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Effective PET and ICT Switching of Boradiazaindacene Emission: A Unimolecular, Emission-Mode, Molecular Half-Subtractor with Reconfigurable Logic Gates

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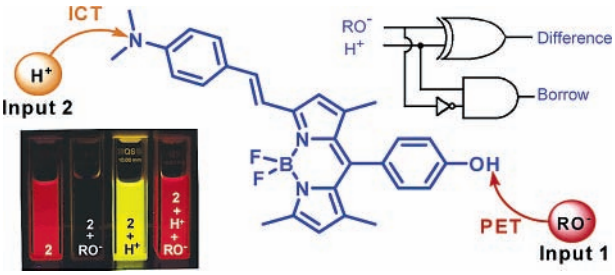
ABSTRACT



We report a unimolecular system functioning as a combinatorial logic circuit for half-subtractor. The emission characteristics can be modulated by chemical inputs, and when followed at two different wavelengths, two functionally integrated logic gates XOR and INHIBIT are obtained. Both logic gates function in the emission mode, and with very large differences in the signal intensity allowing unequivocal assignment of logic-0 and logic-1.

Within the past decade, many inspirational examples of molecular logic gates have been reported.[1] Ion-induced photophysical phenomena yield signals varying in intensity and/or color, and when viewed from a different vantage point, these changes can be correlated with the digital action of Boolean logic gates. The photoinduced electron transfer (PET)[2] is particularly appropriate for this purpose, because the changes observed by the modulation of the thermodynamics of PET with different inputs (analytes) usually yields "off-on" type, clear digital action. For two binary variables, there are 16 different types of Boolean functions, and molecular logic gates are available for most of them. Recently, the proof-of-principle for the important goal of molecular arithmetic was successfully demonstrated by de Silva and co-workers.[3] Following the publication of this article, other examples of addition[4] and subtraction[4b,5] using

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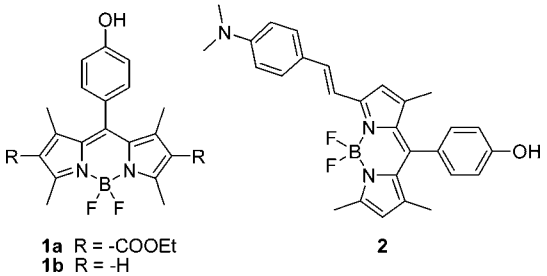
molecules were reported. While there are considerable hurdles to overcome in reaching practically useful information processing at the molecular level, such as individual addressability and higher levels of integration, further refinement of functionally integrated combinatorial circuits is essential. It would be highly desirable to have arithmetic operators which produce the same kind of output with very sharp changes in the studied parameter. Fluorescence, being an essentially zero-background technique, has clear advantages as output. The changes in the emission spectrum can also be followed at more than one wavelength, resulting in more than one logic function in a single molecular or supramolecular system. This has been first demonstrated by us[6] and then recognized as a powerful tool for obtaining multiple logic expressions.[4b,7]

With these considerations in mind, we targeted a single molecular entity, which could function as a unimolecular half-subtractor based on a boradiazaindacene (borondipyrromethenes, BODIPYs, BDPs)-type ICT (internal charge transfer) fluorophore. Among other applications, boradiazaindacenes were utilized in a number of fluorescent switches and chemosensors.[8] Extension of conjugation by the condensation reaction of dialkylaminobenzaldehydes with 3,5-dimethyl-substituted boradizaindacenes yields[9] red-emitting dyes with acid-switchable emission. To obtain a molecular system capable of carrying out arithmetic operations, we decided to introduce an additional, PET-sensitive functional group. This design is expected to yield wavelength-reconfigurable logic gates and thus produce two different logic operators at two different wavelengths, which would function in accordance with the operation of a half-subtractor.

8-(4-Hydroxyphenyl)-substituted boradiazaindacene (**1a**) was reported to display quenched emission upon deprotonation of the phenolic −OH.[10] The quenching has all the hallmarks of photoinduced electron transfer (PET) from the phenolate unit to the boradizaindacene fluorophore. To obtain a fluorophore which has two independent signaling units, we only had to react a boradiazaindacene (**1b**) with *p*-dimethylaminobenzaldehyde. The reaction, as reported previously,[8e] was carried out in toluene with azeotropic removal of water. The emission properties of the target compound (**2**) were studied in THF. Optically dilute solutions



1a R = -COOEt
1b R = -H

2

of **2** in THF have an absorbance peak at 565 nm and an emission peak at 660 nm. Addition of a drop of perchloric acid results in a considerable hypsochromic shift in both absorbance (−40 nm) and the emission (−100 nm) spectra. This is of course expected, considering the ICT nature of the emission. The addition of a strong base (potassium *tert*-butoxide) deprotonates the phenolic hydroxyl group, but this time the emission is quenched without any shift in either absorption or emission peaks. The quantum yields were also determined; without any added modulator, the quantum yield of the red emission in THF was 0.25. Upon addition of acid, a bright yellow emission is observed with increased quantum yield (ϕ_{em} = 0.84). However, addition of base yields a significantly quenched emission (ϕ_{em} = 0.032) at the same wavelength (660 nm). The digital photograph (Figure 1) of

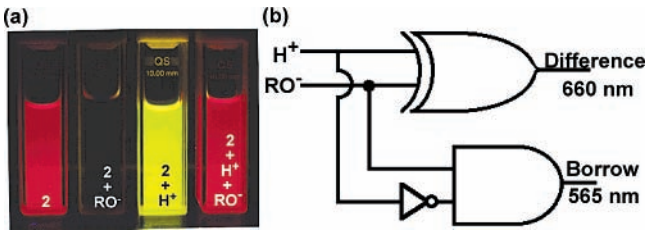


Figure 1. (a) 5 × 10^{-6} M solutions of **2** in THF illuminated with a UV lamp at 360 nm. From left to right, dye alone, dye in the presence of 0.5 mM potassium *tert*-butoxide, dye in the presence of 0.5 mM $HClO_4$, dye with equimolar acid and base. (b) Logic diagram of the half-subtractor. The "difference" and "borrow" outputs were collected at two different wavelengths, 660 and 565 nm, respectively.

the solutions of the dye **2** with different modulators (inputs) clearly demonstrates the strongest aspect of this unimolecular operator, which is the sharp changes in the emission characteristics. When the emission was followed at two different channels, 565 and 660 nm, the clear digital nature of the signal becomes apparent (Figures 2 and 3). A half-

input		output		
base[a]	acid[b]	borrow[c] (***B***) (λ_{max}:565 nm)	difference[c] (***D***) (positive logic) (λ_{max}:660 nm)	difference[c] (***D***) (negative logic) (λ_{max}:660 nm)
0	**0**	**0** (low, 1.8)	**1** (high, 32)	**0** (high, 32)
0	**1**	**1** (high, 100)	**0** (low, 1.5)	**1** (low, 1.5)
1	**0**	**0** (low, 1.2)	**0** (low, 1.8)	**1** (low, 1.8)
1	**1**	**0** (low, 1.8)	**1** (high, 32)	**0** (high, 32)

Figure 2. Truth table for the operation of the molecular half subtractor **2**. When followed at 565 nm, the molecule functions as an INHIBIT gate, but it can be reconfigured by the selection of wavelength. At 660 nm, and when negative logic is applied XOR outputs are obtained. Key: (a) potassium *tert*-butoxide (0.5 mM); (b) $HClO_4$ (0.5 mM); (c) assigned output values for the two logic functions. The emission intensity values at the indicated wavelengths are shown in parentheses.

subtractor can be implemented with a combinatorial logic circuit composed of an XOR gate and an INHIBIT gate (Supporting Information). The emission output at 565 nm

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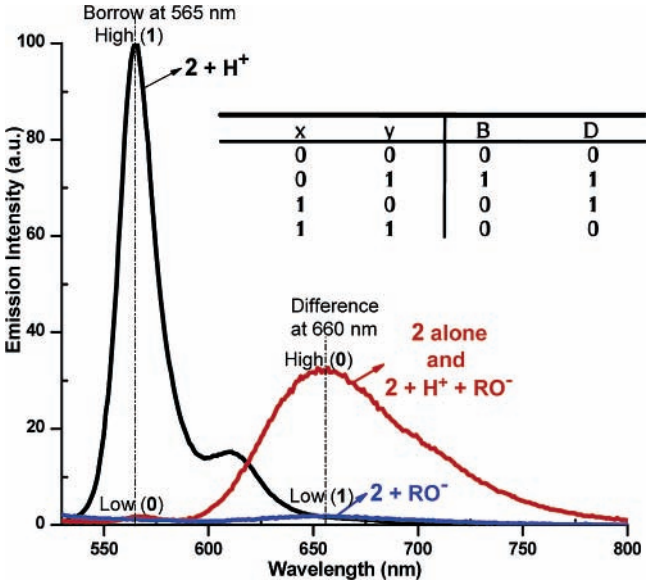

x	y	B	D
0	0	0	0
0	1	1	1
1	0	0	1
1	1	0	0

Figure 3. Emission spectra of compound **2** in THF in the presence of chemical inputs. When excited at 520 nm (5 nm slit widths), compound **2** shows an emission peak at 660 nm. The addition of either acid or base decreases the emission intensity at this wavelength. But, when both acid and base are added together there is no change at 660 nm. When acid is added as an input, there is a new intense emission band at 565 nm. Inset: The truth table for a half-subtractor; the outputs are Borrow (B) and Difference (D).

correlates very well with an INHIBIT logic gate. The output at 660 nm results in an XNOR logic. XNOR logic and XOR logic operators are "duals" of each other.

Since the assignment of logic-0 and logic-1 to inputs and outputs is arbitrary (assignment of logic polarity), low (or 0) concentration inputs and low intensity outputs can also be assigned to logic-1 and vice versa. In digital design, where both the inputs and the outputs are voltages, this is referred to as negative logic.[11] However, as in most molecular logic gates, in our system the inputs are chemical and the outputs are photonic. The fact that the inputs and the outputs are of different kind, allows us an application of negative logic only on the outputs. Two logic gates are independent of each other, so it is fully acceptable to run one channel in positive logic while applying negative logic on the outputs of the other channel. Thus, following this procedure for the outputs at 660 nm, XNOR gate is effectively transformed into an XOR gate.

Thus, we demonstrate that a single molecule with very large differentials of emission intensity, can carry out an arithmetic operation (subtraction) at the molecular level. "In solution" logic gates are more likely to evolve into components of a wet computer, much like our brains, rather than integrate with the current paradigm of silicon based systems. The addressability issue has been approached very elegantly in a recent communication.[12] Based on our unimolecular half-subtractor, we are also targeting similar nanosystems with molecular arithmetic capabilities. Work along these lines is in progress.

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Supporting Information Available: Syntheses, experimental details, ^{1}H and ^{13}C NMR spectra, additional spectroscopic data, and logic diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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