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[2,2′-Bipyridyl]-3,3′-diol as a Molecular Half-Subtractor

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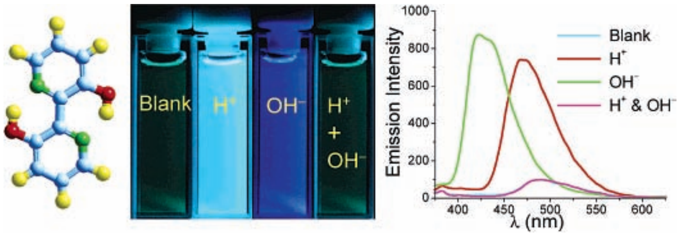
ABSTRACT



Spectral responses at two different wavelengths revealed that BP(OH)$_2$ ([2,2′-bipyridyl]-3,3′-diol) can function as a combinatorial logic circuit for a molecular half-subtractor with acid and base as input variables.

The idea of a molecular computer has emerged, since chemists have shown that certain molecular systems are capable of performing arithmetic logic operations.[1−3] This area of research has attracted considerable attention since the first molecular AND logic gate was reported by de Silva and co-workers.[4] Examples of the molecular arithmetic systems are available in the literature which demonstrate AND,[4] XOR,[5] INHIBIT,[6] NOT,[7] OR,[8] NOR,[9] XNOR,[10] NAND,[11] logic operations independently. However, literature reports on molecular systems that are capable of integrating simple logic gates into combinatorial circuits are rare. Such

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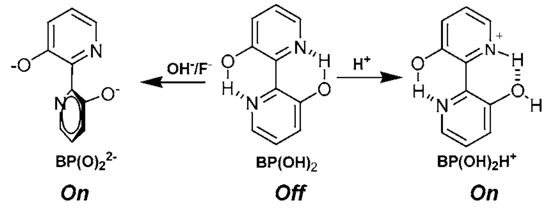
operations are important for the realization of complex information processing.[12,13]

A half-subtractor is a combinatorial circuit that subtracts two bits and produces their difference. It needs two outputs: one generates the difference (D), and the other generates the borrow (B). These outputs are generated through XOR and INHIBIT gates, respectively. Examples of a molecular system based on a single molecule, which is capable of exhibiting operations for a half-subtractor, are rare in the literature.[13]

In this paper, we have demonstrated that $BP(OH)_2$ ([2,2′-bipyridyl]-3,3′-diol) can be used to exhibit a complex algebraic operation, such as a half-subtractor process with acid and base/fluoride ion as binary ionic inputs. Output signals were monitored through changes in emission intensity and/or optical density values.

$BP(OH)_2$ and its derivatives have potential as laser dyes and solar energy collectors[14] and are known to undergo excited-state intramolecular double proton transfer in solution.[15] The strong intramolecular H-bonds (Scheme 1) lead to the planar structure of the molecule in the ground state. This has also been confirmed by the single-crystal X-ray structure of $BP(OH)_2$.[16]

Scheme 1. Schematic Representation of the $BP(OH)_2$



There are sites for protonation and deprotonation in $BP(OH)_2$ (Scheme 1), and this molecule exhibits appreciably different luminescence and electronic spectra in protonated and deprotonated states. Optical spectra for $BP(OH)_2$, $BP(OH)_2H^+$, and $BP(O)_2^{2-}$ in acetonitrile are shown in Figure 1. Absorption maximum for the neutral molecule $BP(OH)_2$ at 344 nm was attributed to a $\pi-\pi^*$-based electronic ($S_0 \rightarrow S_1$) transition. Excitation of this molecule at 344 nm showed a weak emission band with maxima at 500 nm. An earlier report reveals that this molecule might exist in the corresponding keto form in the excited state and luminescence is substantially quenched due to the photoinduced electron transfer.[15]

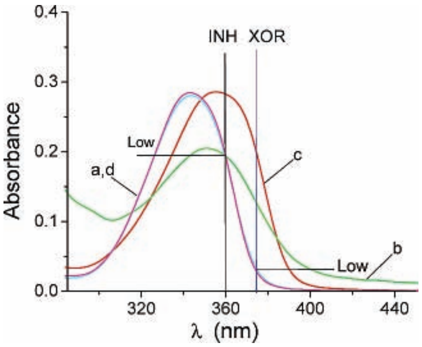


Figure 1. Electronic spectra for (a) $BP(OH)_2$, (b) $BP(O)_2^{2-}$ at pH $\approx$ 10.8, and (c) $BP(OH)_2H^+$ at pH $\approx$ 4.0 (Scheme 1), (d) $BP(OH)_2$ in the presence of equimolar amounts of H^+ and OH^-. Concentraion of $BP(OH)_2$ used for the study was 2.0×10^{-4} M.

No color change could be detected by the naked eye on addition of $HClO_4$ or $[^n(Bu)_4N]OH$ (TBAH)/$[^n(Bu)_4N]F$ (TBAF). However, spectrophotometric measurements revealed that addition of H^+ (pH $\approx$ 4.0) in the form of $HClO_4$ caused a shift of the absorption maxima to the lower energy by 10 nm (Figure 1). A similar shift (~7 nm) with lower absorption intensity was observed on addition of OH^- (pH ~10.8)/ F^- (excess) to the acetonitrile solution of $BP(OH)_2$ (Figure 1). Profiles for these two independent titrations with $HClO_4$ and TBAH revealed that monoprotonated species $BP(OH)_2H^+$ at pH $\approx$ 4.0 and bisdeprotonated form $BP(O)_2^{2-}$ at pH $\approx$ 10.8 were prevalent in solution (Scheme 1). Thus, the new absorption spectra recorded on addition of 1 equiv of H^+ or 2 equiv of OH^- were assigned to $BP(OH)_2H^+$ or $BP(O)_2^{2-}$, respectively. The observed red shift was attributed to facile intramolecular charge-transfer process (ICT).

Luminescence spectra recorded for $BP(OH)_2$, $BP(O)_2^{2-}$, and $BP(OH)_2H^+$ in acetonitrile are shown in Figure 2. Relative emission quantum yield for $BP(OH)_2$, $BP(O)_2^{2-}$, and $BP(OH)_2H^+$ (with respect to anthracene as reference, $\phi_{\mathrm{anthracene}} = 0.27$) in acetonitrile were found to be 0.0024, 0.025, and 0.018, respectively. Higher emission quantum yields for $BP(O)_2^{2-}$ and $BP(OH)_2H^+$, compared to $BP(OH)_2$, were due to the enhanced ICT transition.[13b,17] Blue-shifted emission was observed for $BP(OH)_2H^+$ and $BP(O)_2^{2-}$ at 470 and 422 nm, respectively.

A closer look at the set of electronic spectra for $BP(OH)_2$ at different pH (Figure 1) revealed that with two different modulator (inputs), $BP(OH)_2$ demonstrated the basic aspect of a unimolecular operator. The change in absorption spectra

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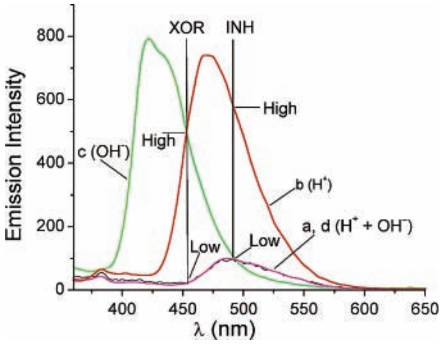

Figure 2. Steady-state luminescence spectra for (a) $BP(OH)_2$, (b) $BP(OH)_2H^+$ at pH ≈ 4.0, (c) $BP(O)_2^{2-}$ at pH ≈ 10.8, and (d) $BP(OH)_2$ in the presence of equimolar amounts of H^+ and OH^- following excitation at 344 nm. Concentration of $BP(OH)_2$ used for the study was 2.0×10^{-7} M.

of the neutral $BP(OH)_2$ molecule was monitored at two different wavelengths, i.e., 360 and 374 nm, with two inputs in the form of H^+ and OH^-. Consequently, the clear digital nature of the signal became apparent (Figure 3 and Table 1), and a half-subtractor operation could be implemented with a combination of a XOR gate and an INHIBIT gate.

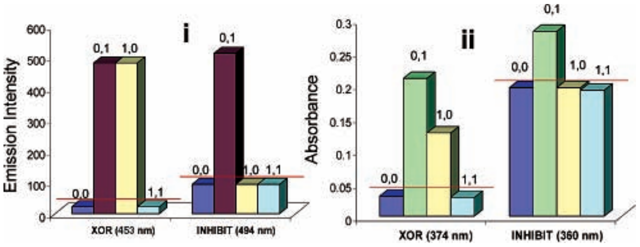

Figure 3. Bar diagram of the half-subtractor: (i) change in emission; (ii) change in absorbance values.

Table 1. Truth Table for Absorption-Based Half-Subtractor.

input		ouput (λ_{abs})	
OH^-	H^+	XOR (D), 374 nm	INH (B), 360 nm
0	0	0 (low, 0.031)	0 (low, 0.196)
0	1	1 (high, 0.210)	1 (high, 0.282)
1	0	1 (high, 0.127)	0 (low, 0.196)
1	1	0 (low, 0.029)	0 (low, 0.196)

To examine that this molecule behaved as a XOR gate, the output signal was monitored at 374 nm and the threshold value was kept at 0.031 for $BP(OH)_2$). The changes in the absorbance at this wavelength were used as an output to derive a truth table based on two chemical inputs (H^+ and OH^-). Output was found to be high, i.e., 1, with either one of these two inputs, H^+ or OH^-. Further, two simultaneous inputs in the form of H^+ and OH^- annihilated each other's action (Figure 1) generating the spectrum of the neutral from, i.e., $BP(OH)_2$. Thus, this observation correlated very well with XOR logic gate as it generated an *on* output when either input was *on*; but not when the inputs were both *on* or both *off* (Table 1). Next, absorbance change at 360 nm was monitored as an output signal with threshold value of 0.196. Increase in absorbance value (i.e output value is 1) was noticed only with H^+ as an input. For all other options as shown in Table 1, output was 0. These observations complied with the function of an INHIBIT gate and are presented in truth table (Table 1 and Figure 3). Thus, the combination of XOR and INHIBIT gates at these two monitoring wavelengths indicate that $BP(OH)_2$ molecule behaves as a unimolecular half-subtractor.

Binary half-subtractor operation of $BP(OH)_2$ can also be explained by monitoring the luminescent intensity at two different wavelengths, 453 and 494 nm. For 453 nm as monitoring wavelength, output remained in the *on* state (1), in presence of either H^+ or OH^-. While, it was in the *off* state when either none or both chemical inputs were present (Table 2). Thus, this study could also explain the XOR gate operation for $BP(OH)_2$.

Table 2. Truth Table for Fluorescence-Based Half-Subtractor

input		ouput (λ emission)	
OH^-	H^+	XOR (D), 453 nm	INH (B), 494 nm
0	0	0 (low, 22.5)	0 (low, 93.6)
0	1	1 (high, 480.3)	1 (high, 511.2)
1	0	1 (high, 480.3)	0 (low, 93.6)
1	1	0 (low, 22.5)	0 (low, 93.6)

Further, luminescence intensity at 494 nm was monitored to examine the INHIBIT function. Only in presence of H^+ as input, emission was *on* (i.e output value is 1) (Figure 2). For all other circumstances as shown in Table 2, the output signal was 0 and thereby complied with an INHIBIT operation.

In binary subtraction, XOR gate output (monitoring wavelength: $\lambda_{emission} = 453$ nm, $\lambda_{abs} = 374$ nm) was the difference digit (D) and the INHIBIT gate (monitoring wavelength: $\lambda_{emission} = 494$ nm, $\lambda_{abs} = 360$ nm) was the Borrow digit (B) (Figure 3). Thus, we could interconnect two arithmetic operations like INHIBIT and XOR gates to implement half-subtraction in $BP(OH)_2$.

A small number of reports, including one from this group, have shown that the phenoxy functionality can act as a specific receptor for fluoride ion and shows an appreciably high affinity constant value.[18] At lower $[F^-]$, an adduct formation between $BP(OH)_2$ and F^- occurs through H-bond ($-O-H\cdots F^-$) formation. However, at higher $[F^-]$, stability

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of HF_2^--species is expected to lead to the deprotonation to the corresponding phenoxide ion. We have monitored the output signal (*on* or *off* state) by changes in the electronic and luminescence spectra of $BP(OH)_2$ with two ionic inputs (H^+ and F^-) at two specific wavelengths. To ensure bis-deprotonation in $BP(OH)_2$, we added 5 mol equiv of F^- for the study. Changes in spectra (Figure 4) were almost similar to the situation when OH^- was added as ionic input (Figure 1 and 2). Differences in absorbance values at monitoring wavelength of 361/ 374 nm and luminescence intensity values at probe wavelength of 451/ 490 nm, with use of two ionic inputs in the form of H^+ and F^-, were used as output to derive a truth table (Supporting Information). The truth table revealed that the digital nature of the signals matched with the one for half-subtractor. Electronic spectral output at 361 nm and emission output at 490 nm correlated very well with a INHIBIT logic gate; while same at 374 and 451 nm could be linked with the XOR logic gate. A half-subtractor operation could be implemented with a combination of a logic circuit composed of these two logic gates.

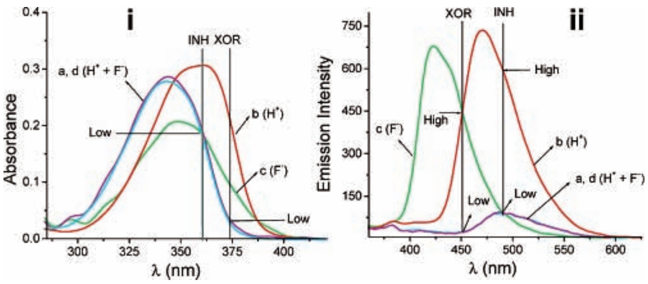

Figure 4. Changes in (i) absorption and (ii) luminescence spectra of (a) $BP(OH)_2$, (b) $BP(OH)_2H^+$ at pH ≈ 4.0, (c) 5 molar equiv of F^-, and (d) equimolar amounts of H^+ and F^-. Concentraion of $BP(OH)_2$ used for the study was 2.0×10^{-7} M.

In conclusion, we have studied the electronic and luminescence spectral properties for $BP(OH)_2$ in presence of [$HClO_4$] and/or [TBAH]/[TBAF]. For TBAF, the strong affinity of the phenolic OH toward F^- and high stability of HF_2^- eventually led to the generation of $BP(O)_2^{2-}$. Changes in the absorbance data/ emission intensities at two chosen wavelengths with two independent ionic inputs like H^+ and OH^-/F^- leads to a truth table that demonstrates the arithmatic operation of a molecular half-subtractor and thus may be used as an arithmetic processor in a wet computer.

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Supporting Information Available: Individual optical and luminescence spectra for $BP(OH)_2$ with different ionic inputs; H^+ and OH^-/ F^- demonstration of the XOR and INHIBIT operations at two different monitoring wavelengths. This material is available free of charge via the Internet at http://pubs.acs.org.

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