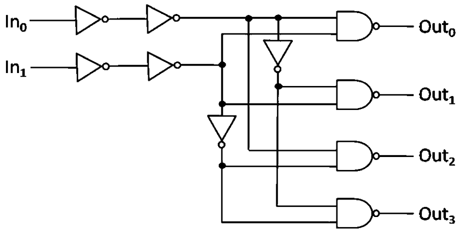

***Figure 6.*** Combinational logic scheme of the commercially available 2-to-4 decoder from Texas Instruments.[25]

In conclusion, by using electronic and photonic inputs, we have shown that a molecule as simple as $[Ru(bpy)_3]^{2+}$ can act both as a 4-to-2 encoder and 2-to-4 decoder. The system can be reconfigured in situ without addition of chemical reagents. Leaving aside the vision of a molecular computer,[9] systems such as that described herein may find applications for more conventional chemical purposes, such as sensing and labeling.[26]

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**Keywords:** electrochemistry · luminescence · molecular devices · photochemistry · ruthenium

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