Unimolecular binary half-adders with orthogonal chemical inputs†

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Unimolecular half-adders based upon an arylvinyl-bipyridyl fluorophore platform were demonstrated where all the chemical input combinations were fully processed by half-adder molecules to generate the arithmetic results of the entire truth table.

Binary logic gates are basic operational components of a central processing unit (CPU) in a computer.[1] A molecular logic gate is a molecule, or a molecular system, that performs a binary logic function upon externally administered input signals.[2–5] The development of molecular logic gates or logic functions was propelled by the realization that the growth of information processing capacity per unit area of conventional, silicon-based CPUs will slow down soon and eventually reach a plateau through incremental optimization according to Moore's Law.[6] Further miniaturization of computing devices requires revolutionary approaches. Inspired by biological information transduction and processing mechanisms, chemists have begun to develop molecules and molecular systems that perform logic functions in response to various types of input signals.[7,8]

The study of molecular logic functions began in the early 1990s.[9] In the past 15 years, numerous molecular logic gates have been created. These examples utilize a plethora of input and output signals of different types including chemical, optical, electrical, and magnetic,[10] which mirrors the diversity of stimuli that natural logic systems such as neural systems respond to. Advanced informational processes such as a few arithmetic functions have also been accomplished using elaborately constructed logic circuits.[5,11]

A molecular binary half-adder is a prototypical challenge in the pursuit of wiring individual molecular logic gates into functional circuits that are able to perform advanced functions. The CARRY and SUM digits resulted from a binary half-adder calculation can be represented by an AND and an XOR gates, respectively. The logic truth tables, showing the results of four combinations of binary inputs (0 and 1) of both gates and a half-adder, are shown in Fig. 1. Many molecular half-adders have been developed over the last seven years.[12–21]

While these accomplished systems are commendable for their ingenious designs and clever interpretations of physical signals, several issues need to be addressed to greatly improve the performance and practicality of molecular half-adders. Notably, chemically interacting input signals (*e.g.* acid and base) have often been used so that when both inputs are present, they annihilate each other rather than being processed by the molecular logic function. Other issues include the applications of different molecules as AND and XOR gates separately to achieve the half-adder function and the heavy reliance on output signal interpretation (*e.g.* judicious choice between positive and negative logic conventions, employing different types of output signals to separately configure AND and XOR gates) and threshold setting. Our objective is to develop unimolecular half-adders with non-interacting (*i.e.* orthogonal) chemical inputs with straightforward interpretation of output signals following positive logic convention.

Herein we describe unimolecular half-adders (**1a** and **1b**, Scheme 1) that accept chemically orthogonal inputs based upon the structures of heteroditopic fluorescent ligands (fluoroionophores) for transition metal ions. In our system, two different metal ions of a given concentration are considered as input signals; the fluorescence intensities at two different wavelengths (channels) are designated as output signals. As shown in Fig. 2, the interactions between different combinations of chemical inputs and an elaborately designed ditopic fluorescent ligand give rise to different coordination states of the ligand, which lead to corresponding photophysical processes upon excitation. The coordination-dependent fluorescence intensity at different wavelengths are interpreted as output signals of a binary half-adder.

We previously prepared **1a** as a prototype fluorescent probe for quantification of zinc ion (Zn^{2+}) over a large concentration range.[22] In acetonitrile (MeCN), the affinity of di(2-picolyl)amino group in **1a** to Zn^{2+} is larger than that of 2,2′-bipyridyl to Zn^{2+}.[22] Three coordination states of **1a** (non-, mono- and di-coordinated) at different Zn^{2+} concentrations give rise to three different fluorescence states (fluorescence off, emission at one wavelength, and emission at another wavelength). The promiscuous coordination chemistry of the di(2-picolyl)amino moiety in **1a** prompted us to examine the coordination-driven photophysical processes of **1a** with other metal ions. It was found that the fluorescence

A

I1	I2	Q
0	0	0
0	1	0
1	0	0
1	1	1

AND

B

I1	I2	Q
0	0	0
0	1	1
1	0	1
1	1	0

XOR

C

I1		I2		CARRY	SUM
0	+	0	=	0	0
0	+	1	=	0	1
1	+	0	=	0	1
1	+	1	=	1	0
				AND	XOR

Fig. 1 Truth tables of (A) AND, (B) XOR logic gates, and (C) a binary half-adder. I1, I2 – Inputs; Q – Output.

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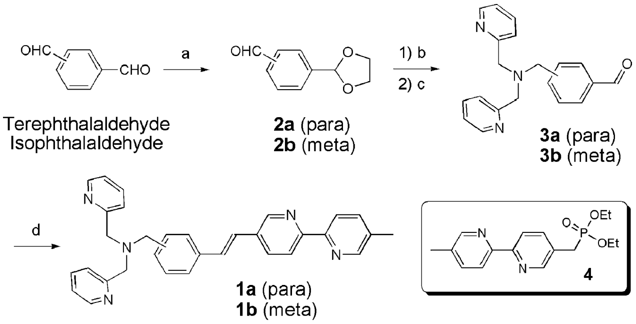

Scheme 1 Synthesis of **1a** and **1b**. *Reagents and conditions*: a. ethylene glycol, TsOH (cat.), Dean–Stark, reflux, 4 h; b. di(2-picolyl)amine, NaBH(OAc)$_3$, rt, 6 h; c. HCl–THF–H$_2$O, rt, 14 h; d. NaH, dimethoxyethane, **4**, rt, 14 h.

modulations of **1a** induced by Zn^{2+} and Cd^{2+} coordination are similar (see ESI†). This observation led us to the design of unimolecular half-adders with stipulated amounts of Zn^{2+} and Cd^{2+} as inputs using a ditopic phenylvinyl-bipyridyl structural platform. Examples of ditopic fluorescent ligands for metal ions have been reported before.[23–26] However, the coordination-driven photophysical processes in those known systems are not amenable to interpretations as binary half-adders.

Compounds **1a,b** were prepared as shown in Scheme 1. Mono-protection of benzenedialdehydes by ethylene glycol afforded **2a,b**, which underwent reductive amination with di(2-picolyl)amine followed by acidic deprotection to give **3a** and **3b**. Horner–Wadsworth–Emmons reactions between **3a,b** and **4** provided the targets **1a,b**. The binary half-adder function is demonstrated using **1a** in MeCN in this paper. The half-adder interpretation of **1b** is shown in the ESI.†

The emission of the phenylvinyl-bipyridyl fluorophore undergoes a bathochromic shift when the 2,2′-bipyridyl site is bound with Zn^{2+}. For the ease of discussion, we designate the emission of **1a** when 2,2′-bipyridyl is *unbound* as the "Blue" channel, and the emission when 2,2′-bipyridyl is *bound* with Zn^{2+} as the "Red" channel (390 nm and 449 nm, respectively, in MeCN). According to the positive logic convention, a *high* fluorescence intensity in either channel is assigned the logic value "ON" or "1"; a *low* fluorescence intensity is assigned the logic value "OFF" or "0". The coordination-driven fluorescence changes of **1a** are illustrated in Fig. 3. Fluorescence spectra of **1a** in MeCN in the presence of four combinations of two inputs, I1 and I2 (1.0 eq. of Zn^{2+} and 1.0 eq. of Cd^{2+}, respectively), are shown in Fig. 4. The quantum yields (Φ_F) of **1a** and **1b** at different coordination states are listed in Table 1.

In the absence of metal ion (input 0,0, Fig. 3(A)), **1a** displays weak fluorescence (Fig. 4), which suggests that the non-radiative relaxation of the excited state of **1a** through efficient photoinduced electron transfer (PET) is occurring.[27] As a result, both "Blue" and "Red" channels are assigned "OFF".

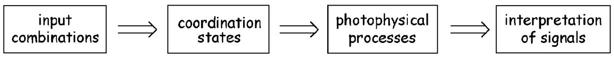

Fig. 2 Design principle of fluoroionophore-based logic and arithmetic functions.

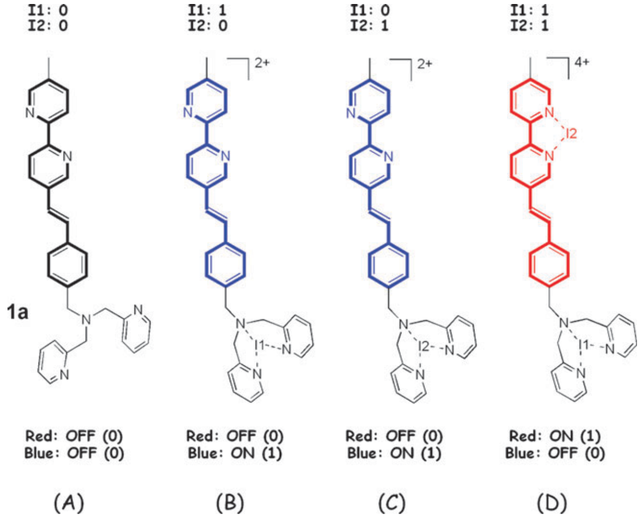

Fig. 3 Coordination and photophysical states of **1a** in response to four combinations of inputs I1 and I2 in MeCN. I1 and I2 represent 1.0 eq. of Zn^{2+} and Cd^{2+}, respectively, with respect to **1a**. "ON" and "OFF" represent high and low fluorescence intensity, respectively.

In the presence of either I1 or I2 (inputs 1,0 or 0,1, Fig. 3(B,C)), the emission band centered at 390 nm ("Blue" channel) is greatly enhanced (Fig. 4). Therefore, the "Blue" channel is assigned "ON" and "Red" channel "OFF" when either input combinations is applied. The enhancement is attributed to the fact that PET is terminated through metal coordination at the electron donor di(2-picolyl)amino site.[28]

In the presence of both I1 and I2 (input 1,1, Fig. 3(D)), both coordination sites, di(2-picolyl)amino and 2,2′-bipyridyl, are occupied. The coordination at 2,2′-bipyridyl site enhances the charge-transferred character of the fluorophore. Consequently, a longer emission band at 449 nm replaces that at 390 nm (Fig. 4). The "Red" channel is assigned "ON"; the "Blue" channel "OFF".

The fluorescence intensities of **1a** at 390 nm ("Blue") and 449 nm ("Red") in response to the four combinations of I1 and I2 are collectively interpreted as AND and XOR gates, respectively (Fig. 5). Hence, unimolecular half-adder **1a** with

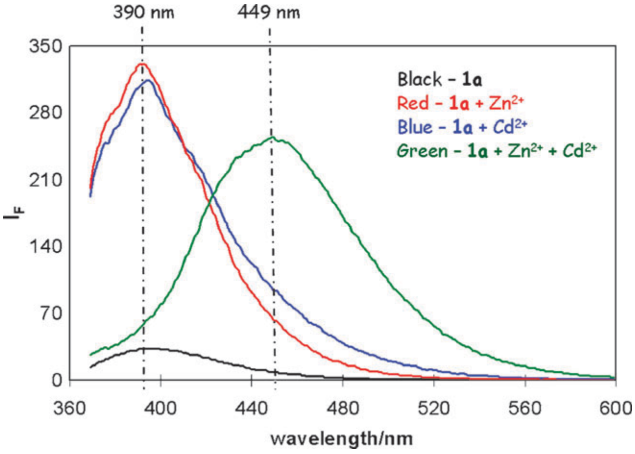

Fig. 4 Fluorescence spectra (λ_{ex} = 357 nm) of **1a** (2.0 μM) in MeCN in the presence of four combinations of I1 (1.0 eq. of Zn^{2+}) and I2 (1.0 eq. of Cd^{2+}).

Table 1 Fluorescence quantum yields (Φ_F)[a] of **1a** (2.0 μM) and **1b** (2.0 μM) at different coordination states in MeCN at 25 °C

	No metal	$+Zn^{2+}$ [b]	$+Cd^{2+}$ [b]	$+Zn^{2+}$ and Cd^{2+} [b]
Φ_F (**1a**)	0.04 ± 0.01	0.47 ± 0.05	0.58 ± 0.07	0.53 ± 0.09
Φ_F (**1b**)	0.06 ± 0.01	0.37 ± 0.04	0.32 ± 0.03	0.60 ± 0.02

[a] Fluorescence quantum yields (Φ_F) were determined in MeCN (with 1.0 eq. of DIPEA and 5 mM TBAP) at 25 °C by using solutions of anthracene (Φ_F = 0.27, ethanol) and quinine sulfate (Φ_F = 0.546, 0.5 M H_2SO_4) as references.[29] [b] Zn^{2+} and Cd^{2+} were added as quanta of 1.0 and 0.7 eq. for **1a** and **1b**, respectively.

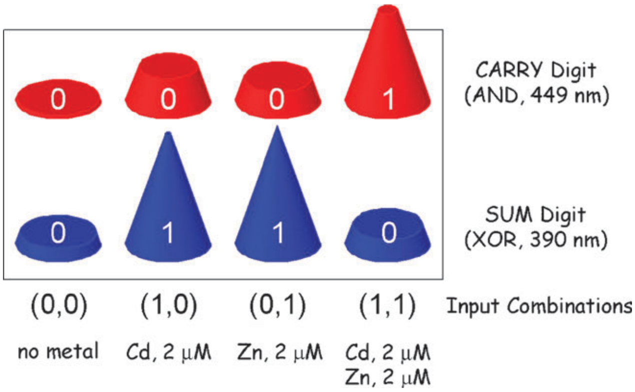

Fig. 5 Fluorescence intensity of **1a** in MeCN, reflected as the heights of the cones, at 449 nm ("Red" channel) and 390 nm ("Blue" channel) are interpreted as CARRY and SUM digits of a binary half-adder, respectively. The numbers on the *x*-axis are input combinations. "0" represents no addition of metal ion; "1" represents 2.0 μM of Cd^{2+} (I2) or 2.0 μM of Zn^{2+} (I1). The numbers on the cones are output values. "0" represents low fluorescence intensity; "1" represents high fluorescence intensity.

metal ions (Zn^{2+} and Cd^{2+}) of given quantities as inputs is successfully demonstrated (Fig. 3).

In summary, we have demonstrated unimolecular half adders **1a** and **1b** that accept non-interacting, hence orthogonal chemical inputs of Zn^{2+} and Cd^{2+} of given quantities. The generation of output signals of the binary half-adder truth table is fully based upon the processing power of the molecular half-adders on both chemical inputs, rather than the chemical reactivities of the two inputs toward each other. The design of the binary half-adders is based upon sound photophysical and coordination principles of heteroditopic arylvinyl-bipyridyl fluorophore platform established in our laboratory;[22] the interpretation of output signals as fluorescence intensities at two different wavelengths is straightforward. The system is of high performance in terms of the large signal contrasts between "0"s and "1"s; therefore, subtle threshold settings are not needed. The arithmetic function is based upon the facile reversible coordination between small molecules and metal ions. Therefore, this system can be reset if needed by treating with EDTA (see Fig. S10, ESI†).

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