

# Half-subtractor operation in pH responsive N-heterocyclic amines

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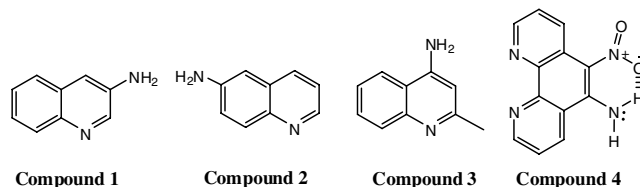
**Abstract**—Intramolecular charge transfer processes in simple molecules can be exploited to implement combinational digital operation.

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In recent years, there has been a surge of interest in mimicking the function of silicon chips using either readily available or easily synthesizable chemicals.<sup>1–4</sup> In computers, information processing is based on the principles of Boolean algebra; a system for mathematical analysis through logic operation(s). Logic gates are the devices used to perform basic logic operations and are the basis of today's computer processors, which perform logic and arithmetic operations between Boolean variables. The XOR,<sup>5</sup> NAND,<sup>6</sup> INHIBIT,<sup>7</sup> and NOR<sup>8</sup> functions are important in microelectronic circuits since they can be easily implemented using a transistor. The transistor remains the heart of digital computing as it provides the link between logic gates and memory devices. It is believed that an individual molecule can act as a field effect transistor. Having a size more than 100 times smaller than conventional silicon gates, molecules offer excellent component minimization potential.<sup>9</sup> The realization of complex information processing and computation at the molecular level will only be possible with the molecular logic gate, which are capable of integrating simple logic gates into combinational circuits. Such molecular logic gates are composed of a chromophore that responds to an independent ionic input with associated changes in the output signal in the form of changes in spectral pattern.<sup>2,3</sup> A half-subtractor is a combinational circuit that subtracts two bits and produces their difference. This device requires two outputs: one generates the difference (D), while 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 scarce.<sup>4</sup>

In this Letter, we demonstrate that simple quinoline derivatives, such as 3-aminoquinoline (**1**), 6-aminoquinoline (**2**), 4-aminoquinoline (**3**), and 6-nitro-[1,10]-phenanthroline-5-ylamine (**4**) (Scheme 1) can be used to exhibit molecular half-subtractor operations with acid and base as the binary ionic inputs. The cation sensing ability of related derivatives were reported earlier.<sup>10</sup> Output signals were monitored either through change(s) in the fluorescence intensity (for compounds **1–3**) or the optical density values (for compound **4**). All these compounds exhibit an absorption band in the range 300–420 nm owing to the intramolecular charge transfer (ICT) transition with the homocyclic ring and/or amino functionality acting as the donor fragment(s) and the heterocyclic ring acting as the acceptor fragment (Scheme 1). Each compound (**1–4**) has two protonation sites—the amine (N) and the heterocycle (N) atoms. Earlier literature reports revealed that on addition of 1 mol equiv of H<sup>+</sup>, the heterocycle (N) atom became protonated preferentially.<sup>11</sup> Such studies had also established that the –NH<sub>2</sub> functionality could act as an efficient H-bond donor.<sup>12</sup> In the case of **4**, the acidity of one of the two protons (not H-bonded) of the NH<sub>2</sub> functionality was further enhanced due to the intramolecular

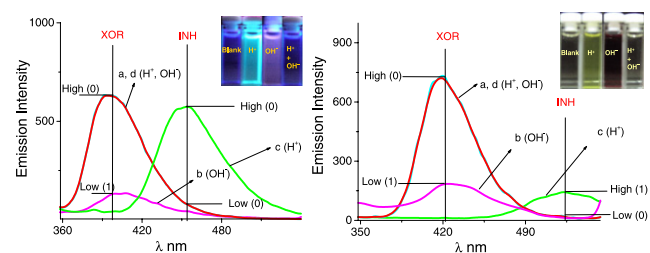


Scheme 1. Chemical structures for compounds 1–4.

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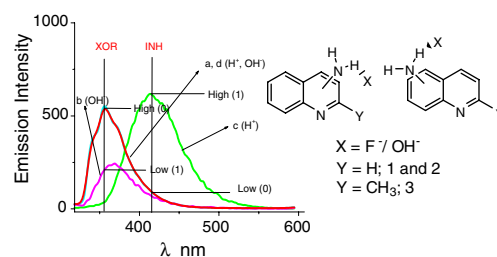
H-bond with the  $-\text{NO}_2$  group (Scheme 1). For amino derivatives of the heterocyclic compounds, it was argued that in the presence of the H-bond acceptor functionality or a polar/aprotic solvent, the planar ICT state was preferentially stabilized. Thus, in a mixed polar solvent such as  $\text{H}_2\text{O}-\text{CH}_3\text{CN}$  (3:7, v/v), one would expect that the lone pair electrons of the  $\text{N}(\text{NH}_2)$ -atom would remain free to participate in the ICT process.<sup>11a</sup> This planar ICT state is expected to be further stabilized on protonation of the ring N-atom. This is expected to be little different for **3** as compared to **1** and **2** where the aryl amine form can exist in equilibrium with the corresponding amidine.<sup>11d</sup> Detailed studies revealed that the spectral pattern for **1–4** differed from that of the neutral species in the presence of  $\text{H}^+$  or  $\text{OH}^-$ . Optically dilute solutions of compounds **1** and **2** in  $\text{H}_2\text{O}-\text{CH}_3\text{CN}$  (3:7, v/v) mixed solvent were found to have absorption maxima at 345 and at 284 and 352 nm, respectively. The emission maxima for these two compounds were observed at 393 and 420 nm, respectively. Addition of  $\text{H}^+$  as an ionic input to compound **1** (at pH 4) and **2** (at pH 3.8) caused protonation of the ring nitrogen and thereby favored the ICT process (Scheme 1).<sup>11b</sup> This was reflected in the red shift for the respective emission maxima (Table 1, Fig. 1) for **1** (454 nm) and **2** (525 nm). Spectral responses for **3** with varying  $[\text{H}^+]$  were different from those of **1** and **2**. Preferred delocalization of the lone pair of electrons of the  $\text{N}(\text{NH}_2)$ -atom in the mono protonated species caused **3** to exhibit spectral properties quite different from those of **1** and **2**.<sup>11b</sup> However, the doubly protonated form of **3** in 18 M  $\text{H}_2\text{SO}_4$  is known to behave as an aryl ammonium ion. This ion is known to exhibit ICT with the homocyclic ring acting as the donor fragment and the heterocyclic ring bearing cationic charges, acting as the acceptor center.<sup>11d</sup> Electronic spectra for compound **3** (neutral species) showed an absorption maximum at 310 nm and an emission band with a maximum at 356 nm. The fluorescence spectrum for compound **3**<sup>2+</sup> in 18 M  $\text{H}_2\text{SO}_4$  shifts to a longer wavelength (415 nm) due to the favored ICT process.

The emission bands for the respective solutions of **1–3** were found to be significantly quenched when 1.2 mol equiv of  $\text{OH}^-$  was added. The  $\text{NH}_2$  (amine) functionality is known to form a relatively strong H-bond with  $\text{OH}^-$ .<sup>12</sup> Thus, in the presence of TBAH, H-bond formation between the electron rich  $\text{OH}^-$  and  $\text{N}(\text{NH}_2)$  was expected to enhance the electron density on the overall adduct. Presumably this would account for the higher solvation and increased vibrational deactivation of the



**Figure 1.** Fluorescence spectra of  $2.0 \times 10^{-6}$  M 3-aminoquinoline (**1**, left) and 6-aminoquinoline (**2**, right) in (a) aqueous-acetonitrile (3:7, v/v), (b) with TBAH at pH 11.7 (1)/11.9 (2), (c) with HCl at pH 4 (1)/3.8 (2), (d) in an equimolar amount of  $\text{OH}^-$  and  $\text{H}^+$  following excitation at 345 (1)/284 (2) nm.

excited state through non-radiative pathways.<sup>4b,13</sup> This could account for the appreciable quenching of the observed emission (Figs. 1 and 2). Similar spectral changes were observed for **1** and **2** when an excess of  $\text{F}^-$  was used as the ionic input, instead of  $\text{OH}^-$ . Analysis of the fluorescence spectral changes for **1–3** with different ionic inputs revealed that the half-subtractor operation could be implemented with a combinational logic circuit composed of an XOR gate and an INHIBIT gate. This can be explained by monitoring the luminescent intensity at two different wavelengths; 393 and 454 nm for compound **1**, 420 and 525 nm for compound **2**, and 356 and 415 nm for compound **3**. Emission outputs at 454, 525, and 415 nm for the respective compounds **1**, **2**, and **3** correlated very well with an INHIBIT logic gate, as it showed output *on* (i.e., output value as 1) only in the presence of  $\text{H}^+$  as an input (Figs. 1 and 2, Tables 1 and 2). The output at 393, 420, and 356 nm for compounds **1**, **2**, and **3**, respectively, resulted in an XNOR logic gate. The output at the aforementioned wave-



**Figure 2.** Fluorescence spectra of  $2.0 \times 10^{-6}$  M 4-aminoquinoline (**3**) in (a) pH 10.2 borate buffer (neutral species), (b) with TBAH at pH 11, (c) in 18 M  $\text{H}_2\text{SO}_4$  (dication), (d) in an equimolar amount of TBAH and  $\text{H}_2\text{SO}_4$  following excitation at 310 nm.

**Table 1.** Truth table for compounds **1** and **2**

Input		Output (emission)					
$\text{OH}^-$	$\text{H}^+$	Compound <b>1</b>			Compound <b>2</b>		
		Borrow	Difference (positive logic)	Difference (negative logic)	Borrow	Difference (positive logic)	Difference (negative logic)
		$\lambda_{\text{emi}}$ : 454 nm	$\lambda_{\text{emi}}$ : 393 nm	$\lambda_{\text{emi}}$ : 393 nm	$\lambda_{\text{emi}}$ : 525 nm	$\lambda_{\text{emi}}$ : 420 nm	$\lambda_{\text{emi}}$ : 420 nm
0	0	0 (Low, 75.8)	1 (High, 628.7)	0 (High, 628.7)	0 (Low, 14.5)	1 (High, 719.8)	0 (High, 719.8)
0	1	1 (High, 575.9)	0 (Low, 35.0)	1 (Low, 35.0)	1 (High, 145.1)	0 (Low, 14.5)	1 (Low, 14.5)
1	0	0 (Low, 39.9)	0 (Low, 128.5)	1 (Low, 128.5)	0 (Low, 14.5)	0 (Low, 185.2)	1 (Low, 185.2)
1	1	0 (Low, 75.8)	1 (High, 628.7)	0 (High, 628.7)	0 (Low, 14.5)	1 (High, 719.8)	0 (High, 719.8)

**Table 2.** Truth table for compounds **3** and **4**

Input		Output (emission)			Input		Output (absorbance)	
OH <sup>-</sup>	H <sup>+</sup>	Compound <b>3</b>			H <sup>+</sup>	OH <sup>-</sup>	Compound <b>4</b>	
		Borrow $\lambda_{\text{emi}}$ : 415 nm	Difference (positive logic) $\lambda_{\text{max}}$ : 356 nm	Difference (negative logic) $\lambda_{\text{max}}$ : 356 nm			Borrow $\lambda_{\text{max}}$ : 444 nm	Difference $\lambda_{\text{max}}$ : 411 nm
0	0	0 (Low, 87.28)	1 (High, 543.2)	0 (High, 543.2)	0	0	0 (Low, 0.18)	0 (Low, 0.47)
0	1	1 (High, 619.0)	0 (Low, 34.6)	1 (Low, 34.6)	0	1	1 (High, 0.58)	1 (High, 0.63)
1	0	0 (Low, 64.16)	0 (Low, 205.6)	1 (Low, 205.6)	1	0	0 (Low, 0.06)	1 (High, 0.63)
1	1	0 (Low, 87.28)	1 (High, 543.2)	0 (High, 543.2)	1	1	0 (Low, 0.18)	0 (Low, 0.47)

lengths for compounds **1**, **2** and **3** remained in the *off* state (0), in the presence of either H<sup>+</sup> or OH<sup>-</sup>, while, it was in the *on* (1) state when either none or both chemical inputs (H<sup>+</sup> and OH<sup>-</sup>) were present (Figs. 1 and 2, Tables 1 and 2). Further, by monitoring these wavelengths, one could also explain the XNOR gate operation. XNOR and XOR are logic operators that are complementary to each other and for the outputs at 393, 420 and 356 nm for **1**, **2** and **3**, respectively, the XNOR gate is effectively transformed into an XOR gate (Tables 1 and 2).<sup>4b,14</sup> Thus, we could interconnect two arithmetic operations like INHIBIT (monitoring wavelengths 454, 525 and 415 nm) and XOR (monitoring wavelengths 393, 420 and 356 nm) gates to implement half-subtraction for compounds **1**, **2** and **3**.

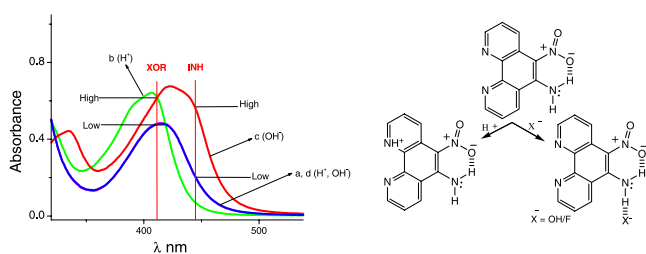
In the case of compound **4**, the absorption maxima (415 nm) shifted to a shorter wavelength (405 nm) on addition of 1.2 mol equiv of H<sup>+</sup>. This could be attributed to the less favored ICT process on protonation of one of the two ring N atoms (Fig. 3). As mentioned earlier, the -NH<sub>2</sub> functionality of 6-nitro-[1,10]-phenanthroline-5-ylamine (**4**) is expected to act as a better H-bond donor toward OH<sup>-</sup>/F<sup>-</sup>. The enhanced acidity of this proton could result in deprotonation at pH 11 or in the presence of excess [F<sup>-</sup>]. The high thermodynamic stability for HF<sub>2</sub><sup>-</sup> is known to favor deprotonation equilibria.<sup>15</sup> Therefore, in the presence of OH<sup>-</sup> or excess F<sup>-</sup>, the deprotonated H-bonded cyclic amine functionality was expected to act as the donor fragment and the heterocyclic ring as the acceptor fragment in the favored ICT process (Fig. 3 and Supplementary information (SI)) and caused a red shift of 8 nm for the absorption maxima (Fig. 3). Analysis of the set of electronic spectra collected for compound **4** at different pHs revealed that with two different modulators (inputs), compound **4** could demonstrate the basic operation of

a unimolecular operator. For this, changes in absorption spectra were monitored at two different wavelengths, that is, 411 and 444 nm, with two independent inputs in the form of H<sup>+</sup> and OH<sup>-</sup>/F<sup>-</sup>. To determine XOR gate behaviors the output signal was monitored at 411 nm with a threshold absorbance value of 0.47. The changes in the absorbance at this wavelength were used as an output to derive a truth table based on two chemical inputs (H<sup>+</sup> and OH<sup>-</sup>/F<sup>-</sup>). Outputs were found to be high, that is, 1, with either one of these two inputs, H<sup>+</sup> or OH<sup>-</sup>/F<sup>-</sup>. Furthermore, two simultaneous inputs in the form of H<sup>+</sup> and OH<sup>-</sup> counterbalanced one another generating the spectrum of the neutral form, that is, compound **4**. This observation correlated very well with an XOR logic gate as it generated an *on* (1) output when either of the two inputs were *on* (1) and an *off* (0) output when both the inputs were *on* (1) or *off* (0) (Table 2) (SI). Next, to match the INHIBIT function; an absorbance change at 444 nm was monitored as an output signal with a threshold value of 0.18. An increase in the absorbance value (i.e., when the output value is 1) was noticed only when OH<sup>-</sup>/F<sup>-</sup> was used as an input. For all other possibilities the output was 0. These observations complied with the function of an INHIBIT gate and are presented in Table 2 and the SI. Thus, the clear digital nature of the signal became apparent and a half-subtractor operation could be implemented with a combination of an XOR gate and an INHIBIT gate. We were led to establish that compound **4** could perform the operation of a unimolecular half-subtractor.

In conclusion, we can explain the integrated half-subtractor arithmetic operation through the emission mode output for compounds **1–3** and absorbance mode output for compound **4** by subtracting two simple XOR and INHIBIT gates. As a rare example,<sup>4b</sup> two wavelengths, which one could select to demonstrate the logic operations for compounds **1–3** mentioned above, are separated by ~100 nm. Thus, these simple molecules could be potential candidates for the development of a new generation of digital devices.

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**Figure 3.** Electronic spectra of  $3.0 \times 10^{-5}$  M (a) compound **4** only, (b) with HCl at pH 1.7 and (c) with TBAH at pH 11, (d) compound **4** in the presence of an equimolar amount of H<sup>+</sup> and OH<sup>-</sup> in H<sub>2</sub>O–DMF (3:7, v/v) solution.

### Supplementary data

Synthesis and characterization of compound **4**. Individual luminescence and optical spectra for compounds **1**, **2**, **3**, and **4** with different ionic inputs. Illustrations of logic operations. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.09.085.

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