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## COMMUNICATION

## Fluorometric/colorimetric logic gates based on BODIPY-functionalized mesoporous silica

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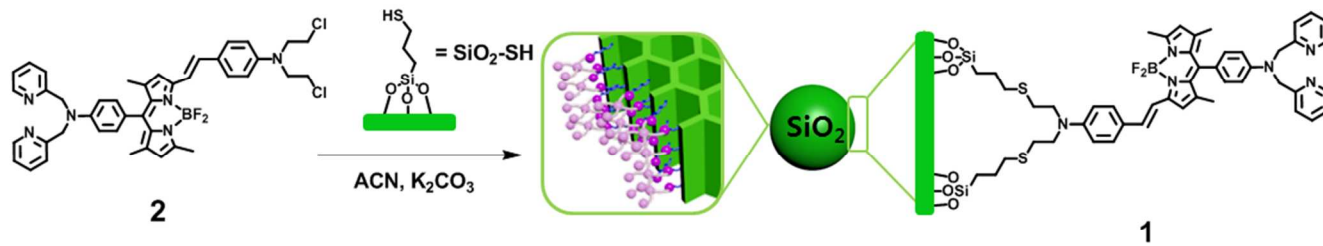
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Functionalized mesoporous SiO<sub>2</sub> nanoparticles are useful as colorimetric and fluorometric logic gates, which with various inputs such as metal ions induce photoinduced electron transfer (PET) and internal charge transfer (ICT) processes of functionalized mesoporous nanoparticles. We have demonstrated that metal ions acting as modulators in BODIPY-functionalized mesoporous SiO<sub>2</sub> can generate absorbance changes in accordance with the operation of a half-adder digital circuit. In addition, a NAND logic gate in the emission mode was obtained which exploited a different binding affinity for metal ions for different ligands.

Molecular logic gate research is built on an initial recognition by de Silva that fluorescence signals obtained in response to cations may be considered as analogous to the digital responses in electronic logic gates.<sup>1</sup> Molecules can undergo changes in the ground or excited states in response to modulators which can be other molecules, ions, or light of a certain wavelength. Molecular logic gates have great potential in the development of molecular-scale computers based on the application of various chemical systems for mimicking logic operations.<sup>2</sup> They have found applications in sensing, small-object recognition, and diagnostics, which have been the focus of great research interest. To identify ideal candidates that satisfy logic operations, considerable efforts have been dedicated in recent years to designing diverse logic gates, such as OR, XOR, AND, NAND, NOR, INHIBIT, half-adder and half-subtractor.<sup>3</sup>

Most of the reported logic gates employ small molecules or biomolecules as their inputs. However, the fluorescent, colorimetric, electrochemical or electrochemiluminescent signals produced by certain molecules as their outputs often suffer from complex labeling or modifying procedures and high cost to produce.<sup>4</sup>

BODIPY derivatives have become the rising star of fluorophores in the fluorescent chemosensor community<sup>5</sup> due to the remarkable fluorescent properties of these reagents, such as a high quantum yield and large extinction coefficients. However, more importantly, these dyes are open to derivatization in a multitude of ways through recently expanded "BODIPY chemistry".<sup>6</sup> Part of this versatile chemistry allowed us to design new BODIPY-based fluorescent molecules with different ligands attached at locations where the modulation of ICT and PET processes can be achieved independently. This is not an easy synthetic task with most other fluorophores. However, with BODIPY dyes, it involves only a few well coordinated sequences in the transformations. In recent years, nanoparticles as signal transducers for outputs have been used to fabricate various logic gates because of their unique physical and optical properties.<sup>7</sup> Gold nanoparticles have been used to fabricate colorimetric logic gates.<sup>8</sup> Various inputs such as metal ions induced the aggregation of functionalized gold nanoparticles, leading to color changes from red to purple as the output. In addition, cerium oxide nanoparticles and quantum dots have been employed as colorimetric and fluorescent logic gates, respectively.<sup>4b,e</sup> Despite this notable progress, the reported logic gate systems based on nanoparticles still have



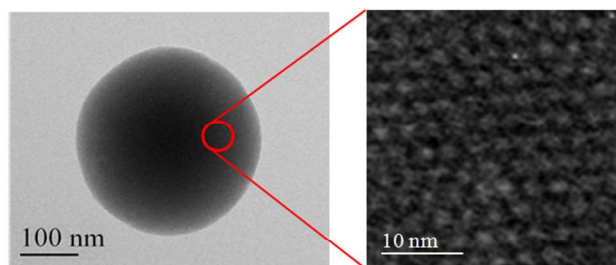
Scheme 1. Preparation for BODIPY dye-functionalized silica nanoparticle (1).

some limitations: 1) some environmental stimuli and quenchers may induce aggregation of the nanoparticles, which leads to fluorescence quenching and false results; 2) the reported logic systems usually need complicated labeling and the participation of enzymes, which inevitably increase the cost and complexity in application; and 3) the performance of logic systems has usually been studied in buffer solutions, and their applicability in real samples has not been explored.

BODIPY-functionalized mesoporous silica has attracted increasing consideration because they incorporate the advantages of mesoporous silica and BODIPY derivatives.<sup>9</sup> So far, the hybrid nanoparticles have found important applications in sensing, imaging and catalysis. In our previous work, we synthesized silica-based hybrid nanoparticles with excellent fluorogenic and colorimetric properties.<sup>10</sup> In the present work, we developed three logic gates (AND, NOR and NAND) based on fluorogenic/colorimetric outputs by taking advantage of the unique property of BODIPY-functionalized nanoparticles. The proposed logic gates were successfully used to detect  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions.

We targeted the styryl-BODIPY derivative **2** (Schemes 1 and S1). In designing this compound, we kept in mind that only the *meso*-substituent is likely to interfere with the excited state processes, partly because of the orthogonal arrangement of the *meso*-(8)-phenyl moiety under the steric influence of the neighboring (1,7) methyl groups, and partly due to the fact that, in the HOMO of the BODIPY chromophore, the C8 position is a nodal point. Therefore, the substituents at the *meso* position can be expected to alter the efficiency of the photoinduced electron transfer process (PET), but not intramolecular charge transfer (ICT). With this consideration, in the design of compound **2** (Scheme 1) the dipicolylamine ligand, which is known to be selective for  $\text{Zn}(\text{II})$ <sup>5f,11</sup> ions, was placed at the 8-position (*meso*) of the BODIPY core. This is easily accomplished by the reaction of dipicolylamine-substituted benzaldehyde (**4**) with 2,4-dimethylpyrrole under the usual conditions for BODIPY synthesis. The BODIPY dye (**3**) was then reacted with the known bis(chloromethyl)amine-tethered benzaldehyde (**7**) under Knoevenagel conditions, thus placing a strong ICT donor in full conjugation with the BODIPY core. The monostyryl-BODIPY dye (**2**) obtained in this way was purified by column chromatography. The ligand containing sulfur atoms is known to have high affinity for  $\text{Hg}^{2+}$  over many other metal ions.<sup>5j,12</sup> Therefore, the thiol group was attached

onto the surface of mesoporous  $\text{SiO}_2$  in toluene. Then, the  $\text{SiO}_2$ -SH nanoparticles were reacted with **2** in the presence of  $\text{K}_2\text{CO}_3$  in acetonitrile with vigorous stirring. The BODIPY-functionalized mesoporous silica (**1**) was fully characterized by

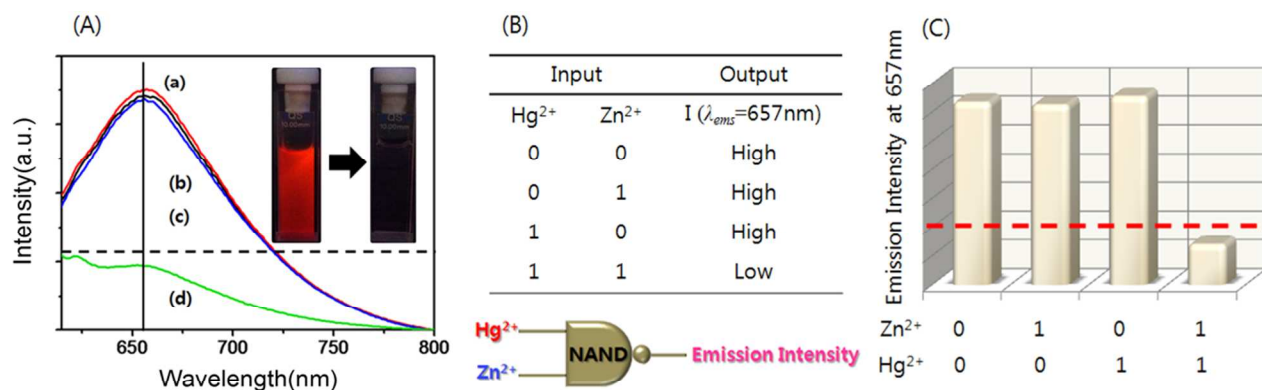


**Fig. 1** TEM images of BODIPY-functionalized mesoporous silica **1**.

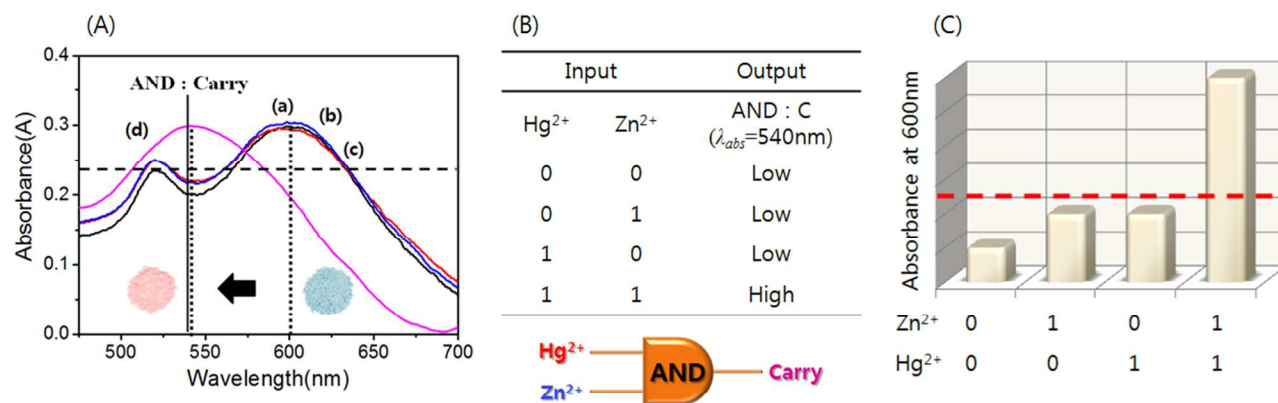
transmission electron microscopy (TEM), FTIR spectroscopy, time-of-flight second ion mass spectroscopy (TOF-SIMS), solid NMR and fluorophotometry.

A TEM image of BODIPY-functionalized silica **1** revealed a mesoporous structure with *ca.* 3 nm pore diameter (Fig. 1). The IR and TOF-SIMS results were in accord with bond formation; the IR spectrum of **1**, showed strong new bands at 3379, 2919, 2850, 2359, 1640, 1568, 1465, 1441, 1389, 1293 and 1054  $\text{cm}^{-1}$  which originated from BODIPY dye **2**, in accordance with **2** now residing on the  $\text{SiO}_2$  nanoparticles (Fig. S1). The TOF-SIMS spectrum of **1** displayed fragments attributable to **2** ( $m/z = 637.57, 754.78$  and  $814.90$ ), thereby providing evidence that **2** was anchored onto the surface of the mesoporous  $\text{SiO}_2$  (Fig. S2). The  $^{13}\text{C}$  CP/MAS spectrum of **1** appeared at 16-140, 135, 60, 55, 25 and 15 ppm.

It is interesting to note that the addition of  $\text{Zn}^{2+}$  ( $11.6 \mu\text{M}$  and  $23.2 \mu\text{M}$ ) ions to an aqueous dispersion of nanoparticles **1** ( $5.0 \text{ mg}$ ) had a minimal effect with very small changes in the emission or peak maximum (Fig. 2); apparently, the ICT donor dialkylaminophenyl group in full conjugation with the BODIPY core determined the spectrum, since  $\text{Zn}^{2+}$  at the applied concentration ( $11.6 \mu\text{M}$ ) had a much lower affinity for the dithiaethylene moiety and charge transfer was not altered to any extent. In addition, PET is known to be less significant in the longer wavelength region of the spectrum (*Vide infra*).<sup>13</sup> On the other hand, the addition of  $\text{Hg}^{2+}$  ( $11.6 \mu\text{M}$ ) alone led to an entirely different result (Fig. 2):  $\text{Hg}^{2+}$  ions preferred the sulfur



**Fig. 2** (A) Emission spectra of nanoparticle **1** ( $5.0 \text{ mg}$ ) without (a; red line) and with (b)  $\text{Hg}(\text{II})$  ( $11.6 \mu\text{M}$ ; black line), (c)  $\text{Zn}(\text{II})$  ( $11.6 \mu\text{M}$ ; blue line) and (d)  $\text{Hg}(\text{II})$  ( $11.6 \mu\text{M}$ )/ $\text{Zn}(\text{II})$  ( $11.6 \mu\text{M}$ ) in aqueous solution. (B) Truth table and (C) emission response for NAND gate in the presence of different input signals ( $\lambda_{\text{ex}}=600\text{nm}$ ).



**Fig. 3** (A) Absorption spectra of mesoporous nanoparticle **1** (5.0 mg) without (a; black line) and with (b) Hg(II) (11.6  $\mu\text{M}$ ; red line), (c) Zn(II) (11.6  $\mu\text{M}$ ; blue line) and (d) Hg(II) (11.6  $\mu\text{M}$ )/Zn(II) (11.6  $\mu\text{M}$ ) in aqueous solution. (B) Truth table and (C) absorption response for AND gate in the presence of different input signals.

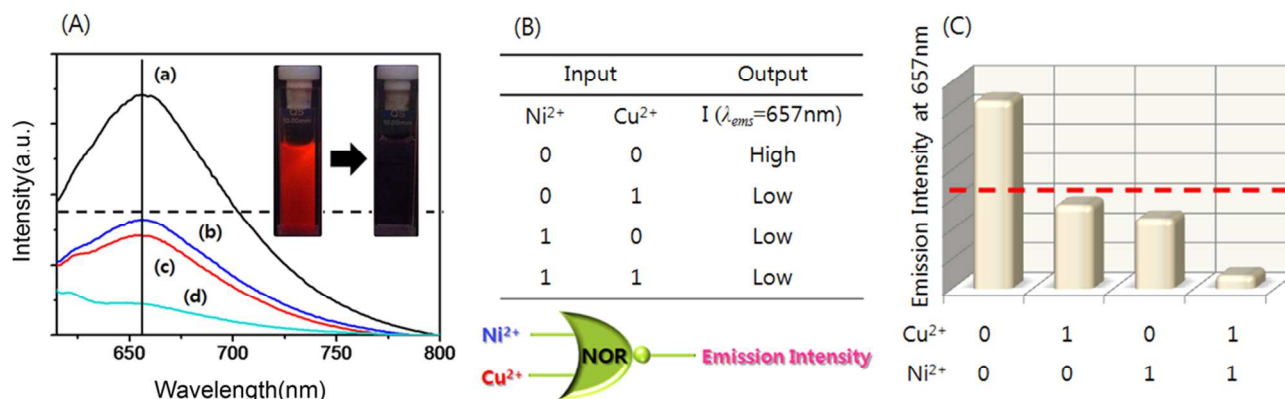
atoms, causing a blue shift of 60 nm. Furthermore, the fluorescence intensity changes of nanoparticles **1** were observed upon addition of 23.2  $\mu\text{M}$  of Zn<sup>2+</sup> or Hg<sup>2+</sup> alone, respectively (Fig. S5). No significant changes were observed in 23.2  $\mu\text{M}$  of Zn<sup>2+</sup> or Hg<sup>2+</sup> alone. These were due to a reduced charge transfer upon metal ion binding, thereby increasing the HOMO-LUMO gap.<sup>14</sup> However, PET from the *meso* substituent became more pronounced, since Hg<sup>2+</sup> does not have a particularly high affinity for the nitrogen atoms; thus the emission intensity at the peak (657 nm) remained high. When both ions were added at the concentrations above, finally the PET from the dipicolylamine substituent and the bis(mercaptoethyl)amine moiety was blocked; a large quenching effect at 657 nm occurred. The inset picture shows the color signaling which is in accordance with the NAND logic when the emission was recorded at 657 nm.

The absorption spectra of hybrid nanoparticle **1** in the presence of metal ion are shown in Fig. 3. The spectral changes are the direct consequence of the relative affinities of the hybrid nanoparticle **1** for Hg<sup>2+</sup> and Zn<sup>2+</sup> (11.6  $\mu\text{M}$  and 23.2  $\mu\text{M}$ ). An aqueous dispersion of the hybrid nanoparticle **1** (5.0 mg) exhibited an absorbance peak at 600 nm. When Zn(II) ions were added in the form of nitrate salt, no significant changes were observed in either the absorbance peak or absorption

wavelength. In addition, the absorbance changes of the hybrid nanoparticle **1** upon addition of higher concentration of Hg<sup>2+</sup> or Zn<sup>2+</sup> (23.2  $\mu\text{M}$ ) alone were almost same to those of obtained from lower concentration of Hg<sup>2+</sup> or Zn<sup>2+</sup> (11.6  $\mu\text{M}$ ) (Fig. S6). Clearly, even an excess of these ions targeted just one of the ligands, thus blocking ICT only partially. However, when both ions were added, the peak shifted further toward the shorter wavelengths and the new metal-bound complex absorbs maximally at 540 nm. When the absorbance was recorded at 540 nm, the data were in accordance with the AND logic gate.

The fluorescent changes of the hybrid nanoparticle **1** were observed upon addition of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions in aqueous solution (Fig. 4 and Fig. S7). Ni<sup>2+</sup> and Cu<sup>2+</sup> ions have intermediate property between soft acid and hard acid.<sup>15</sup> These ions preferred to interact with the nitrogen of the dipicolylamine moiety and the sulfur atoms of **1**. Compared to free **1**, at the concentrations used in the present work (Ni<sup>2+</sup> or Cu<sup>2+</sup> at 11.6  $\mu\text{M}$ , 23.2  $\mu\text{M}$  and Ni<sup>2+</sup>/Cu<sup>2+</sup> at 11.6  $\mu\text{M}$ ), only when cations were added as inputs was emission markedly reduced. These two cations do not induce an enhanced and blue shifted emission from **1**. Thus, inputs from two metal ions were required simultaneously for the large emission quenching at 657 nm; this behavior is in accordance with an NOR logic gate.

In conclusion, we have readily prepared BODIPY-



**Fig. 4** (A) Emission spectra of nanoparticle **1** (5.0 mg) without (a) and with (b) Ni(II), (c) Cu(II) (11.6  $\mu\text{M}$ ) and (d) Ni(II) /Cu(II) (11.6  $\mu\text{M}$ ). (B) Truth table and (C) emission response for NOR gate in the presence of different input signals ( $\lambda_{\text{ex}}$ =600nm).

functionalized mesoporous SiO<sub>2</sub> **1** by a straight forward procedure. The hybrid nanoparticle **1** should be useful as fluorogenic/colorimetric logic gates using different metal ions as inputs. BODIPY derivatives are particularly useful in this regard, because they allow straightforward placement of ICT and PET donors on the same molecule, which greatly increases signal diversity. The proposed logic gate systems have several distinctive advantages. Firstly, the operation is simple, easy to perform and cost-effective. Secondly, the logic systems do not need specific conditions. Thirdly, the logic operations can be carried out not only in an aqueous media, but also in a practical sample. Although this work is at the proof-of-concept stage, we expect it to be an important starting point for research on hybrid logic systems and to have great application potential for fabricating higher-complexity molecular devices with versatile functionalities and a broad range of application in sensing, clinical diagnostics and environmental monitoring.

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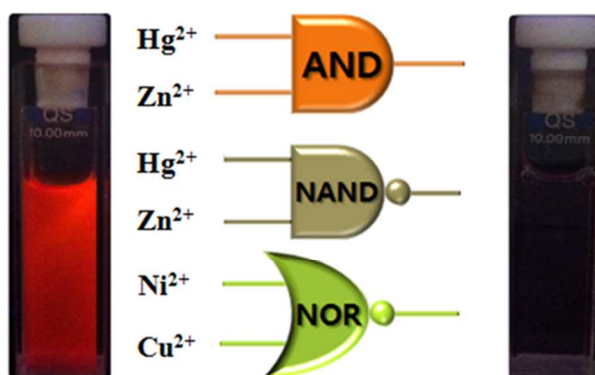
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## Table contents



We have demonstrated that metal ions acting as modulators in BODIPY-functionalized  $\text{SiO}_2$  nanoparticles can generate absorbance changes in accordance with the operation of a half-adder digital circuit.