Molecular Logic

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Fluorescent Logic Gates Chemically Attached to Silicon Nanowires**

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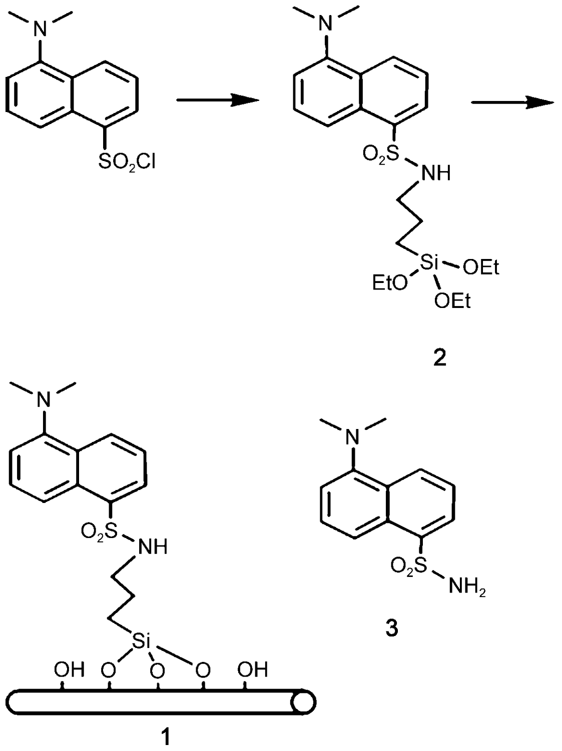
In recent years, the use of organic molecules, which are promising candidates for the realization of digital processing, has made remarkable progress in molecular logic gates because of the wide variety of molecular designs, syntheses, and light-emitting properties that are available.[1–7] Different logic gates based on organic molecules have been constructed, which encompass AND, OR, INH, XOR, XNOR, and NOR gates, and the half-adder and half-subtractor.[8–22] However, molecular logic gates are still far from operational at the single-molecular level.[3,6] In order to achieve practical applications, the functional molecules have to be assembled on carriers of sufficiently small dimensions.[20,22] One approach is to use polymer beads as a carrier and different fluorophores attached to the polymer surfaces to form various logic gates.[6] At the same time, the chemical stability of the materials for logic gates must be improved and the suitability of the logic elements for large-scale integration must also be realized. Silicon nanowires (SiNWs) are an important semiconducting material with high chemical stability and can be prepared in large-area arrays in a controlled fashion.[23–26] In addition, the ease of modification and compatibility of SiNWs with the prevalent integrated technology of silicon make SiNWs promising for construction of future nanosized chemical logic gate systems. Dansylamide (DA, **3**) is a typical intramolecular charge-transfer compound, and has interesting fluorescence properties that can be used in various applications.[27–31] Herein, we report the covalent immobilization of **3** on SiNWs to form **1** (DA-SiNWs) by the synthesis of derivative 3-(dansylamino)propyltriethoxysilane (**2**), and that the fluorescence of **1** exhibited selective responses to pH and Hg^{II} as well as Cl^- or Br^- ions, which permits a three-input chemical logic gate to be built on SiNWs.

SiNWs were prepared by oxide-assisted growth through thermal evaporation using silicon monoxide powder as the sole source.[32] The as-prepared SiNWs with a diameter of 15–28 nm were subsequently modified with **3** using 3-aminopropyltriethoxysilane (APTES) as the linker[33–35] (Scheme 1; the procedure used for the modification of SiNWs is detailed in the Supporting Information). The IR spectrum of **1** (Figure S1 in the Supporting Information) shows two additional peaks at 2920 cm^{-1} and 2958 cm^{-1} that are not present in the IR spectrum of SiNWs, these peaks correspond to the C−H vibration of **2**. Comparison of the XPS spectra of SiNWs before and after modification (Figure S2 in the Supporting Information) shows that the peak located at 402 eV in the XPS spectrum of **1** could be assigned to a nitrogen atom involved in an oxidized environment, which perhaps comes from interaction of nitrogen and oxygen groups near the surface. The peak observed at about 167 eV in the XPS spectrum of **1** could be assigned to the sulfur atom in sulfamide. However, no peaks are observed at similar positions in the XPS spectra of unmodified SiNWs. These



Scheme 1. The structures of the functional molecules and the SiNW modification procedure.

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results, together with the IR observations, further confirm that **2** was covalently attached to the surface of SiNWs.

As **3** and **1** are intramolecular charge-transfer compounds, their fluorescence could be altered by variation of the pH value of the system (Figure S3 in the Supporting Information). The fluorescence intensity of **3** and **1** reached a plateau at pH 5–8 and gradually decreased at lower pH values, as protonation of dimethylamine reduced intramolecular charge transfer, thus reducing the fluorescence intensity.

The fluorescence response of **1** to common metal ions in a neutral medium was investigated; the results showed that Hg^{II} ions have a particular effect on the fluorescence intensity of **1**. The fluorescence of **1** was progressively quenched as the concentration of Hg^{II} ions increased (Figure 1). The fluorescence properties of **1** in the presence of different metal ions are shown in Figure 2a, which indicates that only Hg^{II} ions quench the fluorescence of **1** whereas all other metal ions induce only insignificant changes in the fluorescence intensities. Remarkably, even in the presence of other metal ions at concentrations 10 times more than that of Hg^{II} ions, the quenching behavior of Hg^{II} ions was not altered.

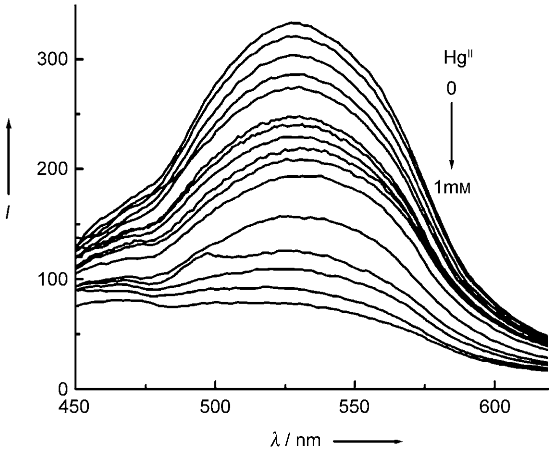


Figure 1. Fluorescence spectra of **1** (48 μg mL^{-1}) with increasing concentration of Hg^{II} ions in aqueous solution containing 4% CH_3CN (λ_{ex} = 330 nm).

To investigate the effects of anions on the fluorescence of **1** in a neutral medium, various anions such as OAc^-, NO_3^-, PO_4^{3-}, HSO_4^-, Cl^-, Br^-, I^-, and F^- were added to a solution containing **1**. Very little change in the fluorescence intensity of **1** was observed, except in the case of the HSO_4^- ion, with the fluorescence quenching probably result from a decrease in the pH value of the solution. Significantly, the presence of Cl^- or Br^- ions can efficiently inhibit the fluorescence quenching by Hg^{II} ions (Figure 2b).

The fluorescence intensity of **1** in the presence of various metal ions and anions is shown in Figure 3 and is explained as follows: 1) At low pH values, the fluorescence of **1** is quenched, irrespective of the presence of any metal ions and anions in the system. 2) Hg^{II} ions can quench the fluorescence of **1** in the absence of Cl^- or Br^- ions. 3) At high pH values, Cl^- or Br^- ions can effectively eliminate fluorescence quenching by Hg^{II} ions. Based on the above

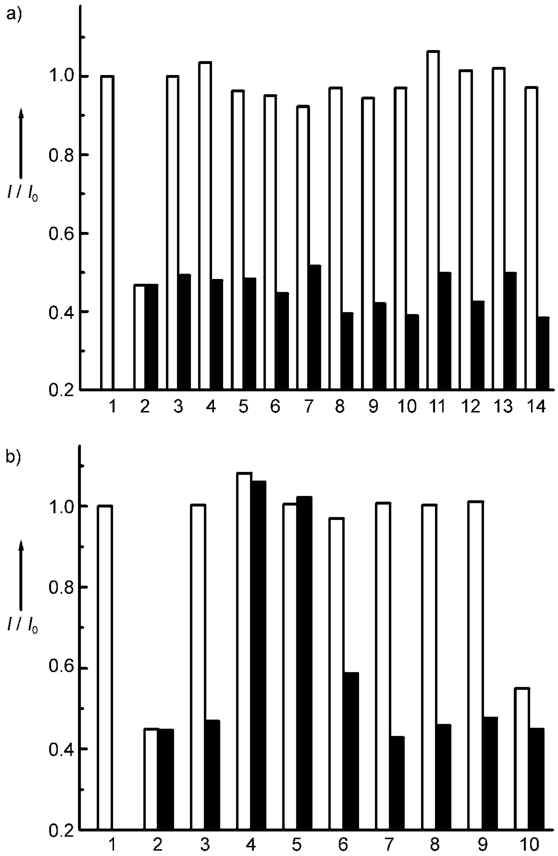


Figure 2. Relative fluorescence intensity of **1** (48 μg mL^{-1}) in the presence of various interfering ions (2 mM, white bars) and coexistence (black bars) of interfering ions (2 mM) with Hg^{II} (0.2 mM), in 4% CH_3CN aqueous solution (λ_{ex} = 330 nm). Interfering ions containing a) metal ions [1) no ions, 2) Hg^{II}, 3) Zn^{II}, 4) Cd^{II}, 5) Fe^{II}, 6) Co^{II}, 7) Ni^{II}, 8) Pb^{II}, 9) Cu^{II}, 10) Ag^{I}, 11) K^+, 12) Ca^{2+}, 13) Na^+, 14) Mg^{2+}]; b) anions [1) none, 2) Hg^{II}, 3) F^-, 4) Cl^-, 5) Br^-, 6) I^-, 7) $H_2PO_4^-$, 8) NO_3^-, 9) AcO^-, 10) HSO_4^-].

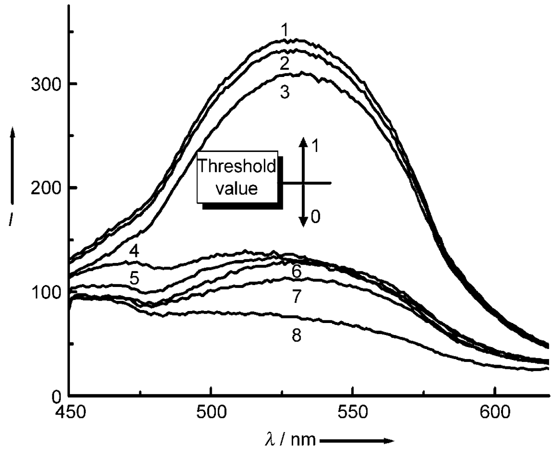
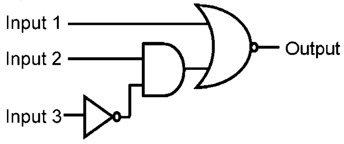


Figure 3. Fluorescence spectra of **1** (48 μg mL^{-1}) under different input conditions. 1) (**1** + Cl^-), 2) **1**, 3) (**1** + Hg^{II} + Cl^-), 4) (**1** + Hg^{II}), 5) (**1** + H^+), 6) (**1** + Cl^- + H^+), 7) (**1** + Hg^{II} + Cl^- + H^+), and 8) (**1** + Hg^{II} + H^+). Fluorescence intensities higher than the threshold value specified at 530 nm are assigned as 1 and intensities lower than that value are assigned as 0.

results, we have designed a logic device that defines a threshold of pH and Hg^{II} as well as Cl^- or Br^- ions as inputs, and the fluorescence signal of **1** as output. For input, the presence and absence of Hg^{II} ions ($> 6\times10^{-5}$ M) and Cl^- or Br^- ions (with 2 equivalents of Hg^{II} added) is defined as 1 and 0, respectively, and pH values greater than 4 and less than 4 as 0 and 1, respectively. For output, we define the normal fluorescence of **1** as 1 and the quenched fluorescence as 0 (detailed in Figure 3). Based on the above definitions and the fluorescence intensity at 530 nm, binary transfer of a logic operation can be realized by controlling the three inputs of pH and Hg^{II} as well as Cl^- or Br^- ions, and by monitoring the fluorescence output from **1**. The truth table and a schematic representation of the logic gates are presented in Table 1.

Table 1: Truth table for the logic gate **1**. The values in parentheses in the output column indicate the experimental fluorescence intensities in arbitrary units. The corresponding binary states are determined by applying a threshold value of $I_F = 200$. The errors were determined by repeating these experiments seven times.



Input 1 pH	Input 2 Hg^{II}	Input 3 Cl^- or Br^-	Output F_1 ($\lambda_{em} = 530$ nm)
0	0	0	1 (332 ± 12)
0	0	1	1 (342 ± 14)
0	1	0	0 (134 ± 8)
0	1	1	1 (308 ± 17)
1	0	0	0 (130 ± 8)
1	0	1	0 (129 ± 10)
1	1	0	0 (76 ± 5)
1	1	1	0 (111 ± 6)

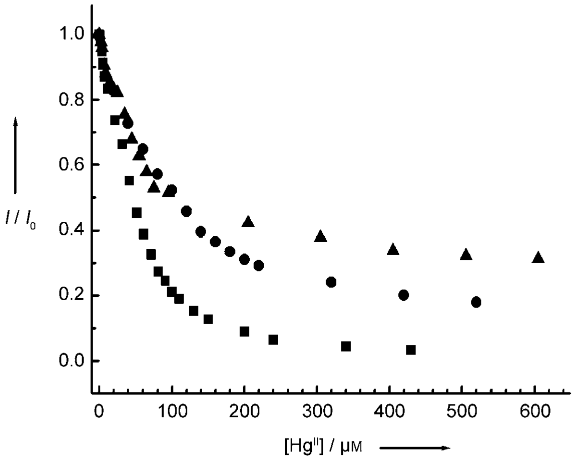


Figure 4. Titration of **3** (■ 1.0×10^{-5} M), **2** (● 1.0×10^{-5} M), and **1** (▲ 48 µg mL^{-1}) with Hg^{II} in aqueous solution containing 4% CH_3CN ($\lambda_{ex} = 330$ nm).

To develop a better understanding of the mechanisms of the logic gate, the dependence of the fluorescence of **3** on metal ions and anions was further investigated. Many different optical applications use **3** as fluorophore when it is linked to a receptor.[27–30] Experimental results suggest that the dependence of the fluorescence intensity of **3** in the presence of various ions is similar to that of **1** (Figures S4–S6 in the Supporting Information). Hg^{II} ions effectively quench the fluorescence of **3**, whereas other metal ions cause a negligible fluorescence change. The fact that Pb^{II} and I^- ions do not quench the fluorescence of **3** (Figure S7 in the Supporting Information) suggests that the quenching action of Hg^{II} ions is unlikely to be associated with the heavy atom effect. Rather, the fluorescence quenching may be attributed to charge transfer within **3** and Hg^{II} ions.[27,28] One can estimate the minimum ratio of Hg^{II} ions to **3** to achieve maximum quenching from the titration data between Hg^{II} ions and **3**. The experimental data (Figure 4) indicate that a Hg^{II}/**3** ratio of about 12 was required for this purpose. For logic gate operation with **1**, 70% more Hg^{II} ions were employed than the minimum amount required for maximum quenching of the fluorescence of **3**, so as to assure maximum quenching, since more Hg^{II} ions are required to quench the fluorescence of **1** than that of **3** (Figure 4).

By titration of the **3**–Hg^{II} and **1**–Hg^{II} systems with Cl^-, Br^-, or I^- ions, we found that the fluorescence of **3** and **1** gradually recovered and reached a point of inflexion at a concentration ratio Cl^-, Br^-, or I^-/Hg^{II} ratio of 2:1 (Figure S8 in the Supporting Information). The titration experiments of **3**–Hg^{II} also showed that the addition of Cl^-, Br^-, or I^- ions caused precipitation of $HgCl_2$, $HgBr_2$, or HgI_2. The amount of visible precipitation is in accordance with the solubility of these Hg^{II} halides. In contrast to the addition of Cl^- or Br^- ions, addition of a small quantity of I^- ions caused the formation of a heavy yellow precipitate, which complicated the fluorescence measurement. The yellow precipitate was identified as the beta form of HgI_2 by using X-ray diffraction. By monitoring the fluorescence intensity of **3**, we determined that more than 83% of the fluorescence of **3** could be recovered by addition of iodide ions after centrifugation and removal of HgI_2; the remaining fluorescence quenching may be attributed to the loss of **3** that arises from its adsorption to HgI_2. On the other hand, a ^{1}H NMR titration with **3** (Figure S9 in the Supporting Information) also indicated that the addition of Cl^- ions led to the effective recovery of the original ^{1}H NMR spectrum of **3** after the changes caused by the addition of Hg^{II} ions. These results demonstrated that the interaction between Hg^{II} and Cl^-, Br^-, or I^- ions is stronger than that between Hg^{II} ions and **3** or **1**. As a result, HgX_2 was formed, which led to the recovery of the fluorescence signal of **3** and **1**. Therefore, for logic gate operation, it is more desirable to use Cl^- or Br^- than I^- ions, as the precipitation of HgI_2 complicates the detection and reduces the fluorescence intensity. Two equilibrium reactions exist in this system:

$$\mathrm{Hg^{II}} + \mathrm{DA-SiNWs(orDA)} \rightleftharpoons \mathrm{DA-SiNWs(orDA)-Hg^{II}}$$

$$\mathrm{Hg^{II}} + 2\,\mathrm{X^-} \rightleftharpoons \mathrm{HgX_2}$$

The results of a titration of **3**, **2**, and **1** with Hg^{II} ions is shown in Figure 4. Addition of 12 equivalents of Hg^{II} ions caused 80 % quenching of fluorescence of **3**, but only 60 % quenching of fluorescence of **2**, thus showing that the same amount of Hg^{II} quenched **3** more effectively than **2** since the long alkyl chains in **2** obstruct the approach of Hg^{II}. Thus, it is understandable that the ability of Hg^{II} ions to quench the fluorescence of **1** is weaker than that of **3**.

In addition, we found that the reduced fluorescence of **1** could be restored by addition of EDTA to a solution containing **1** and Hg^{II} (Figure S10 in the Supporting Information). This observation suggests that the present SiNW-based chemical logic gate could be readily reset by the addition of EDTA and adjustment of pH values to each logic state, which is a crucial property for the practical applications of chemical logic gates.

In conclusion, a SiNW-based three-input chemically controlled logic gate, which combines the YES and INH operations, was realized by surface modification of SiNWs with **3**. Changes in pH and addition of Hg^{II} as well as Cl^- or Br^- ions were employed as the three inputs, and the fluorescence intensity of **1** was monitored as the output. Significantly, the present SiNW-based fluorescent logic gate is compatible with silicon-based semiconductor technology, thus providing a good approach to build various logic gates to integrate more logic operations. It can be envisaged that a chemical logic gate array may be formed by attaching several different fluorophores on an individual SiNW in an array of SiNWs, and the logic gates that have various functions within such an array could be further integrated for more complex operations at the nanoscale.

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