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INHIBIT logic operations based on light-driven β-cyclodextrin pseudo[1]rotaxane with room temperature phosphorescence addresses†‡

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INHIBIT logic gates based on light-driven β -cyclodextrin pseudo[1]rotaxane were conveniently fabricated in aqueous solution utilizing induced circular dichroism (ICD) and photocontrolled reversible room temperature phosphorescence (RTP) as output addresses respectively.

The design and construction of molecular systems capable of information processing potentially used to develop molecular scale electronics, chemical and biological computers on the molecular level have attracted considerable attention and may have technological potential. Since the proposal of the first molecular AND gate by de Silva and co-workers about 20 years ago,¹ a variety of molecule-based systems capable of realizing Boolean logic gates (AND, OR and NOT gates, *etc.*) have been realized, with the prospect of creating more sophisticated and complex circuits.² Many of these systems employ stimuli-responsive rotaxanes and pseudorotaxanes,³ in which the relative positions of the interlocked components can be altered by external stimuli to create logic gates with chemical or photonic inputs and recognizable output signals such as UV/Vis absorption, fluorescence, electrochemical signals, circular dichroism, *etc.*

Phosphorescence, especially the room temperature phosphorescence (RTP), is an excellent method expected to obtain the output signals of rotaxanes and pseudorotaxanes to construct more complex devices. RTP possesses some remarkable merits such as fewer interferences, high selectivity, quick response, easily measurable and long lifetimes, high signal-to-noise ratios, *etc.*⁴ However, only a few examples of RTP logic gates have been reported up to now.^{2h}

Cyclodextrins (CD) continue to be extensively used in the construction of various rotaxanes and pseudorotaxanes.⁵ They can admit a variety of appropriately sized guest molecules

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into the cavity and form inclusion complexes in aqueous solution. Moreover, many kinds of chemically modified CDs have been designed and synthesized to enhance the original binding ability, the molecular selectivity and the spectral changes upon inclusion complexation with guests.⁶

Since the establishment of cyclodextrin induced room temperature phosphorescence (CD-RTP) by Cline Love *et al.* first in 1984,⁷ it has developed rapidly with its wide applications in environmental science, agricultural chemistry, biological and medical science.⁸ Numerous phosphor–CD systems were developed, and the most typical one is the α -bromonaphthalene– β -CD system.⁹ Phosphor molecules enter the CD cavity, which provides a protective environment for the emitted triplet state of phosphor from interaction with oxygen molecules and other dissolved quenchers, and form an inclusion complex. We have reported a photocontrolled reversible room temperature phosphorescence encoding β -CD pseudorotaxane based on a ternary system including β -CD, α -bromonaphthalene (α -BrNp) and a photo-responsive azo dye in aqueous solution.¹⁰

Herein, a binary system with light-driven pseudo[1]rotaxane based on azobenzene modified β -CD (β -CD-Azo) and α -BrNp was constructed to investigate the CD-RTP as an efficient tool to address the threading and dethreading of pseudorotaxanes (Scheme 1).



Scheme 1 Synthetic routes of pseudo[1]rotaxane $\beta\text{-CD-Azo}$ and its inclusion phenomenon with $\alpha\text{-BrNp}$ in water.

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[†] This communication is dedicated to Prof. Seiji Shinkai on the occasion of his 70th birthday.

[‡] Electronic supplementary information (ESI) available: Experimental details, ¹H NMR, UV-Vis, ICD and RTP spectra and other characterization data mentioned in the text. See DOI: 10.1039/c3cc49820d

In this β -CD-Azo- α -BrNp system, light irradiation on β -CD-Azo can reversibly control its isomerization and the subsequent complexation with α -BrNp due to which the association constant order is β -CD/*trans*-azo > β -CD- α -BrNp > β -CD/*cis*-azo.¹⁰ The ICD responses of β -CD-Azo to the light irradiation with different frequencies correspond to an INHIBIT logic gate. While using 360 nm as well as α -BrNp as two inputs and RTP emission as output, compound β -CD-Azo was demonstrated to be an AND logic gate. Furthermore, its RTP emission output with oxygen or heat as the third input can express INHIBIT logic functions in aqueous solution. To the best of our knowledge, this is the first light-driven β -CD pseudo[1]rotaxane platform which can conveniently achieve INHIBIT logic operations with adjustable ICD and RTP as output addresses.

The photoisomerization of the pseudo[1]rotaxane β-CD-Azo was measured by ¹H NMR spectroscopy, 2D ¹H ROESY NMR spectroscopy as well as absorption spectroscopy (see details in ESI^{\ddagger}). It suggested that the β -CD-Azo preferentially exhibited self-inclusive conformation in which the azobenzene moiety is deeply self-included in the cavity of the β -CD in the original state rather than forming a polymer.¹¹ Upon irradiation with UV light at 360 nm, β-CD-Azo could be photoisomerized from trans to cis until it reaches the photostationary state (the photoisomerization efficiency is about 60%, see ESI‡) and the cisazobenzene unit dethreads from the β -CD cavity. It can be reversibly shifted back after light irradiation at 430 nm. Compared with the ternary system we reported previously,¹⁰ the β -CD-Azo- α -BrNp binary system undergoes E/Z photoisomerization to reach the photostationary state for a shorter time (2 than 15 min, respectively).

It is well known that the azobenzene unit can be induced to generate an ICD signal when it is included into the cavity of CD.¹² As seen in Fig. 1A, the ICD spectrum of aqueous β -CD-Azo solution (curve black) showed positive Cotton peaks at about 258 nm (20.45 cm⁻³ mol⁻¹ cm⁻¹) and 436 nm (17.90 cm⁻³ mol⁻¹ cm⁻¹) and

a negative Cotton peak at about 318 nm ($-10.55 \text{ cm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$), which, respectively, correspond to the n– π^* and π – π^* transition bands of the azobenzene group located in β -CD.¹³ Owing to the *trans–cis* photoisomerization of the azobenzene unit in the pseudo[1]rotaxane β -CD-Azo and its subsequent dethreading out of the β -CD cavity, the prolonged irradiation with 360 nm light leads to a gradual increase in the intensity of the Cotton peak at 258 nm and 436 nm, but a decrease at 320 nm (curve red). And the ICD spectral changes can be shifted back by irradiation at 430 nm (blue curve, overlapped with the black curve).

Based on the above results, we designed a logic device that defined the light irradiation at 360 nm and 430 nm as inputs and the ICD signal of the β -CD-Azo as output. For output, the intensity of ICD signals above 30 mdeg at 436 nm is denoted as **1** and the one below as **0** (Fig. 1B). Based on the above definitions, β -CD-Azo was demonstrated to be an INHIBIT logic gate with optical inputs and outputs in aqueous solution.

The RTP spectrum of this binary system β -CD-Azo- α -BrNp in aqueous solution is shown in Fig. 2A (for more detailed data see ESI[‡]). In the original state, β -CD-Azo in aqueous solution prefers forming trans-configuration, and then the azobenzene moiety attached to the β -CD rim can be deeply embedded into the β -CD cavity to form the intramolecular inclusion complexes in aqueous solution. Most of the α -BrNp molecules were free in the solution without obvious RTP emission owing to the oxygen guenching while only a little α -BrNp was included by the β -CD cavity, which engendered weak RTP signals (green curve in Fig. 2A). Upon irradiation by 360 nm light for 60 min, the inducing RTP emission of β-CD-Azo-α-BrNp in aqueous solution is obviously enhanced (red curve in Fig. 2A) due to which the azobenzene unit is photoisomerized to dethread from β-CD and more α-BrNp molecules are included into the β-CD cavity. The RTP lifetime was found to be about 0.58 ms (Fig. S9, ESI‡).9a After the photoisomerization of the β -CD-Azo- α -BrNp system, the equilibrium



Fig. 1 (A) ICD emission spectra of β -CD-Azo under different light irradiation:¹³ (a) black, on the initial state; (b) red, after irradiation by 360 nm light for 2 min; (c) blue, irradiated by light at 430 nm for 2 min. (B) Output (ICD intensity at 436 nm) response to the absence and presence of light irradiation at 360 nm and 430 nm; (C) corresponding truth tables; and (D) scheme representation for the INHIBIT logic gates.



Fig. 2 (A) RTP emission spectra of β-CD-Azo under different input conditions: (a) black, initial state; (b) red, irradiation by 360 nm light and addition of α-BrNp; (c) green, α-BrNp; (d) purple, irradiation by 360 nm light, adding α-BrNp and purging with O₂; (e) blue, irradiation by 360 nm light, adding α-BrNp and heated to 60 °C. (B) Output (RTP intensity at 528 nm) responding to different external stimuli; (C) corresponding truth tables; and (D) scheme representation for the INHIBIT logic gates.

can be reversed by irradiation at 430 nm for 60 min. Owing to the good photoreversibility of the β -CD-Azo pseudo[1]rotaxane, the photochemical process of this binary system is highly reproducible over more than five cycles with UV irradiation alternating between 360 and 430 nm in 60 min intervals (ESI,‡ Fig. S8).

The potential of the pseudo [1] rotaxane β -CD-Azo to execute logic function with RTP as output was also demonstrated. The change in the RTP signals in the binary system is obtained by both the photoisomerization and the complexation with α -BrNp of the β -CD-Azo, which means both the light irradiation and the addition of α -BrNp are needed to induce the strong RTP emission. This pattern of RTP intensity as output is read as an AND logic response according to the truth table (Fig. 2C). Moreover, the RTP is sensitive to the obvious environment conditions, including oxygen and temperature of the solution etc. In the event, RTP output is nearly quenched by purging oxygen or heating to 60 °C, respectively. This behavior pattern exactly fits the NOT truth table. NOT and AND logic gates are integrated within the unimolecule, which makes the system suitable for the execution of INHIBIT functions. So two INHIBIT logic gates were manipulated by utilizing UV irradiation at 360 nm, temperature change, purging with O_2 and addition of α -BrNp as inputs, and the RTP emission of the binary system at 528 nm as the output. For inputs, we defined the presence and absence of 360 nm light, α -BrNp and O₂ as 1 and 0, and the temperature above and below 60 °C as 1 and 0, respectively. For output, the normal RTP of the β-CD-Azo-α-BrNp system is denoted as 1 and the quenched RTP as 0 (Fig. 2B). In addition, the excitation-emission wavelengths and other factors related to RTP emission intensities as inputs are additional selections to construct more logic gates.

In summary, a reversible photocontrolled pseudo[1]rotaxane based on the azobenzene-modified β -CD was prepared in aqueous solution, and its photoisomerized movement was characterized by 1D and 2D ¹H NMR, circular dichroism and UV-Vis absorption spectra *etc.* Their complexation behavior with the typical phosphor α -BrNp was addressed with RTP signals. INHIBIT logic gates based on this system were fabricated with the light irradiation, temperature change, O₂ purging, α -BrNp as the inputs and ICD or RTP as output, respectively. Significantly, the strategy based on the RTP intensity as output in this work provides a feasible approach for the fabrication of other integrated, complicated and multifunctional molecular logic devices. A possible way to immobilize the above operation supramolecular system onto carriers or substrates for further practical applications in information technology is underway.

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- 13 It should be noted that the intensity of the maximum peak of the ICD spectra was beyond the limit when using 1 cm quartz, so 1 mm quartz cell was more appropriate to be used at the same concentration during the RTP measurement ([β -CD-Azo] = 2.0 × 10⁻³ mol L⁻¹).