CHEMILUMINESCENT AND PHOTOLUMINESCENT SWITCHES AND THEIR RELATION TO LOGIC GATES

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INTRODUCTION

The central processing unit (CPU) in digital devices sends electronic signals through a series of gates that perform logic functions to produce the desired response. While this process is standard in computing devices, by 2012, the components of the process (i.e. silicon chip and electronic wiring) will reach a theoretical size barrier due to current leakage in the wiring.[1] One step toward finding a solution to this problem has been the design of compounds, whose physical properties of which can function as logic gates. These molecular-scale logic gates may lead to the replacement of their electronic predecessors. Examples of molecular logic to date are comprised of compounds which undergo photoinduced reversible structural changes or supramolecular ionic binding upon exposure to external stimuli to elicit responses similar to logic operations.

The foundation of logic is based on binary operations similar to those in a modern computer. This base 2 form of arithmetic utilizes only two numbers: "0" indicating the absence of a signal, and "1" indicating the presence of a signal.[2] In many molecular logic operations, the output signal of "1" would be the digital representation of a spectroscopic output (i.e. fluorescence, phosphorescence, transmittance, absorption). The three fundamental types of logic gates are AND, NOT, and OR (Figure 1).[3] The definitions of these simple logic gates may be explained by using *connective* words. An AND logic gate gives an output only if both input 1 *and* input 2 are present. NOT logic produces an output if input 1 is *not* present. OR logic produces an output signal when either input 1 *or* input 2 is present. These simple logic operations may be combined to perform more complex operations including addition and subtraction.[4] The results of logic operations are typically tabulated in truth tables. While there have been examples of logic operations at the macromolecular scale including polymers[5] and DNA,[6] this review will focus on experimental work using multiple input chemi- and photoluminescent small molecules as potential digital processors.

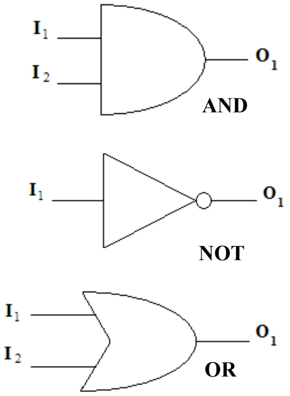


Figure 0. Simple Logic Gates

CHEMILUMINESCENT MULTIPLE INPUT LOGIC GATES

Many molecular logic gates function by cation binding that produces a fluorescent response.

These compounds undergo a photoinduced electron transfer (PET) mechanism from a receptor to the fluorophore, quenching or producing emission. In order for this donor/acceptor process to occur, the excited fluorophore must be able thermodynamically to drive the electron transfer. One may quantitatively predict this process by utilization of the Weller equation (1)[7] in which E_s is the singlet

$$\Delta G_{ET} = - E_{S.fluor} - E_{red.fluor} + E_{ox.receptor} - E_{i.p.} \qquad (1)$$

energy of the fluorophore, $E_{red.fluor}$ is the reduction potential of the fluorophore, and $E_{ox.receptor}$ is the oxidative potential for the receptor. The last term, $E_{i.p.}$, represents the free energy gained from bringing the ions into encounter distance and may be considered a constant parameter in the following situations due to the donor and acceptor being covalently linked together.[8] Quenching from receptor binding is depicted schematically in Figure 2.[9] Upon electronic excitation, a HOMO electron of the free receptor is transferred to the HOMO of the fluorophore to quench any emission. Thermal relaxation from the fluorophore LUMO to free receptor HOMO occurs through a nonradiative electron transfer. However, upon receptor binding, the HOMO of the bound receptor is reduced and no electron crossing takes place, allowing emission. In other instances, PET does not induce quenching, but instead produces a charge-separated excited state which may be monitored through absorbance or fluorescence.

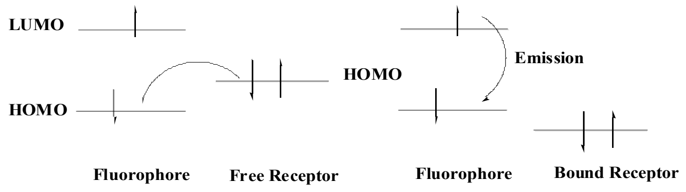
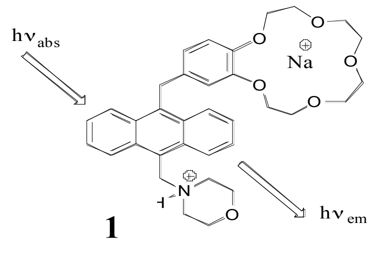


Figure 1. Emission Quenching with PET

Simple Chemiluminescent Molecular Logic: AND Gate

In 1993, de Silva[10] and coworkers introduced the first example of a multiple input molecular logic gate which was improved in 1997.[11] The improved anthracene derivative **1** (Figure 3) was designed[12] with two binding sites, one for H^+ one for and Na^+. When excited at the isobestic point (377 nm), the anthracene excited state was formed; however before emission can occur, this excited state was quenched by either electron transfer from the benzo crown ether or the lone electron pair on the tertiary nitrogen of morpholine. This prevention of fluorescence, quantified by a quantum yield (Φ_F) of 0.0031, is defined by a digital output of “0” in the truth table



1

I_1 (H^+)	I_2 (Na^+)	Output
0	0	0 (Φ_F = 0.0031)
1 (10^{-3}M)	0	0 (Φ_F = 0.0063)
0	1 (10^{-2}M)	0 (Φ_F = 0.0046)
1 (10^{-3}M)	1 (10^{-2}M)	1 (Φ_F = 0.24)

Figure 3. Molecular AND Gate **1** and Corresponding Truth Table[11]

(Figure 3). When H^+ or Na^+ ions are added to **1** (10^{-6} M in MeOH), quenching PET still occured and virtually no emission was observed. However, in the presence of both stimuli, both receptor sites became electron deficient and no PET was observed, and fluorescence occured ($\Phi_F = 0.24$). The design of this multiple input sensor mimics AND logic where both inputs are needed to produce an output. Digital representation of "on" and "off" forms of **1** are shown in the truth table (Figure 3).

Complex Chemiluminescent Molecular Logic

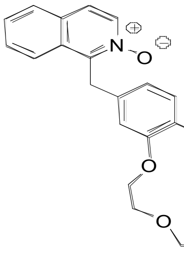


Figure 4. Complex Logic Gate **2**

Recently, several examples displaying more complex logic through merging several simple logic gates have been reported. Perez-Inestrosa[13] and coworkers presented this integration with isoquinoline-*N*-oxide-benzocrown ether derivative **2**. The structure of **2** incorporates multiple output fluorescent channels through fast electron transfers. Since PET is strongly dependent on the redox potentials of the donor-acceptor pair (equation 1), compounds similar to **2** were displayed both locally excited (LE) and charge transfer (CT) emissions by modifying the donor ability.[14] Upon excitation at 336 nm, LE emission at 400 nm was the only emission observed when isoquinoline-N-oxide was in its deprotonated form. Protonation of the *N*-oxide, **2** allowed for dual emission. When excited at the same wavelength, the emission was blue shifted to 380 nm. In addition, excitation at a higher wavelength (400 nm) allowed for PET emission at 550 nm. When K^+ was coordinated to the benzo-crown ether, PET was quenched in all situations, and if no H^+ is present, only LE emission was observed at 400 nm; however, in the presence of both stimuli, only blue shifted LE emission at 380 nm was observed. With the addition of Zn^{2+}, which coordinates preferentially to the *N*-oxide, the emission shifted and trends are similar to that of H^+. A three-input, three-output logic circuit may be constructed to predict the results (Figure 5). OR logic is present and observed as emission at 380 nm in the presence of H^+ or Zn^{2+}. NOR logic, defined as the inverted results of OR, was demonstrated with emission at 400 nm in the absence of either input. NOT logic was the major control for output 3 (λ_{em} 550 nm) which was observed when either input 1 or 2 are present but not 3.

I_1 (H^+)	I_2 (Zn^{2+})	I_3 (K^+)	O_1 λ_{em} 400nm	O_2 λ_{em} 380nm	O_3 λ_{em} 550nm
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

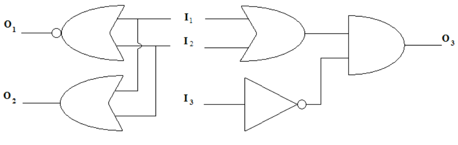
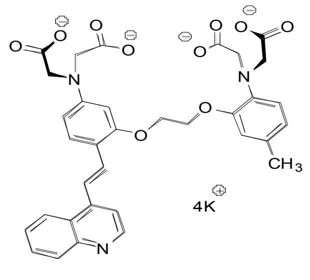


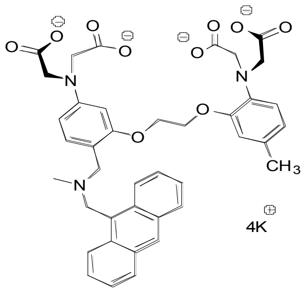
Figure 5. Complex Molecular Circuit **2** and Truth Table

Chemiluminescent Molecular Half-Adder

When combining an AND in addition to an exclusive OR (XOR) gate in parallel, one is able to perform simple arithmetic operations in an electrical device. The logic of XOR is that in which an output is detected in the presence of only one of the inputs, but in the presence of none or both inputs, no output is observed. Both AND and XOR logic operations perform different functions for addition. The XOR gate acts as a sum digit. Because binary code operates with only two digits, adding 1+1 requires that the sum be transferred to a carry digit and have a 0 remain in the sum digit. The transferred sum from the sum digit is now represented by a 1 in the carry digit. Therefore, the binary code of 10 is equal to 2. De Silva[15] and coworkers demonstrated this concept at the molecular level using chemiluminescent sensors **3** and **4**. Compound **3** possesses binding sites for Ca^{2+} and H^{+}. In the presence of only Ca^{2+}, binding of the cation to the tetracarboxylate motif destabilizes the receptor excited state to produce a blue shift in the absorbance (λ_{abs} 390nm → 347nm). When only H^{+} was introduced, a red shift in the absorbance is observed (λ_{abs} 390nm → 492nm). In the presence of both stimuli, no net shift was observed. When **3** was monitored by % transmittance, XOR logic was fulfilled. Compound **4** contains the same tetracarboxylate motif for Ca^{2+} binding in addition to a tertiary amine for H^{+} binding. When alone or in the presence of one cation, the fluorescence was quenched by PET. However, in the presence of both cations, binding produced two electron-deficient receptor sites and no electron transfer is possible, enabling emission. Combining **3** and **4** in the same solution study, both logic operations were fulfilled in parallel to construct a half-adder. Results are listed in the truth table (Figure 7). It was shown that when only one input was added (0+1 or 1+0), 01 was the result corresponding to 1. When both inputs were added (1+1), 10 was the result corresponding to 2.



3
XOR



4
AND

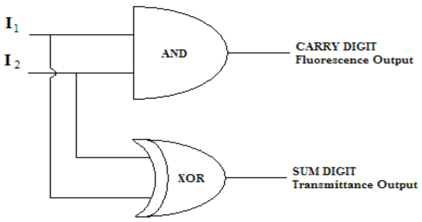


Figure 6. Molecular Half-Adder and Circuit

I_1 (H^{+})	I_2 (Ca^{+})	Carry Digit (λ_{Fluor} 419nm)	Sum Digit (% Trans 390nm)
0 ($10^{-9.5}$M)	0 ($10^{-9.5}$M)	0 ($\Phi F = 0.003$)	0 (8%)
1 (10^{-6}M)	0 ($10^{-9.5}$M)	0 ($\Phi F = 0.009$)	1 (40%)
0 ($10^{-9.5}$M)	1 ($10^{-2.3}$M)	0 ($\Phi F = 0.005$)	1 (33%)
1 (10^{-6}M)	1 ($10^{-2.3}$M)	1 ($\Phi F = 0.100$)	0 (12%)

Figure 7. Half Adder Truth Table

While the previous chemiluminescent examples are good examples of molecular logic, they provide more of a proof of concept due to their several limitations. The limited reusability of the gates hinders their practical utility due to problematic removal to the alkaline cation input. Developing a way to remove the inputs to reuse the gates would greatly improve the effectiveness of these examples. Limitations also are caused by the different input and output signals. Coupling the output signal from one gate to the input of another to mimic the connectivity in an electrical device without some type of transducer would not be possible.

PHOTOLUMINESCENT MOLECULAR LOGIC GATES

Complex Photoluminescent Molecular Logic

Molecular logic operations have also been demonstrated using photosensitive switches to produce different output signals. Raymo[16] and coworkers investigated spiropyran **5 (**Figure 8) that, upon different photo and chemical stimuli, produced a complex sequence of logic operations. Heterocycle **5** (10^{-4} M in MeCN) displayed no absorption above 400 nm, however; upon irradiation with UV light (254 nm), transformation to the fully conjugated and deprotonated merocyanine **6** occured with absorption and emission wavelengths at 563 nm and 647 nm respectively. Upon addition of acid to the solution of **6**, the protonated merocyanine **7** was generated. Both absorption and emission bands of **6** were replaced by an absorption band at 401nm for iminium ion **7**. Upon irradiation with visible light (524nm), **7** was converted back to the unconjugated **5** with consequent disappearance of the absorption band at 401nm. Following the reaction scheme in the opposite direction (Figure 8), **5** → **7** → **6** → **5** may be performed by acidification, basification, and irradiation with visible light. All absorption and emission spectra were identical to the previous cycle.

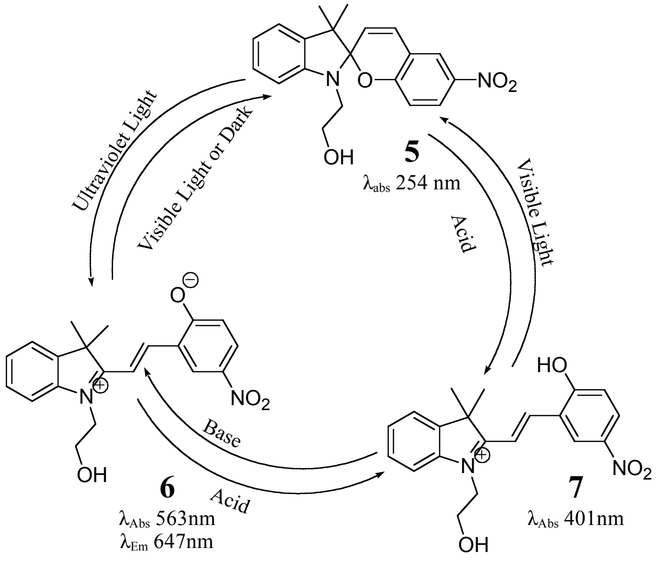


Figure 8. Swiching Cycle of **5**, **6**, and **7**

This photosensitive switch has also shown to communicate to and from fluorescent emitters[17] and other switches.[18] In another study by Raymo[19] and coworkers, energy transfer to **5** from pyrene **PY** was studied. When excited at 336 nm, one of the two emission maxima was detected at 373nm for **PY**. In the presence of **5**, the fluorescence intensity of **PY** decreased to 60% due to **5** absorbing the excitation light and the emitted light (reabsorption) from **PY**. It should be noted that the absorbance maxima of **5** is less than **7** and **6** which are equal in intensity. Upon conversion of **5** to **7** and **6** in the presence of **PY**, emission of **PY** at 373 nm decreased to 50% due to the increased absorbance of **7** and **6**. Upon conversion back to **5**, the reabsorption of emission decreases causing an increase of emission of **PY** back to 60%. By converting the emission intensity of **PY** to a digital representation of "on" (60%) and "off" (50%) Raymo constructed a truth table describing the results (Figure 9). A combinational logic circuit may also be constructed to represent and predict the outcome of this system which consists of seven interconnected gates which express AND, NOT, and OR logic.

I_1 (UV light)	I_2 (Visible Light)	I_3 (H^+)	O_1 (λ_{em} 373nm)
0	0	0	1
0	0	1	0
0	1	0	1
1	0	0	0
0	1	1	1
1	0	1	0
1	1	0	0
1	1	1	0

Figure 9. Truth Table of **PY** and Switch **5**

Photoluminescent Molecular Half Adder

Addition at the molecular level through photoluminescence is also possible and shown by Gust[20] and coworkers. Triad **8** consists of a porphyrin core (P), a fullerene (C_{60}), and a dihydropyrene photochrome (DHP) (Figure 10). Laser excitation of the porphyrin in triad **8** ($2{\cdot}10^{-5}$ M in 2-methyltetrahydrofuran) at 650 nm initiated PET from the DHP to C_{60} to form **DHP$^{\cdot+}$-P-**$C_{60}^{\cdot-}$ which $C_{60}^{\cdot-}$ has an observed absorbance at 1000 nm.[21] Irradiation with visible light (532 nm), photoisomerized of DHP to cyclophanediene (CPD) produced traid **9**. While a charge separated excited state is produced, it was short lived due to the high oxidation potential of CPD and no absorbance was observed in this state. Isomerization back to DHP was accomplished with irradiation with 355 nm light. Using this triad as an AND gate, the "off" setting is in the CPD-P-C_{60} form. When laser inputs set to 1064 nm (I_1) or 532 nm (I_2) were used, no isomerization of CPD to DHP was observed and the gate remains in the "off" setting. However, simultaneous irradiation at both wavelengths through a third-harmonic-generating (THG) crystal produced light at 355 nm (Figure 11). This induced isomerization of CPD to DHP producing the excited state DHP$^{\cdot+}$-P-$C_{60}^{\cdot-}$ with λ_{max} at 1000nm.

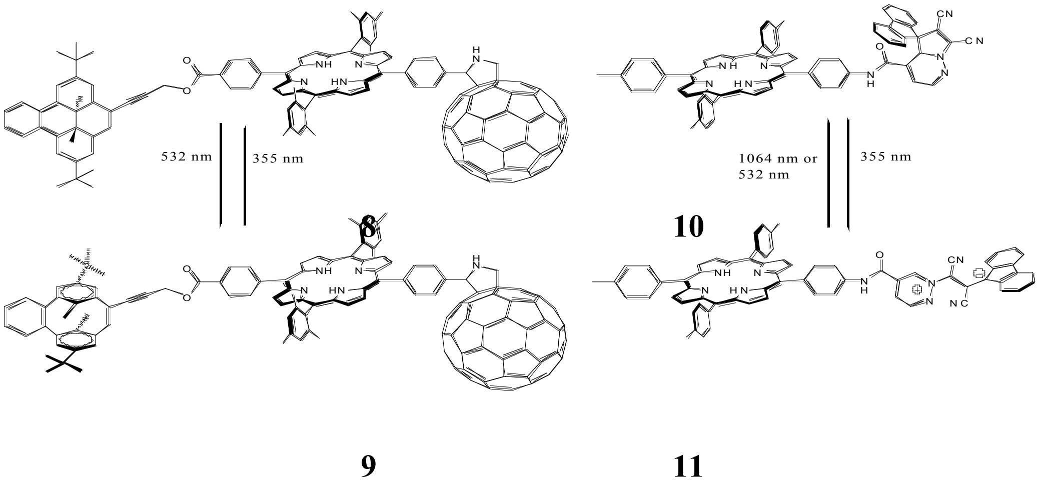


Figure 10. Photoluminescent Molecular Half Adder

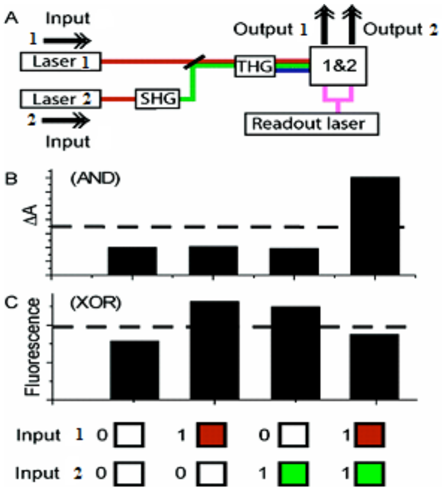


Figure 11. Experimental Setup of Half Adder (A) and Spectral Thresholds (B and C)

XOR logic with only light inputs and outputs were also established. Dyad **10** contains a porphyrin with a covalently linked dihydroindolizine (DHI). Irradiation of **10** ($1 \cdot 10^{-5}$ M in 2-methyltetrahydrofuran) with $\lambda \geq 590$ nm produces a strong porphyrin fluorescence at 720 nm.[22] However, upon irradiation with 355nm light, isomerization of DHI to betaine (BT) took place to produce dyad **11**. Light absorption by **11** produced a PET excited state $P^{\cdot +}$-$BT^{\cdot -}$ which strongly quenched prophyrin fluourescence. Laser excitation of this state with 1064 nm or 532 nm caused isomerization of BT back to DHI. P-BT may be set up to express XOR logic. The "off" state was set at P-BT **11** where no fluorescence was observed. Upon irradiation with either 1064 nm or 532 nm light, isomomerization to DHI takes place and fluorescence of P-DHI was observed. However, upon irradiation with both wavelengths, the third wavelength (355 nm) produced by THG does not allow net isomerization to DHI and no fluorescence was observed. Designating XOR logic as the sum digit and AND logic as the carry digit of a combined solution of **9** and **11** expresses simple addition when both lasers were irradiated (1+1) to produce an output of 10.

Photoluminescent logic gates have overcome two of the limitations of their chemiluminescent counterparts in that they utilize that same form of input as output, and that they are reusable. However, limitations in these examples are still apparent and hinder their use in practical devices. Photochemical pathways with spyropyran **5** exemplifies complex logic; however, conversion of isomers, **6** → **5** (10^{-4} s^{-1}), **5** → **7** (10^{-2} $M^{-1}s^{-1}$), and **7** → **5** (10^{-4} s^{-1}) is too slow to be of practical use in computing devices. A solution to this slow isomerization was overcome with fast isomerization of gates **8** → **9** and **9** → **8** (10^{7} s^{-1}) and isomerization between gates **10** and **11**. While the half adder function was demonstrated over 8 cycles, photodecomposition of **10** was observed through reduction of fluorescence quenching.

CONCLUSION

Several different logic operations were demonstrated at the molecular scale. Of these, the overlying modes of detection occurred through: (a) the presence of a PET to quench or initiate fluorescence, or (b) photoisomerization to alter or induce absorbance/fluorescence. Simple and complex logic operations, in addition to elementary mathematics, were demonstrated through supramolecular cationic binding to produce fluorescence. While these examples have yet to provide a practical purpose in regards to nanoscale devices, they provide more of a "proof of concept" to molecular digital processing. The photoluminescent complex logic operation and half adder presented are examples of proximate, practical utility due to similar inputs and outputs (photons) and have recently been shown to operate in the solid phase.[23] The concept of molecular computing, while challenging to develop, may not be that obscure considering information in all living organism is processed chemically and/or photochemically.

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