A light-driven [1]rotaxane *via* self-complementary and Suzuki-coupling capping†

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A light-driven [1]rotaxane was prepared conveniently and directly through self-inclusion complexation of an azobenzene-modified β-CD and Suzuki-coupling capping in aqueous solution, and its photoisomerization was thoroughly investigated.

Optical rotaxanes, beyond all doubt, have self-evident positive characteristics, such as fast response times, low detection costs in small spaces, highly sensitive output signals and feasible remote-detection, despite the fact that a large number of rotaxane molecular machine systems have been prepared recently.[1] Cyclodextrins (CDs) continue to be attractive wheel components in constructing rotaxanes,[2,3] and the foundation for the construction of a CD-based rotaxane is the interactions between the hydrophobic cavity of the CD and the special hydrophobic unit in the linear component. The first CD-based [1]rotaxane was synthesized starting from a [2]rotaxane *via* an indirect method by fixing a covalent linkage between the stilbene axis and the CD ring.[4] Herein, we report a fully optical CD-based [1]rotaxane *via* self-complementary and Suzuki-coupling capping, for the first time,[5] and the investigation of its photoisomerized absorption and induced circular dichroism (ICD) spectra.[6] To the best of our knowledge, there are no previous reports of CD-based [1]rotaxanes prepared using direct methods.

It is well-known that the stability constants of the β-CD inclusion complexes are influenced by the solvent effect because of the hydrophobic property of the β-CD cavity. Liu[7] *et al.* have reported the self-inclusion conformation of a β-CD modified by an azobenzene group in DMSO–H_2O solutions of varied proportion. In a 10% DMSO aqueous solution of **3**, the azobenzene group attached to the β-CD rim can be deeply embedded in the β-CD cavity to form the intramolecular inclusion complex.[7] [1]Rotaxane **6** was synthesized by Pd-catalyzed Suzuki coupling, where phenylboronic acid **4** reacted with azobenzene-modified β-CD **3** in an argon-saturated 10% DMSO Na_2CO_3 aqueous solution. However, in 90% DMSO solution, **3** represents an exclusion of the azobenzene side arm from the β-CD cavity.[7] Then, treating **3** with **4** can lead to the formation of compound **5** as illustrated in Scheme 1 (for synthesis details see ESI†).[8]

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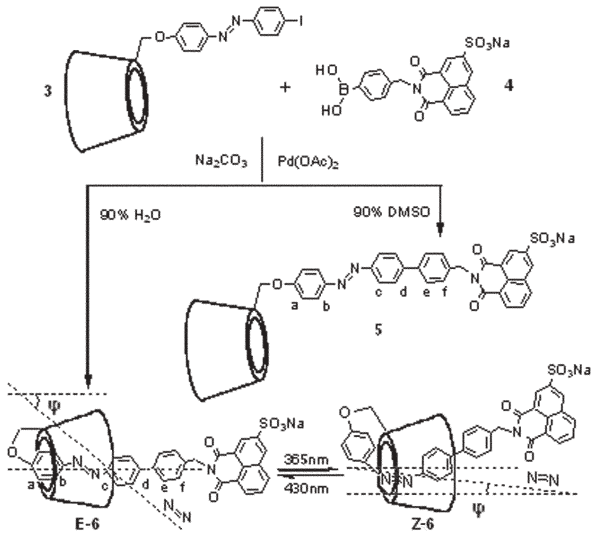
† Electronic supplementary information (**ESI**) available: Synthetic procedures for the compounds, MALDI-TOF mass spectra of [1]rotaxane **6** and reference compound **5**, 2D ^{1}H ROESY NMR spectra of [1]rotaxane **6** and reference compound **5**, and a brief description of analytical methods. See DOI: 10.1039/b615900a



Scheme 1 The syntheses of compound **5** and [1]rotaxane **6** and sketch maps of transition dipole moments of the reversible configuration change of the [1]rotaxane **6** under different stimuli (---, φ stands for the rough angle between the transition moment of the azobenzene unit and the axis of the β-CD cavity).

Both [1]rotaxane **6** and reference compound **5** were characterized by ^{1}H NMR spectroscopy, 2D ^{1}H ROESY NMR spectroscopy and MALDI-TOF mass spectrometry.† Fig. 1 shows the ^{1}H NMR spectra of **6** and **5** in [d_6]DMSO (298 K). The signals for H_d, H_e and H_f of the thread are shielded by δ = 0.06, 0.18 and 0.13 ppm in the [1]rotaxane **6** with respect to compound **5**, and the signal for H_a is deshielded by δ = 0.04 ppm, which is due to the influence of

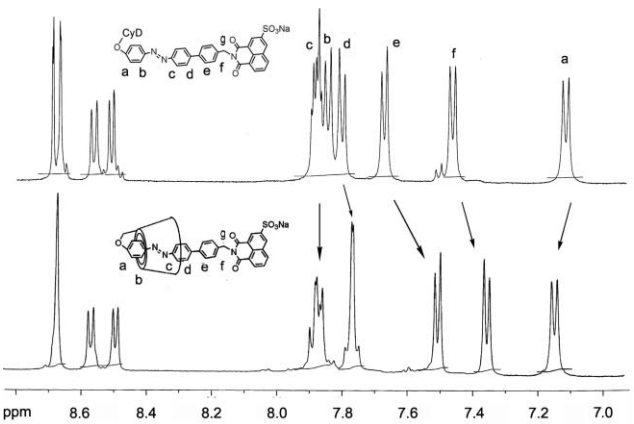


Fig. 1 Partial ^{1}H NMR spectra of compound **5** (top) and rotaxane **6** (bottom) in [d_6]DMSO.

the β-CD ring. The MALDI-TOF spectra of **6** and **5** are similar and both exhibit the same signal at *m*/*z* 1724.4, which corresponds to [**6** (or **5**) + Na]$^+$, respectively since the *m*/*z* of **6** and **5** are identical (ESI, Fig. S1 and Fig. S2†). The presence of the azobenzene moiety inside the β-CD cavity in **6** has been confirmed using 2D ^{1}H NMR ROESY spectroscopy (ESI, Fig. S3†). The NOEs between the azobenzene protons and the H_3 and H_5 protons on the interior of the β-CD show that the azobenzene is deeply embedded in the β-CD cavity to form [1]rotaxane **6**. However, there are no obvious NOEs between the H_3 and H_5 protons on the interior of the CD annulus and the aromatic protons in the 2D ROESY spectrum of **5**, and cross-peaks were found between the H_a and H_b protons of the azobenzene moiety and the hydroxyl groups of the primary side of the CD in the ROESY spectrum of **5** (ESI, Fig. S4†), indicating the location of the azobenzene moiety above the CD cavity and the exclusion of the thread out of the CD cavity, thereby confirming the structures of rotaxane **6** and reference compound **5**.

The *E*/*Z* photoisomerization reaction of [1]rotaxane **6** in D_2O solution was investigated by monitoring the changes in its ^{1}H NMR spectra. Irradiation at 365 nm for 3 h leads to several new signals for *cis*-azobenzene (Fig. 2), appearing at δ = 6.75 (H_a), 6.95 (H_b, H_d), and 7.49 (H_c) ppm, corresponding to the initial peaks appearing at δ = 6.94, 7.75 and 7.90 ppm, respectively. This is reasonable because the signals of the aromatic protons of the azobenzene unit generally shift upfield upon their isomerization from *trans* to *cis* configuration, as a result of the magnetic shielding effect of aromatic rings. Integrals of the two signals for H_a appear with a 1 : 1 ratio, which suggests that, at the photostationary state, about 50% of *E*-**6** was transformed to the *Z*-**6** isomer. In this case, the efficiency of the photoreaction is not high for the reversion process at 365 nm, since some of the photons will be absorbed by the naphthalimide moiety (NS, the stopper) rather than by the azobenzene to undergo the photoisomerization.

The irradiation of the azobenzene-based [2]rotaxanes would induce *E*/*Z* photoisomerization and the shuttling motion of the CD ring, which can also be confirmed by the absorption spectral changes.[3] For [1]rotaxane **6**, the same characteristic spectral changes in aqueous solution (8.5 × 10^{-5} M) were also found, as shown in Fig. 3. Irradiation of the **6** solution at 365 nm for 15 min results in photoisomerization to give an *E*/*Z* mixture, characterized by a rise in the absorption at around 275 nm (ΔA = 0.21), a decrease in absorption at 330 nm (ΔA = 0.52) and a slight increase

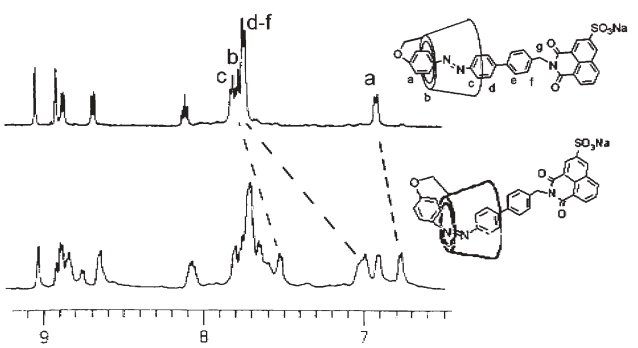


Fig. 2 Partial ^{1}H NMR spectra of rotaxane **6** at the original state (top) and at the photostationary state (bottom) after irradiation at 365 nm for 3 h in D_2O.

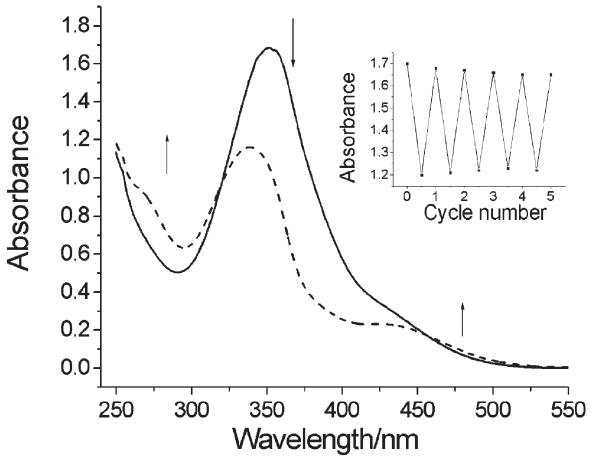


Fig. 3 The absorption spectra of rotaxane **6** in aqueous solution (8.5 × 10^{-5} M) before (—) and after (---) irradiation at 365 nm for 15 min at room temperature. Insert: changes in the absorption spectra of rotaxane **6** (absorption value at around 350 nm) for several cycles. In one cycle, 365 nm and 430 nm irradiation was used to isomerize the azobenzene unit.

in absorption at 465 nm, as well as the presence of an isosbestic point at 318 nm. Compared with [1]rotaxane **6**, the corresponding aqueous solution of compound **5** also undergoes *E*/*Z* photoisomerization by irradiation at 365 nm, but it reaches the photostationary state within a shorter time (5 min). This also demonstrates the fact that *E*/*Z* isomerization becomes more difficult in the presence of the CD ring circling. After the photoisomerization of **5** and **6** from the *E* to the *Z* form, the equilibrium can be reversed by irradiation at 430 nm for 30 min. Because of the good photoreversibility of the azobenzene derivative, the photochemical process of the [1]rotaxane system is highly reproducible over more than five cycles (Fig. 3, insert). As a result, the photoinduced shuttling motion of the CD ring can be carried out repeatedly with reversible absorption signal changes.

Owing to the *trans*–*cis* photoisomerization of the azobenzene moiety and the subsequent shuttling movement of the β-CD ring, the shuttles of [1]rotaxane **6** were accompanied by varied ICD signals.[9] The ICD spectra with respect to the photoisomerization of aqueous [1]rotaxane **6** (1.55 × 10^{-4} M) solution are shown in Fig. 4. It showed a positive Cotton effect at 433 nm and a weaker negative Cotton effect at 322 nm (Fig. 4, curve a). The azobenzene moiety of the [1]rotaxane **6** is located in the β-CD cavity, and its transition dipole moment is by and large aligned parallel to the axis of the chiral β-CD cavity (Scheme 1, *E*-**6**), resulting in the positive ICD signal at 433 nm. The weaker negative Cotton effect at 322 nm is due to the naphthalimide (NS) group, which is located outside of the β-CD cavity and is far from the β-CD (Scheme 1, *E*-**6**). For the reference compound **5** (Fig. 4, curve d), there is a negative ICD signal at 301 nm and a positive one at 352 nm, corresponding to the n–π* and π–π* transition bands of the azobenzene group, respectively.[10]

The *E*/*Z* photoisomerization by prolonged irradiation at 360 nm leads to a similar sign of ICD signals of *cis*-azobenzene *Z*-**6** but only an intensity increase (by about 65% at 433 nm and around 169% at 322 nm) to the *trans*-azobenzene *E*-**6** shown in Fig. 4 (curve b). This may be attributed to the fact that the transition dipole moment becomes further parallel to the axis of the chiral

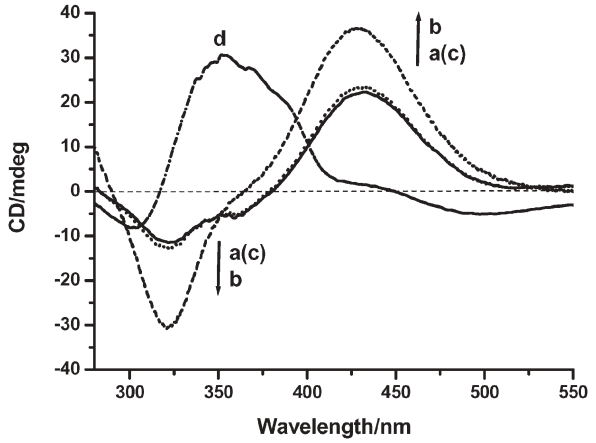


Fig. 4 ICD spectra of [1]rotaxane **6** (298 K, 1.55×10^{-4} M) aqueous solution (a, —), after the irradiation at 360 nm for 30 min (b, ---). The ICD spectra can be shifted back by irradiation at 430 nm (30 min, c, ···); ICD spectrum of compound **5** (298 K, 1.55×10^{-4} M) aqueous solution (d, -·-).

β-CD cavity with a smaller angle than the *E* form (Scheme 1, *Z*-**6**) when it isomerizes to the *Z* form. Moreover, the photoisomerization from the *E* to the *Z* form results in a closer distance between the β-CD and the NS group (Scheme 1, *Z*-**6**, the rough distance between the β-CD and the NS group is smaller than that in *E*-**6**). The increased effect of β-CD initiates the increase of the negative ICD signal. The ICD spectral changes can be shifted back by irradiation at 430 nm (Fig. 4, curve c).

In conclusion, by taking advantage of the different complexation behaviour and molecular binding models of azobenzene-modified β-CD in aqueous and DMSO solutions, a novel [1]rotaxane **6** and its reference molecular system **5** were synthesized by Suzuki-coupling capping in different media. The [1]rotaxane was confirmed by ^{1}H NMR spectroscopy, 2D ^{1}H ROESY NMR spectroscopy and MALDI-TOF mass spectrometry as well as the induced circular dichroism (ICD) for its conformational identification. Most importantly, this is the first example of a CD-based [1]rotaxane directly and conveniently synthesized *via* self-complementary and Suzuki-coupling capping, and is a prominently optical rotaxane with reversible absorption and ICD signal changes. This direct method, utilizing the interesting self-inclusion complexation, can be used to construct intriguing [1]rotaxanes simply and conveniently.

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