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Photothermal-responsive [2]rotaxanes†

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Cite this: *RSC Advances*, 2013, **3**, 2341

Received 15th September 2012, Accepted 30th November 2012

DOI: 10.1039/c2ra22171c

www.rsc.org/advances

Three photothermal-responsive α-cyclodextrin-based [2]rotaxanes were prepared *via* the copper(I)-catalyzed azide–alkyne cycloaddition, in which the α-cyclodextrin ring was threaded onto the azobenzene dumbbell component. The difference between the three [2]rotaxanes are the length of the ethylene glycol repeating chains connected between the azobenzene and triazole units in the dumbbell components. The α-cyclodextrin rings in the [2]rotaxanes can be reversibly switched between the azobenzene unit and triazole/ethylene glycol unit driven by the *trans*–*cis* isomerization of the azobenzene unit. The *trans*-to-*cis* isomerization of the azobenzene unit under UV light irradiation (365 nm) leads the α-cyclodextrin ring moving to the triazole/ethylene glycol unit, while the *cis*-to-*trans* isomerization of the azobenzene unit under either visible light irradiation or heating enables the α-cyclodextrin ring shuttling back to the azobenzene station. The different ethylene glycol repeating chains in the [2]rotaxanes can affect (1) the isomerization rates of the azobenzene units, *i.e.* the longer the chain, the faster the isomerization rate, and (2) fluorescent quantum yields of the [2]rotaxanes, *i.e.* the longer the chain, the lower the fluorescent quantum yield. In addition, the quantum yields of the [2]rotaxanes were enhanced by UV light irradiation and decreased back upon visible light irradiation or heating at 65 °C. The current research provides a fundamental understanding of the working mechanism for photothermal-responsive [2]rotaxanes.

Introduction

Numerous endeavors have been directed towards the development of light- and heat-powered molecular machines, since reversible operation of such molecular machines controlled by these stimuli normally does not generate byproducts.[1] Mechanically interlocked molecules (MIMs), such as rotaxanes and catenates, possessing remarkable electronic, photophysical, mechanical, and thermal properties, are suitable building blocks for constructing nanostructured functional materials,[2] molecular switches,[3] molecular logic gates,[4] molecular wires,[5] and memory devices.[6] In particular, rational combination of functionalities, *e.g.* fluorophores,[7] integrated groups,[8] and nanoparticles,[9] with MIMs can further expand extraordinary physical and chemical properties of MIMs, making MIMs excellent entities for a variety of applications in the areas of nanoelectronics,[10] nanocomposites,[11] and mechanical devices.[12] Although light- and heat-powered switchable rotaxanes based on the *trans*–*cis* photoisomerization of the azobenzene dumbbell component threaded into the α-cyclodextrin (α-CD) ring have been investigated,[13,14] rare research attentions have been paid to the construction of photothermal-responsive rotaxanes with fluorescence modulation, and to the investigations for the influence of different molecular lengths of the azobenzene dumbbells on the shuttling rate of the α-CD ring in the rotaxanes. Herein, we report a new class of photothermal-switchable [2]rotaxanes in which the shuttling of the α-CD ring between the azobenzene unit and triazole/ethylene glycol unit was controlled by the *trans*–*cis* isomerization of the azobenzene unit under light irradiation and heating. Different ethylene glycol repeating chains connected between the azobenzene and triazole units in the [2]rotaxanes can affect (1) the isomerization rates of the azobenzene units, *i.e.* the longer the chain, the faster the isomerization rate, and (2) fluorescent quantum yields of the [2]rotaxanes, *i.e.* the longer the chain, the lower the fluorescent quantum yield. The movement of the α-CD ring between the azobenzene unit and the triazole/ethylene glycol unit driven by the *trans*–*cis* isomerization of the azobenzene unit also influences fluorescent quantum yields of the [2]rotaxanes to a certain extent.

Results and discussion

Syntheses of dumbbells and [2]rotaxanes

By following a modified procedure reported by Anderson *et al.*,[14c] intermediate 7-[(4-hydroxyphenyl)diazenyl]naphtha-

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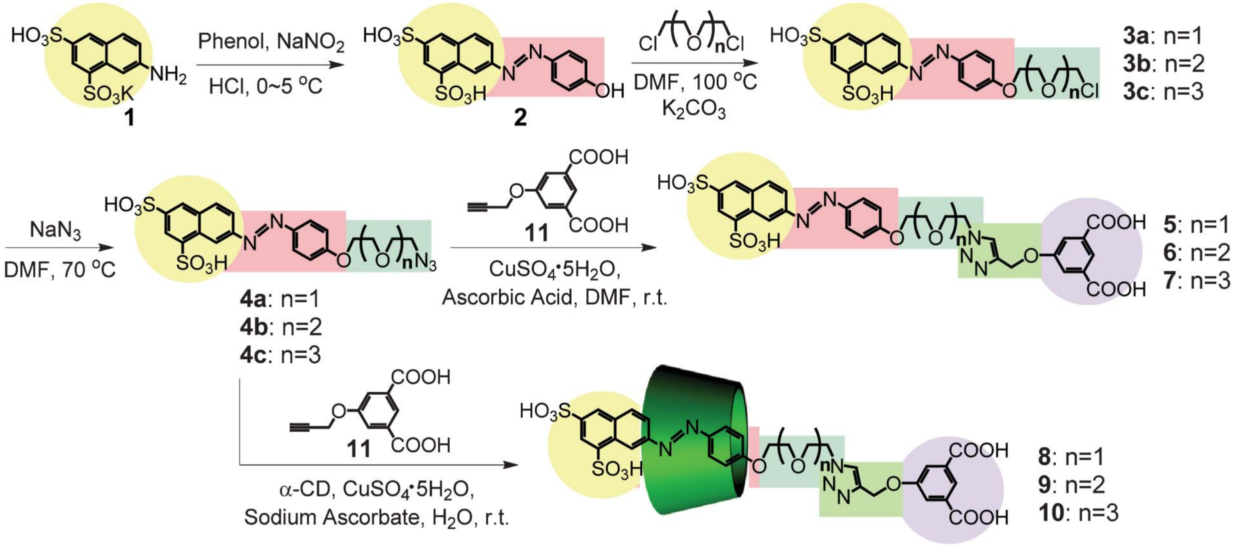
† Electronic Supplementary Information (ESI) available: preparation and characterization data. See DOI: 10.1039/c2ra22171c



Scheme 1 A schematic illustration for the syntheses of [2]rotaxanes and dumbbell molecules.

lene-1,3-disulfonic acid (**2**) was prepared through a diazonium coupling reaction between 7-amino-1,3-naphthalenedisulfonic acid monopotassium (**1**) and phenol (Scheme 1). The azide-containing azobenzene compounds (**4a–4c**) with different ethylene glycol spacers were obtained in 2 steps with *ca.* 65% overall yield. A convenient and sequential combination of template-directed synthetic pathway and the copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC) was adopted for the preparation of photothermal-responsive [2]rotaxanes (**8–10**). In a typical reaction, the compound **4** containing the azide unit and fluorescent stopper was stirred with the α-CD ring in aqueous solution for 2 h in order to form the corresponding [2]pseudorotaxanes [**4**⊂α-CD]. The other stopper isophthalic acid functionalized with alkynyl unit (**11**), $CuSO_4·5H_2O$, and sodium ascorbate were added to an aqueous solution containing [**4**⊂α-CD], and the reaction mixture was stirred under N_2 atmosphere for another 48 h, leading to the formation of [2]rotaxanes (**8–10**). The corresponding dumbbell molecules (**5–7**) as references in the control studies were also prepared from the compounds **4** and **11** in DMF in the absence of the α-CD ring.

Characterizations of [2]pseudorotaxanes and [2]rotaxanes

The [2]pseudorotaxane [**4a**⊂α-CD] prepared by mixing one equiv. of the compound **4a** and two equiv. of the α-CD ring in aqueous solution was clearly characterized by ^1H NMR spectroscopy as shown in Fig. 1. The excess addition of the α-CD ring is to ensure that the compound **4a** was completely complexed with the α-CD ring. To avoid the isomerization of *trans*-azobenzene to its *cis*-isomer, the mixture solution was shielded from light. The downfield shifts of corresponding proton signals $H_{a–g}$ of the azobenzene unit in the presence of the α-CD ring indicate that the α-CD ring encircles the *trans*-azobenzene unit of the compound **4a**, forming the [2]pseudorotaxane [**4a**⊂α-CD] (Fig. 1b). The proton signals of the compound **4a** present no obvious changes after stirring the sample in the dark at room temperature even after 1 day, indicating that there was no *trans*-to-*cis* isomerization occurring in the dark environment (Fig. 1c,d). The appearances of some new peaks, corresponding to the protons of *cis*-azobenzene, were observed by putting the sample-containing NMR tube under an ambient light (Fig. 1e–g). The intensities of these new peaks were increased upon exposure time, and reached their photostationary state after 5 h. All of the new peaks disappeared after heating the sample in the dark at 65

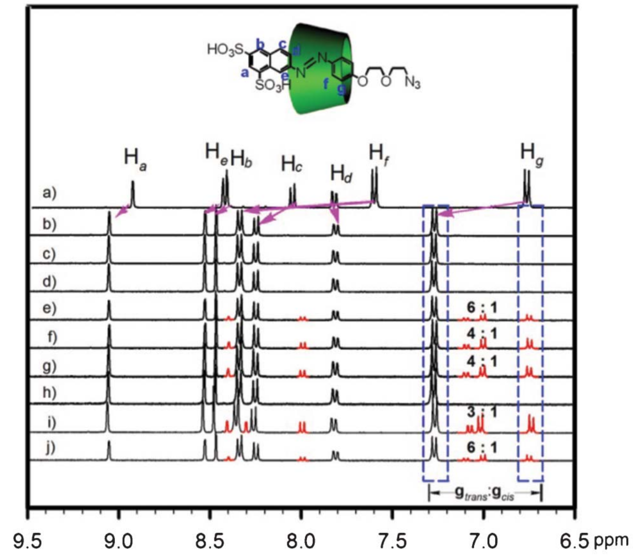


Fig. 1 ^1H NMR spectra of (a) compound **4a**, after the addition of the α-CD ring at room temperature in the dark for (b) 2 h, (c) 5 h, and (d) 1 d, then putting the NMR tube under an ambient light at room temperature for (e) 2 h, (f) 5 h, and (g) 1 d, (h) followed by heating the sample at 65 °C for 2 h, (i) then irradiated the sample by UV light at 365 nm for 30 min, and finally (j) irradiated the sample by visible light for 30 min. The proton peaks H_{b-d} of the azobenzene unit were incorrectly assigned in our previous report.[20] This correction leaves the discussions and the conclusion unchanged.

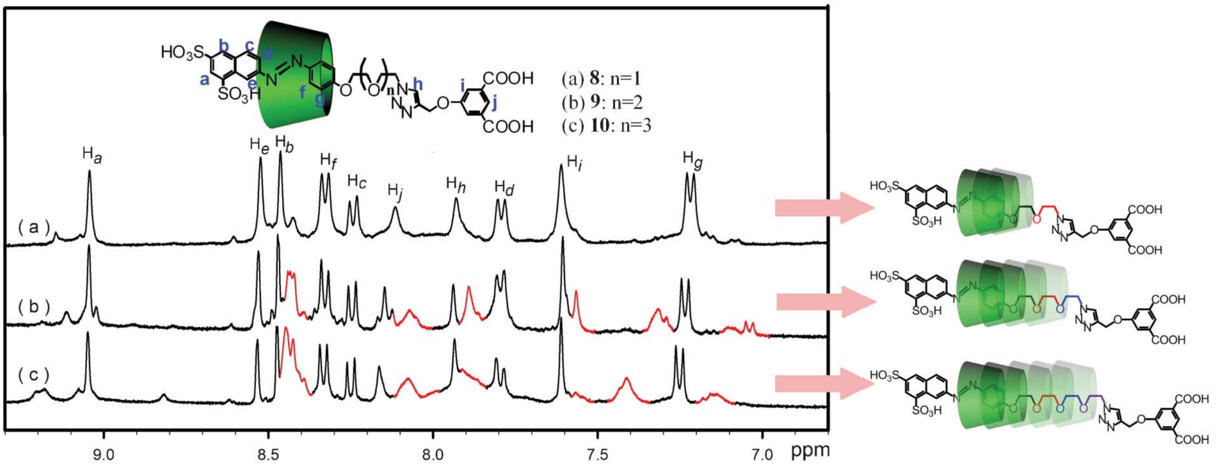


Fig. 2 Partial ^{1}H NMR spectra of [2]rotaxanes (a) **8**, (b) **9**, and (c) **10** in D_2O.

°C for 2 h (Fig. 1h), and appeared again under the UV light irradiation. The molar ratio between *trans*-isomer (g_{trans}) and *cis*-isomer (g_{cis}) reached to 3 : 1 after the UV light irradiation for 30 min as shown in Fig. 1i. The recovery of the *cis*-azobenzene to its *trans*-form by visible light irradiation was also investigated. Unlike the treatment of heating, the proton peaks of the *cis*-isomer cannot completely disappear after visible light irradiation (Fig. 1j). These observations indicate that the *trans*–*cis* isomerization of the [2]pseudorotaxane powdered by alternating UV light irradiation and heating is reversible and controllable. Similar phenomena were observed in the cases of the [2]pseudorotaxanes [**4b**⊂α-CD] and [**4c**⊂α-CD] (Fig. S2 in the ESI†).

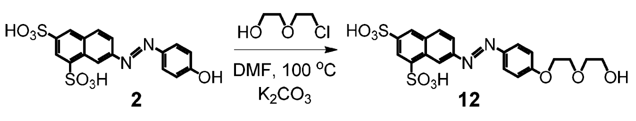
The [2]pseudorotaxanes [**4**⊂α-CD] underwent click chemistry with the alkynyl unit-containing isophthalic acid in aqueous solution, forming corresponding [2]rotaxanes **8–10** as shown in Scheme 1. Since the α-CD ring has two sides and the dumbbell component is non-symmetrical, two stereoisomers of each [2]rotaxane can be formed. We were unable to separate the stereoisomers by using conventional methods. For the sake of clarity, we present only one stereoisomer in which the secondary side of the α-CD ring faces the naphthalene stopper in Scheme 1. Fig. 2 shows partial ^{1}H NMR spectra of [2]rotaxanes **8–10** in D_2O with emphasis on the aromatic protons of the azobenzene axles. As compared with the ^{1}H NMR spectrum of [2]rotaxane **8**, some new peaks were observed in the cases of [2]rotaxanes **9** and **10** upon increasing the length of the ethylene glycol chains connected between the azobenzene unit and triazole moiety. It is known[15] that ethylene glycol chains can also form the inclusion complexes with the α-CD ring under relatively low binding constants. Increasing the length of the ethylene glycol chains in the [2]rotaxanes changes the location distribution of the α-CD ring to a certain extent. Partial encirclement of the α-CD ring on the ethylene glycol chains leads to the signal shifts of some protons on the ethylene glycol units. These interesting observations suggest the influence of the ethylene glycol chains on the co-conformation of the [2]rotaxanes.

The fact that the azobenzene unit can be included inside the α-CD cavity in the [2]rotaxanes was confirmed by ^{1}H ROESY NMR spectra. The ^{1}H ROESY NMR spectra (Fig. S3 in the ESI†) of the [2]rotaxanes **8–10** show that the aromatic protons H_f and H_g of the azobenzene unit are spatially close to the internal protons H_5 and H_3 of the α-CD ring. The formations of the [2]rotaxanes **8–10** were further evidenced by electrospray ionization mass spectrometry (ESI–MS). MS spectra exhibit the molecular weights at 1713.94 ($[M+H]^+$, calculated: 1713.4) for [2]rotaxane **8**, 1757.84 ($[M+H]^+$, calculated: 1757.45) for [2]rotaxane **9**, and 1802.03 ($[M+H]^+$, calculated: 1801.48) for [2]rotaxane **10** (Fig. S4 in the ESI†). The MS spectra also indicate good purity of [2]rotaxanes **8–10**.

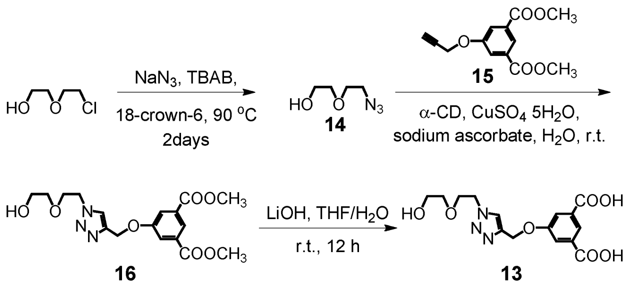
Switching process of [2]rotaxanes

Detailed studies to characterize and prove the molecular shuttling of the α-CD ring between the azobenzene moiety and the triazole/ethylene glycol unit triggered by reversible *trans*–*cis* isomerization of the azobenzene unit were performed on the reference compounds **12** and **13**, and [2]rotaxanes **8–10** by using ^{1}H NMR, UV-vis and circular dichroism (CD) spectra. The synthetic procedures for the preparations of the reference compounds **12** and **13** were shown in Schemes 2 and 3, respectively.

The association constants (K) of the azobenzene compound **12** with α-CD ([**12**⊂α-CD]) present significant differences before and after UV light irradiation (Fig. 3). The details for calculating the K values were shown in the ESI.† The K values of 4666 and 164 M^{-1} were obtained for [**12**⊂α-CD] before and after UV light irradiation at 365 nm, respectively. Interestingly, the K value of the triazole/ethylene glycol **13** with the α-CD ring



Scheme 2 A schematic illustration for the synthesis of the reference compound **12**.



Scheme 3 A schematic illustration for the synthesis of the reference compound **13**.

[**13**⊂α-CD] was calculated to be 2600 M^{-1}, which lies between the *K* values of [**12**⊂α-CD] before and after UV light irradiation. These association constants theoretically support the feasibility of controlled forth and back shuttling of the α-CD ring between the azobenzene unit and the triazole/ethylene glycol recognition site in the [2]rotaxanes.

The changes in UV-vis absorption at 370 nm (Fig. 4), CD spectra at 360 nm (Fig. 5), and ^{1}H NMR spectra (Fig. 6), corresponding to the azobenzene unit in the [2]rotaxanes upon alternating treatments by UV light irradiation and visible light irradiation/heat, reveal that the photo-switching process of the α-CD ring driven by the *trans*-to-*cis* and *cis*-to-*trans* isomerization of the azobenzene unit is reversible and controllable. Fig. 4 shows representative spectral evolutions of the [2]rotaxanes **8–10** in aqueous solution upon alternating irradiation of UV and visible light at 5 °C, when the thermal-triggered isomerization of the azobenzene unit is negligible during the measurements under this temperature. In general, the spectral evolutions of the [2]rotaxanes for both the *trans*-to-*cis* and *cis*-to-*trans* isomerization of the azobenzene unit present two isosbestic points at 325 and 435 nm. The *trans*-to-*cis* and *cis*-to-*trans* isomerizations reach their photostationary states within 5 min and 3 min, respectively. Interestingly, the rate of these spectral changes depends on the structural nature of the [2]rotaxanes. Based on the kinetics of the spectral evolution with either the decrease or increase of the π–π* absorption band at 370 nm (Fig. 4G), apparent rate constants were derived by fitting the time dependence of the maximum absorbance with either an exponential decay (K^a, 1st-order) upon UV light irradiation or an exponential growth (K^b, 1st-order) upon visible light irradiation.[16] Under the same concentration (0.5×10^{-4} M) of the [2]rotaxanes, the resulting decay constants display an order of **10** ($6.2 \times 10^{-3}\ s^{-1}$) > **9** ($5.5 \times 10^{-3}\ s^{-1}$) > **8** ($3.7 \times 10^{-3}\ s^{-1}$) by UV light irradiation. Importantly, the recovery constants by visible light irradiation were again found to be an order of **10** ($3.62 \times 10^{-2}\ s^{-1}$) > **9** ($3.09 \times 10^{-2}\ s^{-1}$) > **8** ($1.86 \times 10^{-2}\ s^{-1}$). These results indicate that the short [2]rotaxane **8**, containing two ethylene glycol repeating units connected between the azobenzene unit and the triazole ring, has the slowest spectral evolution rate than those of longer [2]rotaxanes **9** and **10** during the *trans*-to-*cis* and *cis*-to-*trans* isomerization of the azobenzene units. The increased isomerization rates in the [2]rotaxanes **8–10** may be attributed to the increased ethylene glycol length with an increased molecular flexibility. Similar constant orders were also observed for the *trans*–*cis* isomerization of their corresponding dumbbell molecules (Fig. S5 in the ESI† and Table 1). Such general trend is well consistent with previous reports where the size of the molecular framework affects the *trans*–*cis* isomerization of azobenzene.[17]

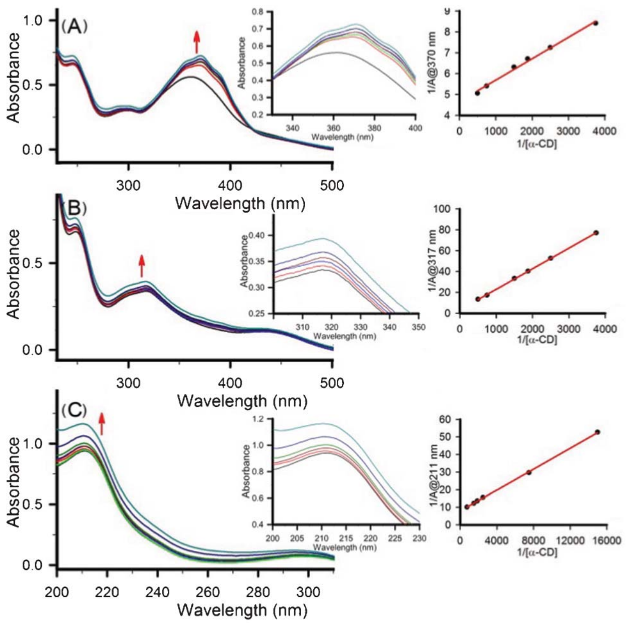


Fig. 3 The UV-vis absorbance changes of the reference compounds **12** and **13** upon stepwise addition of excess α-CD at 298 K. (A) UV absorbance changes of the reference compound **12** upon stepwise addition of excess α-CD before UV light irradiation. (B) UV absorbance changes of the reference compound **12** after UV light irradiation (365 nm, 50 Hz) followed by stepwise addition of excess α-CD. (C) UV absorbance changes of the reference compound **13** upon stepwise addition of excess α-CD in the dark. The concentrations of **12** and **13** were kept at 1.0×10^{-4} M. The association constant *K* was obtained from the double reciprocal plot of 1/Δ*A versus* 1/[α-CD]. Inserts are magnified spectra of the key absorption region and the maximum absorbance changes of compounds **12** and **13** upon stepwise addition of excess α-CD.

Furthermore, the dumbbell molecules present quicker isomerization rates than corresponding [2]rotaxanes, demonstrating the encirclement of the α-CD ring in the [2]rotaxanes can restrict the *trans*–*cis* isomerization of the azobenzene unit to a certain extent, in other words, the host–guest interaction between the α-CD ring and the azobenzene unit in the [2]rotaxanes provides a braking force for the isomerization.

Similar light-responsive switching process of the [2]rotaxanes was confirmed by CD spectra (Fig. 5 and Fig. S6 in the ESI†). Fig. 5 shows representative CD spectra for [2]rotaxanes **8–10** under alternating UV and visible light irradiation. In the control experiments, neither the azobenzene dumbbell molecules **5–7** nor the α-CD ring show the signals at the region of 300–600 nm in the CD spectra. The [2]rotaxanes **8–10** present positive Cotton effects at around 360 nm in aqueous solution, on account of the fact that the azobenzene unit in the [2]rotaxanes is located inside the α-CD ring with the transition dipole moment aligned parallel to the axis of the α-CD chiral cavity.[18] The signal around 360 nm was decreased upon the UV light irradiation for 10 min, indicating that a certain amount

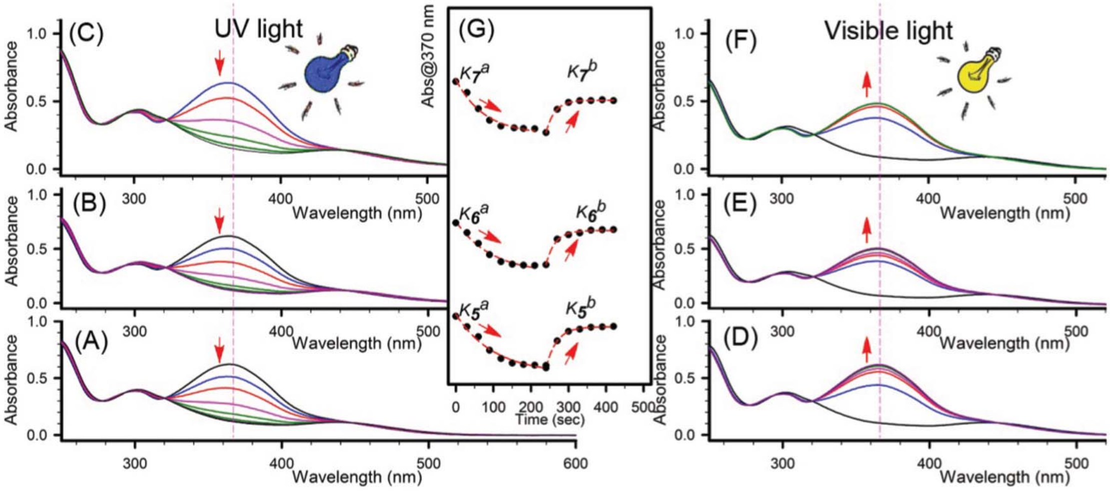


Fig. 4 UV-Vis spectral changes of [2]rotaxanes (A) **8**, (B) **9**, and (C) **10** in aqueous solution (0.5×10^{-4} M) at 5 °C in response to the UV light irradiation for 5 min, and then the spectral changes of [2]rotaxanes (D) **8**, (E) **9**, and (F) **10** upon the visible light irradiation for 3 min. (G) Kinetics for the absorbance at 370 nm for [2]rotaxanes **8–10** in response to the UV and visible light irradiation. Decreased dot lines represent 1st-order exponential decay fitting ($y = y_0 + ae^{-kx}$) under UV light irradiation and increased dot lines represent 1st-order exponential growth fitting ($y = y_0 + a(1 - e^{-kx})$) under visible light irradiation.

of the azobenzene unit in the [2]rotaxanes underwent the *trans*-to-*cis* isomerization. The signal changes around 360 nm as a function of the cycle numbers of alternating UV and visible light irradiation were shown as the inserts in Fig. 5, further revealing that the light-switching process of the [2]rotaxanes is reversible.

The shuttling of the α-CD ring driven by *trans–cis* isomerization of the azobenzene unit was examined by ^{1}H NMR spectroscopy. Fig. 6 shows representative ^{1}H NMR spectra for [2]rotaxane **8** before and after the co-conformation change. It can be noted that some tiny peaks (indicated in red in Fig. 6b) from [2]rotaxane **8** were further enhanced after UV light irradiation, indicating that these peaks belong to the aromatic protons of *cis*-azobenzene unit. It has been demonstrated[19] that the *trans*-to-*cis* isomerization efficiency of azobenzene is generally low even under UV light irradiation, on account of the presence of the *trans*-isomer. According to the NMR spectrum (Fig. 6c), the ratio between the *trans*-azobenzene unit and its *cis*-isomer is about 1.3 : 1 after UV light irradiation. Interestingly, all the increased proton peaks disappeared after heating the sample at 65 °C for 3 h, demonstrating that the *cis*-isomer was completely transformed back to the *trans* one under heating. In the control experiments, the ^{1}H NMR spectra of the reference compound **13** before and after the complexation with the α-CD ring were also obtained (Fig. 6d,e). It can be clearly seen that the protons h and i were shifted downfield about 0.02 and 0.04 ppm, respectively, after the complexation with the α-CD ring. The trend is consistent with the corresponding proton changes of [2]rotaxane **8** caused by the encirclement of the α-CD ring on the dumbbell component. Similarly, the enhancement and decrease of some aromatic proton signals associated with the *trans–cis* isomerization of the azobenzene unit in the [2]rotaxanes **9** and **10** triggered by alternating UV light irradiation and heating can also be observed (Fig. S7 and S8 in the ESI†). The [2]rotaxanes **9** and **10** with longer ethylene glycol chains present a bit more

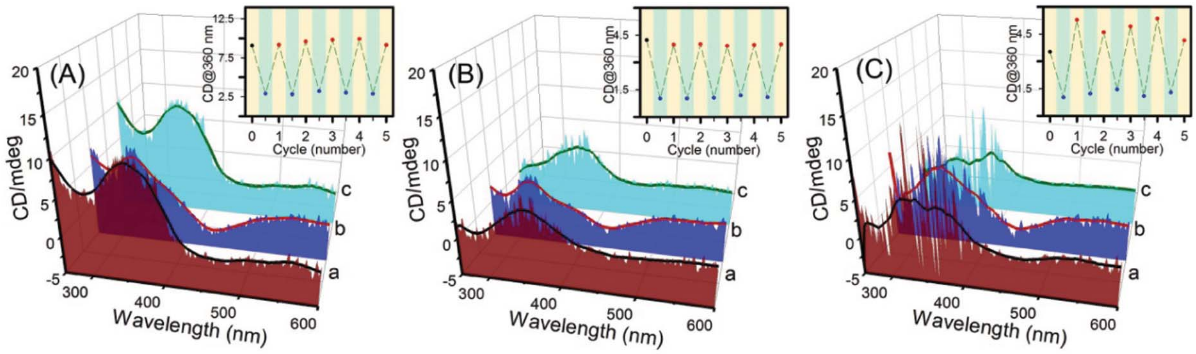


Fig. 5 CD spectra of [2]rotaxanes (A) **8**, (B) **9**, and (C) **10** in aqueous solution (0.5×10^{-4} M) (a) at initial state, (b) after 365 nm of UV light irradiation for 10 min, and (c) after visible light irradiation for 15 min. The solid lines were simulated by SigmaPlot smoothing algorithm. The inset slots show the CD signal changes at 360 nm as a function of the cycle numbers of alternating UV and visible light irradiation.

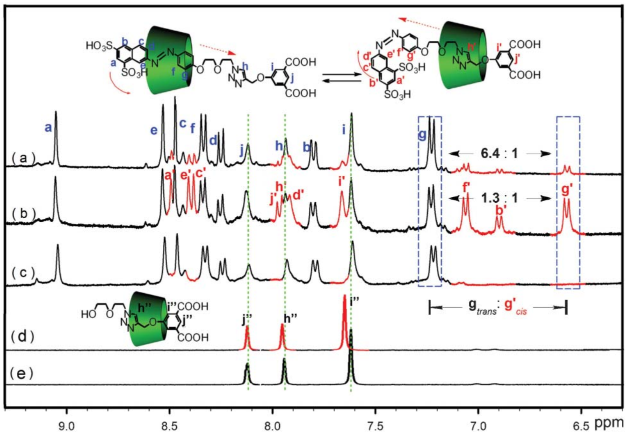


Fig. 6 ^{1}H NMR spectra of [2]rotaxane **8** in D_2O (a) in initial state, (b) after UV light irradiation at 365 nm for 30 min, and then (c) after heating at 65 °C for 3 h. The red peaks were assigned to the protons of the *cis*-azobenzene unit. ^{1}H NMR spectra of (d) the complex of α-CD with compound **13** and (e) compound **13** itself in D_2O.

Table 1 Summary of apparent rate constants for compounds **5–10** derived from the kinetic fitting of the π–π* absorption band at 370 nm during the *trans*-to-*cis* and *cis*-to-*trans* isomerization processes

Molecules	No.	K^a $(s^{-1})^a$	K^b $(s^{-1})^b$
Dumbbell molecules	**5**	0.99×10^{-2}	3.55×10^{-2}
	6	1.06×10^{-2}	4.13×10^{-2}
	7	1.32×10^{-2}	4.27×10^{-2}
[2]Rotaxanes	**8**	3.65×10^{-3}	1.86×10^{-2}
	9	5.50×10^{-3}	3.09×10^{-2}
	10	6.20×10^{-3}	3.62×10^{-2}

[a] Kinetics for the absorbance at 370 nm in response to UV light irradiation. [b] Kinetics for the absorbance at 370 nm in response to visible light irradiation.

complicated spectra as compared with that of [2]rotaxane **8**. The recovery process from the *cis*-isomer to its *trans*-form in the [2]rotaxanes through visible light irradiation was also conducted. However, the aromatic proton peaks from the *cis*-isomer cannot completely disappear after visible light irradiation, indicating that the heating method is more efficient for completing the *cis*-to-*trans* isomerization.

Effects of temperature and viscosity on *cis*-to-*trans* isomerization

The *cis*-azobenzenes can be isomerized back to the corresponding *trans*-isomers powered by either visible light irradiation or heat. The influence of molecular structures on the *cis*-to-*trans* isomerization of azobenzene under visible light or heat was reported previously.[17] In our study, the differences in the co-conformation changes in response to visible light irradiation and heating among these [2]rotaxanes and their dumbbell molecules were assessed by examining the spectral kinetics in aqueous solution and in viscosity-different solvents, respectively. Fig. 4D and 7A show representative UV-vis spectral recovery process of [2]rotaxane **8** after initial treatment with UV light irradiation for 15 min followed by either visible light irradiation or heating. Upon visible light irradiation onto the sample solution, a spectral evolution showing (1) a clear increase of the π–π* absorption band around 324–428 nm and (2) the decreases of the absorbance band around 280–324 nm and the n–π* absorption band around 430–500 nm was observed, demonstrating the *cis*-to-*trans* isomerization occurred. However, a spectral evolution by heating the sample at 65 °C for 30 min showed a slow increase of the π–π* absorption band around 324–428 nm. Based on the kinetics of the spectral evolution of the π–π* absorption band at 370 nm (Fig. 7B), apparent isomerization rate constants (K) derived by fitting the time dependence of the maximum absorbance with an exponential growth (1st-order) are 1.86×10^{-2} s^{-1} for visible light irradiation and 1.48×10^{-4} s^{-1} for heating.

As compared with the initial state of [2]rotaxane **8** (black curve in Fig. 7D), the spectrum (red curve in Fig. 7D) after the

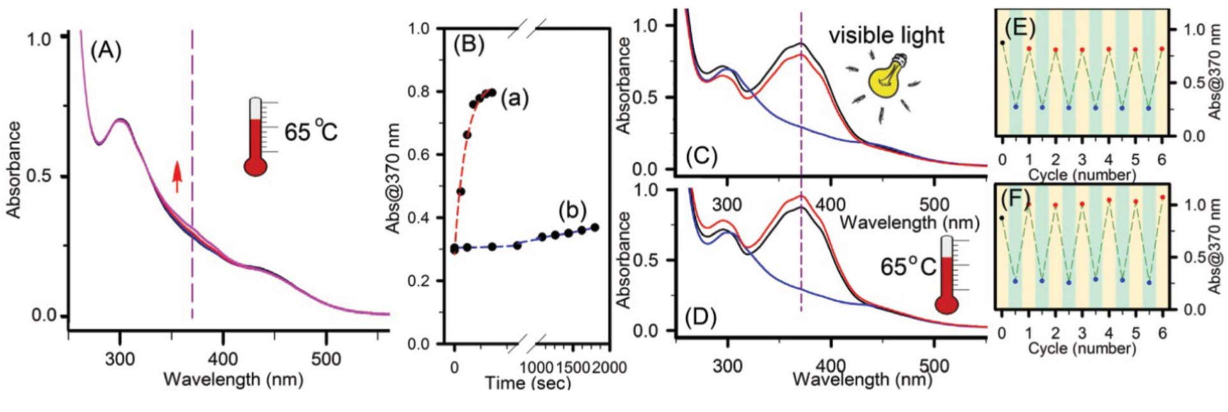


Fig. 7 UV-Vis spectral changes of the [2]rotaxane **8** (0.5×10^{-4} M) treated by UV light irradiation (not shown here) followed by either (A and D) heating at 65 °C or (C) visible light irradiation. (B) Kinetics of the absorbance changes at 370 nm upon (a) visible light irradiation for 3 min and (b) heating at 65 °C for 30 min. In figures C and D, the black lines are the spectra of the [2]rotaxane in the initial state, the blue lines are the spectra at the photostationary state after UV light irradiation, and the red lines are the spectra at photostationary state after either (C) visible light irradiation for 5 min or (D) heating at 65 °C for 3 h. The absorbance changes at 370 nm as a function of the cycle numbers of alternating UV light irradiation and (E) visible light irradiation or (F) heating are presented.

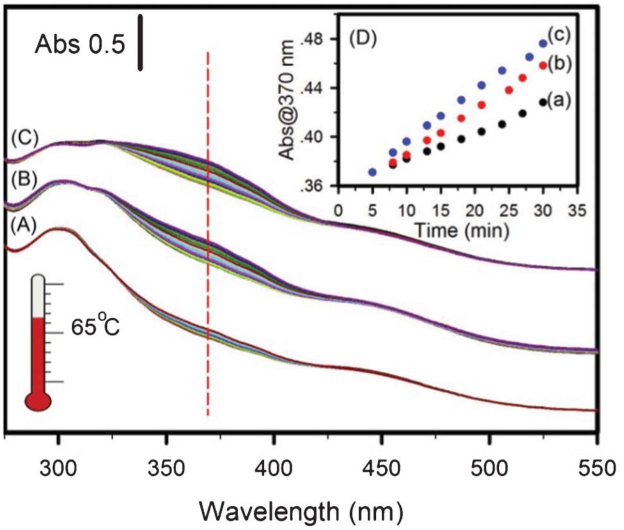


Fig. 8 UV-Vis spectral changes of (A) **8**, (B) **9**, and (C) **10** in aqueous solution (0.5×10^{-4} M) in response to heating at 65 °C for 30 min. (D) Kinetics of the absorbance changes at 370 nm for (a) **8** (black dots), (b) **9** (red dots), and (c) **10** (blue dots).

Table 2 Summary of quantum yields (%) and dependent constants of [2]rotaxanes **8–10** and dumbbell molecules **5–7** under different conditions. Q_{Initial} indicates the quantum yield in the initial state, Q_{UV} represents the quantum yield after UV light irradiation, Q_{Vis} indicates the quantum yield after visible light irradiation, and Q_{Δ} represents the quantum yield after heating at 65 °C for 3 h

	No.	Q_{Initial}	Q_{UV}	Q_{Vis}	Q_{Δ}	Dependent constant
Dumbbell molecules	**5**	0.53	6.38	1.66	1.79	0.1807
	6	0.51	3.71	0.90	1.07	0.2856
	7	0.32	2.61	0.49	0.60	—[a]
[2]Rotaxanes	**8**	1.87	6.82	2.12	2.00	0.0351
	9	1.21	3.26	1.33	1.30	0.0497
	10	0.96	2.53	0.97	1.06	0.0641

[a] Dumbbell molecule **7** did not show obvious viscosity response as indicated in Fig. S13.†

cis-to-*trans* isomerization under heating for 3 h indicates a complete recovery of the isomers. On the contrary, the photostationary state (red curve in Fig. 7C) reached after visible light irradiation for 5 min cannot be completely restored to its initial state. These observations are consistent with the NMR results mentioned above. As an important application, we have studied the [2]rotaxane-functionalized mesoporous silica nanoparticles for controlled drug delivery *in vivo*, in which we observed that the temperature-triggered drug release *in vivo* is efficient.[20] Similar conclusions were achieved for all the [2]rotaxanes **8–10**. The π–π* absorption band changes of the azobenzene unit at 370 nm as a function of the cycle numbers of alternating UV light irradiation and visible light irradiation or heating were present (Fig. 7E and 7F and Fig. S9 in the ESI†), further revealing that the co-conformation change of the [2]rotaxanes is reversible.

The kinetic study of thermal-powered *cis*-to-*trans* isomerization of [2]rotaxanes **8–10** at different temperatures was also performed (Fig. 8 and Fig. S10 and S11 in the ESI†). Fig. S10† shows the UV-vis spectral evolutions for *cis*-[2]rotaxane **8** transforming back to its *trans*-form at different temperatures. The spectral changes (ΔA_{abs}) at 365 nm after 5 h were calculated to be 0.067 at 5 °C, 0.086 at 23 °C, 0.101 at 28 °C, and 0.205 at 37 °C.

Similar studies for the *cis*-to-*trans* conformation recovery were carried out at 65 °C. Fig. 8 shows representative UV-vis spectral changes of [2]rotaxanes **8–10** in response to heating at 65 °C. Upon heating at 65 °C, the spectral evolution shows gradual increase of the π–π* absorption band at 370 nm. The conformation recovery of [2]rotaxane **10** is the quickest one than that of the other two [2]rotaxanes, well matching with the recovery order upon visible light irradiation. However, the kinetic studies show no significant difference between these [2]rotaxanes in response to heating at relatively low temperature such as 37 °C (Fig. S11 in the ESI†). The gradual increase of the π–π* absorption band at 370 nm for the dumbbell molecules **5–7** upon heating at 65 °C was also observed (Fig. S12 in the ESI†), although the difference in the spectral changes between these dumbbell molecules is not obvious.

We then investigated the viscosity effect on the [2]rotaxanes and corresponding dumbbell molecules (Fig. S13 and S14 in the ESI†). The viscosity sensitivity of [2]rotaxanes **8–10** was evaluated by monitoring the maximum emission changes around 440 nm in a mixture solution of ethylene glycol and glycerol. It is well known[25] that increasing glycerol content in the mixture solution leads to the increase of the viscosity with minimal changes of the solvent polarity. Thus, upon increasing the glycerol content (0, 20, 40, 60, and 80%), the viscosity of the solvent mixture was enhanced accordingly (19, 32, 72, 155, and 368 mPa (s). In comparison with the dependent constants of the viscosity sensitivity listed in Table 2, the constants were increased upon increasing the length of the ethylene glycol chain in the [2]rotaxanes **8–10**. This observation indicates that increasing the length of the ethylene glycol chain in the [2]rotaxanes would make the molecule more flexible. In addition, the [2]rotaxanes show smaller dependent constants than that of the corresponding dumbbell molecules, suggesting that the encirclement of the α-CD ring in the [2]rotaxanes makes the molecular structure a bit more rigid.

The studies on the *trans*–*cis* isomerization rates of [2]rotaxane **8** and corresponding dumbbell molecule **5** powered by UV and visible light in viscosity-different solvents were also carried out. The results (Table S1 in the ESI†) indicate that the isomerization rates become slower at high viscosity solvents.

Fluorescence quantum yields of [2]rotaxanes

The integration of fluorophores as stoppers into MIMs exhibits significant advantages over other switches. Reversible changes in fluorescence intensity upon the shuttling of the macrocyclic rings in the rotaxanes present application potentials in molecular memory and molecular logic gates.[21] Study on the suppression and enhancement of the fluorescence through the encirclement of the α-CD ring in rotaxanes was reported by Tian and co-workers.[22] Unlike previously reported protocols where the fluorophores were indirectly connected with photochromic azobenzene components in rotaxanes, in the present case, the naphthalene fluorophore is part of the azobenzene constitution in [2]rotaxanes **8–10**. Thus, the fluorescence of the naphthalene stopper in the [2]rotaxanes is significantly affected by the *trans–cis* isomerization of the azobenzene unit and the length of the ethylene glycol chain.

The fluorescent spectra of [2]rotaxanes **8–10** (0.5×10^{-4} M) were obtained in H_2O with the excitation wavelength (λ_{ex}) of 340 nm, and the emissions at 440 nm were recorded. The emission quantum yields of the [2]rotaxanes and their dumbbell compounds were measured at room temperature by using quinine sulfate in 0.1 M H_2SO_4 as a fluorescence standard (quantum yield = 58%). As seen from Table 2, the quantum yields were significantly decreased upon increasing the length of the ethylene glycol chain, leading to the emission quantum yield order of **8** (1.87%) > **9** (1.21%) > **10** (0.96%). By comparison with the quantum yields of corresponding dumbbell molecules **5–7**, the encirclement of the α-CD ring in the [2]rotaxanes enhances the quantum yields about 3 times. The experimental results agree well with the literature reports[18] that the encirclement of the α-CD ring on fluorophores would normally enhance their fluorescence intensities.

The quantum yields of [2]rotaxanes **8–10** were enhanced after UV light irradiation (Table 2), in which the α-CD ring moves away from the azobenzene unit upon the *trans*-to-*cis* isomerization. These observations indicate that the *trans*-to-*cis* isomerization of the azobenzene unit is the dominant factor for the enhancement of the quantum yield.[23] The enhanced quantum yields of the [2]rotaxanes can be decreased back upon visible light irradiation or heating at 65 °C for 3 h. In the control experiments, we also explored the quantum yield changes of the intermediate compounds **3** and **4** either upon UV light irradiation or in the presence of the α-CD ring. As seen from Table S2 in the ESI†, the enhancement of the quantum yield for compounds **3** and **4** after UV light irradiation is more significant than that after forming the inclusion complex with the α-CD ring.

After integrating fluorophore and photochromic components together within the same molecule, the emission quantum yield of the molecule is highly influenced by the polarity and conformation of the photochromic component, accompanied usually with electron or energy transfer process.[24] In the current [2]rotaxanes, 7-amino-1,3-naphthalenedisulfonic acid was selected as fluorescent stopper because of its high water solubility and high sensitivity to the polarity. The dipole moment (μ) simulation of a model compound **17** was performed on an Opt+Freq computational package implemented in Gaussian 9.0 software. A MeO group was attached to the azobenzene unit instead of the ethylene glycol chain in the model compound **17** (chemical structure shown in Fig. S15 of the ESI†). The dipole moments (μ) of **17** were calculated to be 7.8919 Debye for the *cis*-form and 7.5274 Debye for the *trans*-form, which are in good agreement with the literature reports, *i.e.*, the *trans*-to-*cis* isomerization of the azobenzene unit could lead to the fluorescence increase.[24d]

Conclusion

In conclusion, we have synthesized three photothermal-responsive α-cyclodextrin-based [2]rotaxanes, in which the ethylene glycol chains with different length were employed to connect the azobenzene units and the triazole rings in the dumbbell components. The difference in the length of the ethylene glycol chains endows the [2]rotaxanes with the ability to change the *trans–cis* isomerization rate and fluorescent quantum yield. The occupation stations (*i.e.*, azobenzene moiety and triazole ring) of the α-cyclodextrin ring in the [2]rotaxanes can be controlled by alternating UV light irradiation and visible light irradiation/heating. The present photothermal-controlled [2]rotaxanes with integrated fluorophore show a promising potential for fabricating photothermal-responsive molecular memory.

Acknowledgements

The work was financially supported by the Singapore National Research Foundation Fellowship (NRF2009NRFRF001-015), Singapore National Research Foundation CREATE program – Singapore Peking University Research Centre for a Sustainable Low-Carbon Future, and Nanyang Technological University

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