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A Natural-Product-Inspired Photonic Logic Gate Based on Photoinduced Electron-Transfer-Generated Dual-Channel Fluorescence

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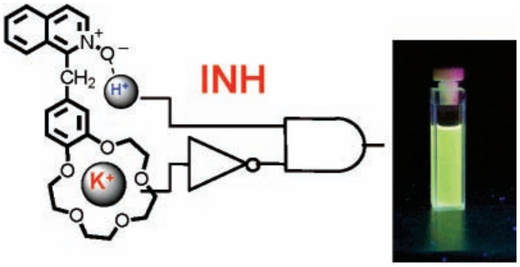
ABSTRACT



Modified 1-benzylisoquinoline *N*-oxides can operate as molecular logic gates. The combination of dual-channel fluorescence emissions and the preferred interaction for selected chemical inputs allows one to design multifunction and self-reprogrammable molecular logic gates.

Logic functions of various types have been arranged within single molecules.[1] Specific sequences of basic logic gates can be programmed in a single molecular switch. Clearly, the complexity that can be achieved with a single molecular switch is limited. The combination of independent molecular gates as basic logic operators could in principle allow one to obtain any combinatorial logic circuit, by combination of two molecules designed by using chemical inputs and optical outputs.[2] The miniaturization and economy of infrastructural needs for data processing and communication is an attractive, essential goal in the design and investigation of molecular-level systems.[3] On the molecular scale, physical "wiring" between two simple gates into more complex ones can be avoided by suitable functionalization. Thus, different functions can be integrated in a molecular or supramolecular system by using appropriate chemical design. While several other research groups have achieved the integration of logic basic functions by operating molecular logic devices in parallel,[2] by applying two excitation pulses,[4] or by operating over more complex systems based on the use of DNA as a

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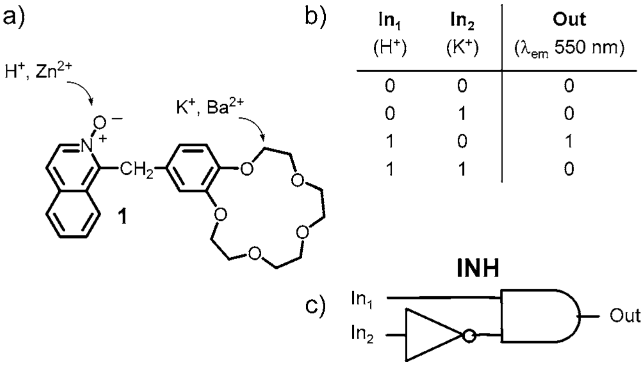


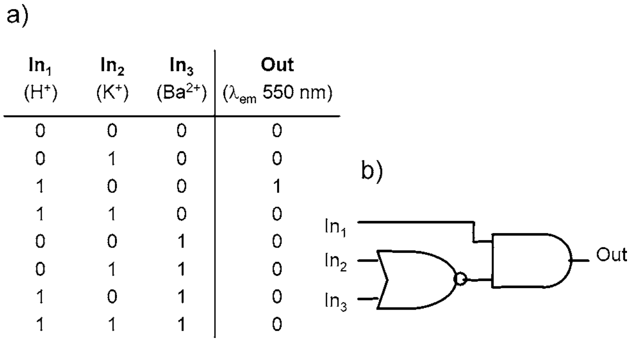
In_1 (H^+)	In_2 (K^+)	Out (λ_{em} 550 nm)
0	0	0
0	1	0
1	0	1
1	1	0

Figure 1. (a) Structure of the molecule used in this study and preferred interaction with selected chemical inputs. (b) Truth table of the input-output relationships for two selected chemical inputs: proton (In_1) operating over the acceptor and potassium (In_2) operating over the donor chromophore; excitation 400 nm, emission (Out) 550 nm. (c) Equivalent combinatorial logic circuit for the Inhibit (INH) gate.

specific supramolecular platform,[5] our goal is to develop systems that operate by integrating two independent output fluorescent channels via fast electron transfers.

Free energy changes in photoinduced electron transfer (PET) are known to be strongly dependent on the redox potentials of the donor/acceptor pair. The isoquinoline *N*-oxide-methylene-arene systems recently studied by our group[6] are dual-channel fluorescent compounds where both locally excited (LE) state and charge transfer (CT) emissions can be modulated simply by modifying the donor ability. These systems can operate as fluorescent monochannels in neutral media, where the LE emission of the free isoquinoline *N*-oxide is the only emission. On protonation of the *N*-oxide, the emission behavior becomes dependent on the excitation wavelength and exhibits dual-channel fluorescence emission. Upon excitation at short wavelengths, the LE emission of the protonated isoquinoline *N*-oxide prevails. At longer excitation wavelengths, fast PET between the positively charged acceptor and the bridged arene donor occurs, leading to a fluorescent CT state. The red-shifted emission is strongly dependent on the donor ability. Dual-channel operation can also be accomplished by coordination of the oxygen atom in the *N*-oxide with appropriate cations allowing for PET and hence for CT fluorescence.[7]

We used this approach to obtain a covalent molecular dyad (Figure 1a) consisting of an isoquinoline *N*-oxide acceptor the reduction potential of which was modulated by proton or transition metal coordination. The methylene-bridged benzo-15-crown-5 acted as the arene-donor, where the inclusion of cations in the chelating cavity governs its electron-donor ability.



In_1 (H^+)	In_2 (K^+)	In_3 (Ba^{2+})	Out (λ_{em} 550 nm)
0	0	0	0
0	1	0	0
1	0	0	1
1	1	0	0
0	0	1	0
0	1	1	0
1	0	1	0
1	1	1	0

Figure 2. Compound **1** operating as a three-input, one-output molecular switch: In_1 operates over the acceptor, whereas both In_2 and In_3 operate over the donor chromophore. (a) Truth table. (b) Combinatorial logic scheme.

Compound **1** behaves as an Inhibit (INH) gate operating via a PET mechanism (see Figure 1b). CT fluorescent emission (Output) is observed when the oxygen in the isoquinoline *N*-oxide is protonated (Input 1). Upon addition of potassium cation (Input 2), however, the donor ability of the benzo-crown ether is canceled. Therefore, CT fluorescence can only be observed when protons rather than potassium ions are present (Figure 1c).

Quenching of PET upon crown ether metal ion complexation was efficient for potassium and barium cations only. Thus, a three-input gate can also be obtained where PET quenching is blocked by both potassium and barium Inputs (Figure 2, In_2 and In_3 respectively), with proton as a third Input (In_1) enabling the device. Therefore, compound **1** can be used as a three-input (one-output) gate in which two inputs (In_2 and In_3) operate over the donor moiety of the dyad and one (In_1) over the acceptor component.

The INH function of Figure 1c can be expanded to the corresponding equivalent logic circuit depicted in Figure 2b. In this circuit, the input data In_2 and In_3 are combined via an NOR operator. The output of the AND gate is fed by this NOR operator and In_1.

The versatility of the double fluorescence emission of compound **1** permits its implementation in a more complex molecular logic system. Altering the three inputs in such a way that two of them (Figure 3a: In_1 and In_2) act over the acceptor and the third (In_3) over the donor moiety, affords a three-input, three-output molecular switch. Proton and zinc cations coordinate preferentially to the oxygen atom in the isoquinoline *N*-oxide, and the LE emission of the isoquinoline *N*-oxide at 400 nm is blue-shifted to 380 nm as a result. Also, the PET from the benzo-15-crown-5 can take place. In this way, In_1 and In_2 enable outputs 2 and 3 and disable output 1. The presence of an alkaline (or alkaline earth) cation such as potassium (or barium) disables output 3. This

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a)

In_1 (H^+)	In_2 (Zn^{2+})	In_3 (K^+)	Out_1 (λ_{em} 400 nm)	Out_2 (λ_{em} 380 nm)	Out_3 (λ_{em} 550 nm)
0	0	0	1	0	0
0	1	0	0	1	1
1	0	0	0	1	1
1	1	0	0	1	1
0	0	1	1	0	0
0	1	1	0	1	0
1	0	1	0	1	0
1	1	1	0	1	0

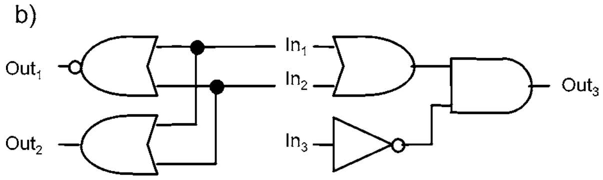

Figure 3. A three-input, three-output molecular switch: (a) truth table for a three-input situation in which two of the inputs (In_1 and In_2) act over the acceptor and one (In_3) over the donor moiety. (b) Combinatorial logic scheme.

corresponds to be integrated logic situation depicted in Figure 3b. In one portion of this complex logic circuit, the AND gate that provides output 3 integrates an OR gate and a NOT gate; in the other portion, outputs 1 and 2 are operated in parallel through a NOR gate and an OR gate.

Compound **1** is related to the family of benzyl isoquinoline alkaloids for which selective receptors have been reported.[8] This synthetic multifunctional compound might be used as a model for understanding the chemical and cellular bases for biological processes.[1c,3] Whereas in molecules with double fluorescence emissions such as LE/ICT the occurrence of a fluorescence mode excludes the other, the Acceptor-Spacer-Donor molecules studied by our group[6] (e.g., **1**) exhibit dual-channel fluorescence emission in an independent mode. This peculiarity allows one to simultaneously integrate two operating channels in these molecules, thus facilitating interesting logic phenomena unlikely to be observed in modular systems. This is a crucial contribution recently accomplished by simultaneously using absorbance and fluorescence emission techniques.[9]

The combination of this intrinsic property with the selectivity of actions by different chemical inputs allows the logic gates operated by compound **1** to be reconfigured. The PET process that operates between the Acceptor and Donor moieties in this dyad upon light excitation bears an INH gate as shown in Figure 1. Therefore, two inputs operating, respectively, over each component of the dyad (the proton over the acceptor and potassium cation over the donor) run this gate. With the introduction of a third input, the molecular device leads to different logic functions in a process that is strongly dependent on the target of this additional chemical input. Thus, if the third input operates over the donor moiety (e.g., barium cations in Figure 2), a three-input (one acceptor-input, two donor-inputs; *A*-In_1, *D*-In_2, and *D*-In_3) can be operated as shown in Figure 2b. However, if the third input operates over the acceptor component (e.g., zinc ions in Figure 3), a different three-input (two acceptor-inputs, one donor-input; *A*-In_1 and *A*-In_2, *D*-In_3) the logic function that can be operated by **1** is represented by a more complicated circuit. All the operations that compound **1** can perform are easily reprogrammed (erased) when operating in a water-immiscible or polymer-supported medium simply by washing with water.

The multiplicity of logic configurations that arises from **1** represents a new kind of reprogrammable molecular logic gate that integrates diverse logic circuits via simple variations over a third input.

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Supporting Information Available: Synthetic work and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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