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# NOR and AND Logic Gates Based on Supramolecular Porphyrin−Fullerene Conjugates

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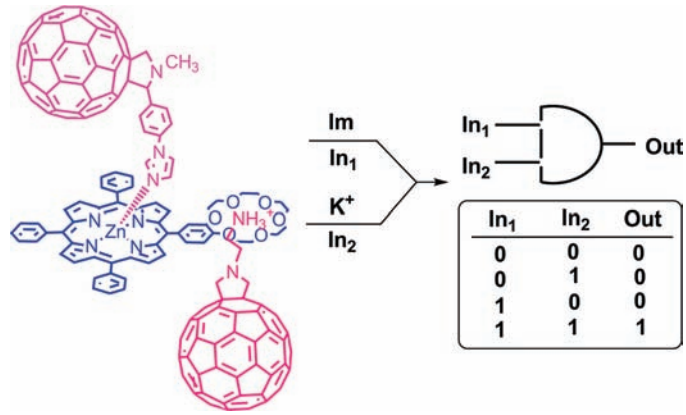
## ABSTRACT




**Supramolecular porphyrin−fullerene conjugates are employed to build NOR and AND logic gates. A crown ether appended zinc porphyrin and an imidazole or an alkyl ammonium functionalized fullerene are utilized. Quenching of zinc porphyrin fluorescence upon addition of binding-site-selective fullerene inputs forms the design basis of the NOR logic gate, while replacing the fullerene entities from the porphyrin−fullerene conjugate and restoring the original fluorescence by chemical inputs form the design basis of the AND logic gate.**

Photochemical events in supramolecular systems are useful for sensing, storing, and information processing.[1] Molecular level logic gates capable of simultaneously treating multiple inputs are extremely appealing as intelligent materials.[2] A wide range of elegant molecular and supramolecular systems responding to chemical, photonic, redox, magnetic, and temperature changes have been designed, synthesized, and tested for this purpose.[1,2] Among the various detection methods of logic gates, the fluorescence technique has been extensively used since detection can be brought down to a single molecule.[3] Often, the fluorescent logic gates operate by biasing a competition between fluorescence emission and photoinduced electron transfer (PET). Consequently, fluo-

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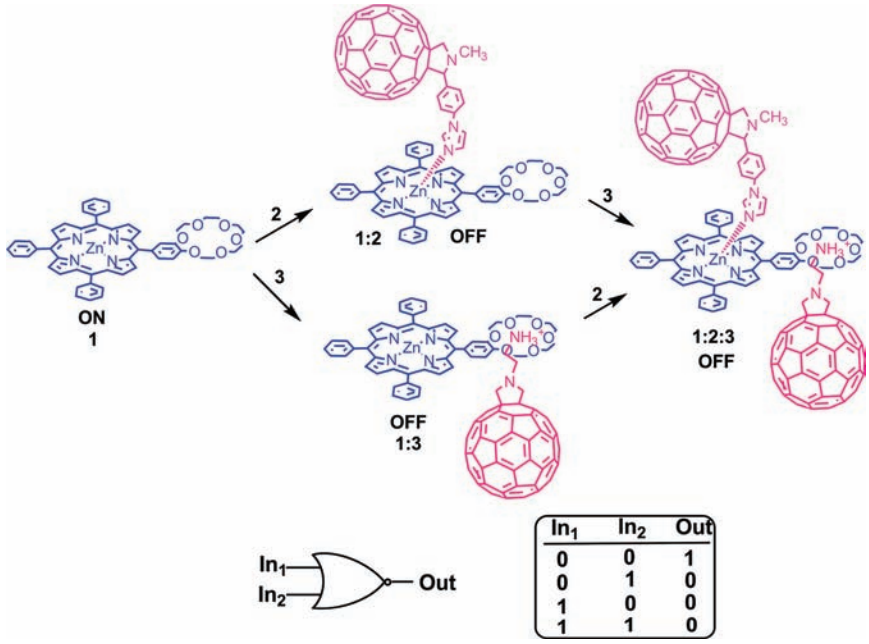
**Scheme 1.** Construction of the NOR Logic Gate via a Self-Assembly Approach[a]




[a] The symbol of the logic gate and the resulting truth table are also shown.

rescent logic gates exhibiting several logical functions have been reported as molecular-level devices.[1,2]

Recently, molecular and supramolecular systems based on porphyrin and fullerene have witnessed a rapid growth largely to understand the structural and mechanistic aspects of photoinduced electron transfer events and also due to their importance in solar energy harvesting by building organic photovoltaic devices.[4] However, utilizing these molecules in developing logic gates has been limited, although the simple PET quenching in supramolecular donor−acceptor dyads could be attributed to ON−OFF switching.[5] Gust and co-workers reported a novel example of a logic gate, that is, a molecule-based photonically switched half-adder using a molecular triad comprised of covalently linked porphyrin, fullerene, and a photochrome as components.[6] Here, we report NOR and AND logic gates using porphyrin−fullerene supramolecular conjugates. The logic functions are derived from controlling the fluorescence quenching as a result of photoinduced electron transfer in these conjugates by chemical inputs. Scheme 1 depicts the NOR logic gate based on the formation of a zinc porphyrin bound to two electron acceptor fullerene entities. The probe, benzo-18-crown-6 appended zinc porphyrin,[7] **1**, possesses two binding sites, viz., a coordinatively unsaturated zinc metal-ion binding site and a cation binding crown ether site. In *o*-dichlorobenzene (DCB), **1** emits at 606 and 651 nm (ON-state, Figure 1a) upon excitation of the Soret band at 430 nm. Equimolar addition of a phenyl imidazole functionalized fullerene, **2**, quenches the emission intensity of **1** over 70% of its original value (OFF-state, Figure 1b).[8] Similarly, equimolar addition

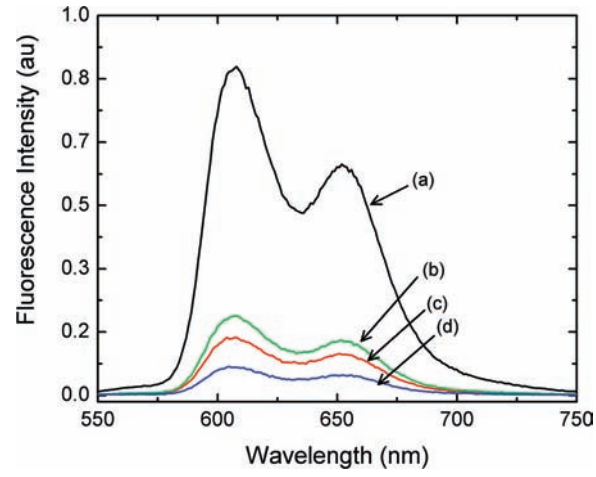



**Figure 1.** Fluorescence spectrum of **1** (20 $\mu$M) (a) in the absence of any addends, (b) upon equimolar addition of **2**, (c) upon equimolar addition of **3**, and (d) upon equimolar additions of **2** and **3** to the solution of **1** in DCB. $\lambda_{ex}$ = 430 nm.

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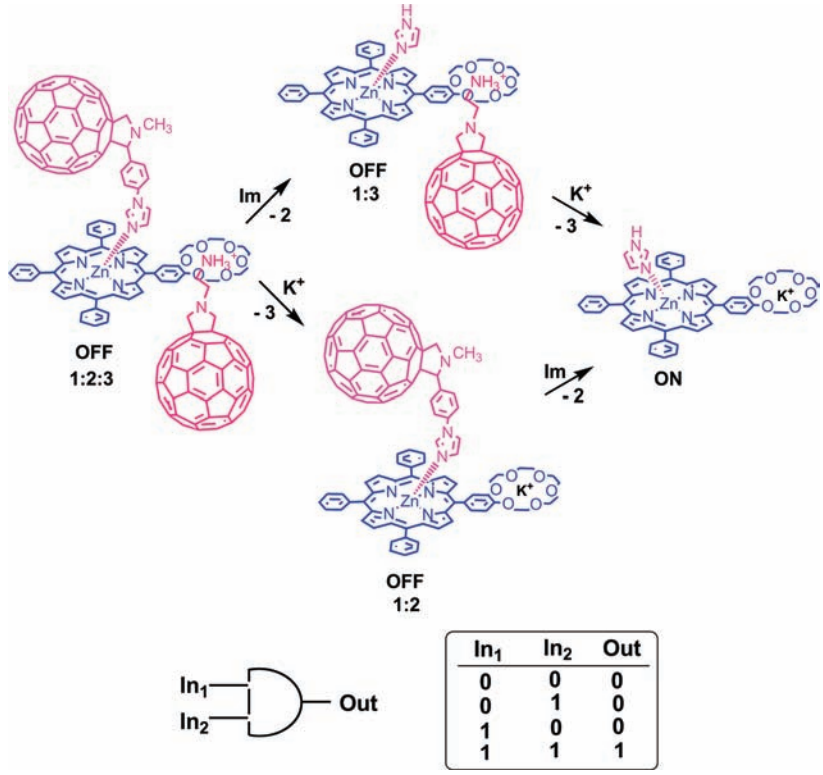
(6) (a) Andreassonk, J.; Kodis, G.; Terazono, Y.; Liddell, P. A.; Bandyopadhyay, S.; Mitchell, R. H.; Moore, T. A.; Moore, A. L.; Gust, D. *J. Am. Chem. Soc.* **2004**, *126*, 15926. (b) Gust, D.; Moore, T. A.; Moore, A. L. *Chem. Commun.* **2006**, 1169.

**Scheme 2.** Functioning of the AND Logic Gate via Chemical Inputs[a]




| $In_1$ | $In_2$ | Out |
|---|---|---|
| 0 | 0 | 0 |
| 0 | 1 | 0 |
| 1 | 0 | 0 |
| 1 | 1 | 1 |

[a] The symbol of the logic gate and the resulting truth table are also shown.

of an alkyl ammonium functionalized fullerene, **3**, to the solution of **1** quenches emission of **1** over 80% (OFF-state, Figure 1c).[10] As expected, equimolar additions of both **2** and **3** to **1** result in the formation of a nonfluorescent **1**:**2**:**3** complex (over 90% quenching, OFF-state, Figure 1d). The resulting truth table based on fullerene input and fluorescence signal output (by setting 70% of the original intensity as a threshold) corresponds to the NOR logic gate as shown in Scheme 1 along with the symbol of the logic gate.

The employed strategy for the development of the AND logic gate is shown in Scheme 2. Here, the nonfluorescent supramolecular complex, **1**:**2**:**3**, forms the initial probe molecule, and owing to the presence of two bound fullerenes, the complex exhibits quenching over 90% of the original fluorescence intensity of zinc porphyrin, **1** (OFF-state, Figure 2a). Systematic elimination of **2** by an axial ligand, imidazole, Im,[12] and **3** by the addition of $K^{+}$[13] forms the basis of the

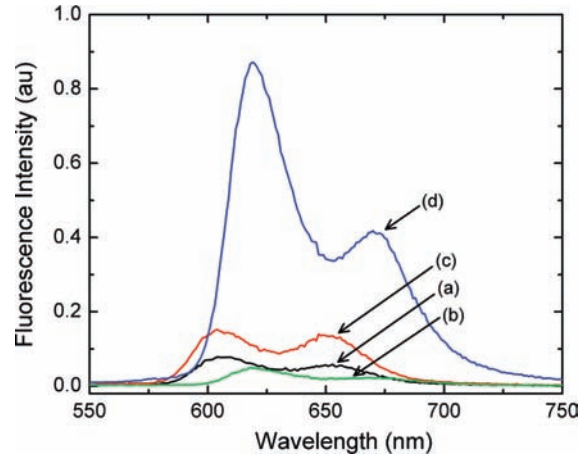



**Figure 2.** Fluorescence spectrum of (a) **1**:**2**:**3** complex formed in situ by equimolar mixing of the components (20 $\mu$M each), (b) **1**:**3** generated by the elimination of **2** by adding Im (2 equiv) to the solution containing the **1**:**2**:**3** complex, (c) **1**:**2** generated by the elimination of **3** by adding potassium tetrakis(4-chlorophenyl)borate (2 equiv) as $K^{+}$ source, and (d) **1** after eliminating both the bound **2** and **3** by the addition of imidazole and $K^{+}$ (both 2 equiv each) in DCB. $\lambda_{ex} = 430$ nm. The small shift in the fluorescence emission maxima is due to zinc porphyrin axial coordination to the basic imidazole ligand.

(7) The syntheses of the employed zinc porphyrin−crown ether and fullerene molecules are given in refs 9 and 11.

(8) The formation of pentacoordinated species via axial coordination of **2** to zinc tetraphenylporphyrin, ZnP, is spectrally characterized with a binding constant of $1.16 \times 10^4$ $M^{-1}$. Photoinduced electron transfer from the $^1$ZnP* to the coordinated **2** occurs at a rate of $1.7 \times 10^{10}$ $s^{-1}$ with a quantum efficiency of 0.97 in DCB. See ref 9 for details.

(9) D'Souza, F.; Deviprasad, G. R.; Zandler, M. E.; Hoang, V. T.; Klykov, A.; VanStipdonk, M.; Perera, A.; El-Khouly, M. E.; Fujitsuka, M.; Ito, O. *J. Phys. Chem. A* **2002**, *106*, 3243.

(10) The formation constant of a porphyrin−fullerene dyad, **1**:**3** via crown ether−cation binding, is reported to be $1.64 \times 10^4$ $M^{-1}$ in PhCN. Photoinduced electron transfer from the $^1$ZnP* of **1** to the coordinated **3** occurs at a rate of $2.6 \times 10^9$ $s^{-1}$ with a quantum efficiency of 0.97 in PhCN. See ref 11 for details.

(11) D'Souza, F.; Chitta, R.; Gadde, S.; Zandler, M. E.; McCarty, A. L.; Sandanayaka, A. S. D.; Araki, Y.; Ito, O. *Chem.−Eur. J.* **2005**, *11*, 4416.

logic function. Here, the utilized chemical inputs, imidazole, and $K^+$ have better affinity to the corresponding binding sites compared to the fullerene derivatives as revealed by their binding constants.[12,13] The **1**:**3** or **1**:**2** complexes obtained by elimination of **2** or **3** in the **1**:**2**:**3** complex still maintain low fluorescence intensity (OFF-state, Figures 2b and c) owing to the presence of the second bound fullerene entity. However, simultaneous elimination of both **2** and **3** from the **1**:**2**:**3** complex by the addition of Im and $K^+$ restores the original zinc porphyrin fluorescence (ON-state, Figure 2d). The resulting truth table based on the chemical input (Im and $K^+$) and fluorescence signal output (by setting 70% of the original intensity as a threshold) represents that of an AND logic gate as shown in Scheme 2 along with the symbol of the logic gate.

In summary, self-assembled supramolecular porphyrin−fullerene conjugates have been successfully employed to build NOR and AND logic gates. The fluorescence quenching−photoinduced electron transfer competition of zinc porphyrin upon addition of binding-site-selective chemical inputs (axial coordination and cation−crown ether complex forming fullerenes) forms the design basis of the NOR logic gate, while replacing the fullerene entities from the supramolecular porphyrin−fullerene conjugate and restoring the original fluorescence of zinc porphyrin by chemical inputs (imidazole and $K^+$ ions) forms the design basis of the AND logic gate. The present study opens up new channels for potential applications of porphyrin−fullerene conjugates in the area of molecular electronic devices. Further studies on building logic gates that are capable of performing repated operations are in progress in our laboratory.

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**Supporting Information Available:** UV−visible spectral changes during imidazole binding to **1** and Scatchard plot to obtain the binding constant. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The binding constant for imidazole coordination to **1** is found to be $2.5 \times 10^4$ $M^{-1}$, roughly twice the magnitude of binding of **2** to **1** in DCB (see Supporting Information for details).

(13) Sandanayaka, A. S. D.; Araki, Y.; Ito, O.; Chitta, R.; Gadde, S.; D'Souza, F. *Chem. Commun.* **2006**, 4327.