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A [3]Rotaxane with Three Stable States That Responds to Multiple-Inputs and Displays Dual Fluorescence Addresses

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Abstract: A [3]rotaxane molecular shuttle containing two α-cyclodextrin (α-CD) macrocycles, an azobenzene unit, a stilbene unit, and two different fluorescent naphthalimide units has been investigated. The azobenzene unit and the stilbene unit can be *E*/*Z*-photoisomerized separately by light excited at different wavelengths. Irradiation at 380 nm resulted in the photoisomerization of the azobenzene unit, leading to the formation of one stable state of the [3]rotaxane (***Z1*-NNAS-2CD**); irradiation at 313 nm resulted in the photoisomerization of the stilbene unit, leading to the formation of another stable state of the [3]rotaxane (***Z2*-NNAS-2CD**). The reversible conversion of the *Z1* and *Z2* isomers back to the *E* isomer by irradiation at 450 nm and 280 nm, respectively, is accompanied by recovery of the absorption and fluorescence spectra of the [3]rotaxane. The *E* isomer and the two *Z* isomers have been characterized by ^{1}H NMR spectroscopy and by two-dimensional NMR spectroscopy. The light stimuli can induce shuttling motions of the two α-CD macrocycles on the molecular thread; concomitantly, the absorption and fluorescence spectra of the [3]rotaxane change in a regular way. When the α-CD macrocycle stays close to the fluorescent moiety, the fluorescence of the moiety become stronger due to the rigidity of the α-CD ring. As the photoisomerization processes are fully reversible, the photo-induced shuttling motions of the α-CD rings can be repeated, accompanied by dual reversible fluorescence signal outputs. The potential application of such light-induced mechanical motions at the molecular level could provide some insight into the workings of a molecular machine with entirely optical signals, and could provide a cheap, convenient interface for communication between micro- and macroworlds.

Keywords: cyclodextrins · fluorescence · molecular shuttle · photoisomerization · rotaxanes

Introduction

Interlocked supramolecules[1,2] such as pseudorotaxanes, rotaxanes, and catenanes have attracted a great deal of attention in recent years because of their challenging construction and potential applications in areas such as molecular logic gates,[3] molecular switches,[4] molecular wires,[5] and information storage.[6] There is a rapidly growing need to design and construct rotaxanes that can be switched reversibly between two different states using different stimuli. There are many external stimuli that can be used to make the molecular machines work: for example, a change in pH,[7] light,[8–10] electrochemistry,[11,12] or entropy.[13] Undoubtedly, photons provide an excellent energy input, because excitation with light can lead to a fast response and can work in a small space without producing any by-products.[8–10] To realize their full potential, rotaxanes should have two basic properties. First, the binary states, "0" and "1", must be reversibly interconvertible. Second, the output signals of the rotaxanes should be easily recognizable. Previously, the binary states of most molecular machines have been distinguished by NMR spectra,[14,15] cyclic voltammetry,[16] differences in the complexation ability of certain ions of the two states,[17] and circular dichromism. It is rather inconvenient to transform these spectral signals into easily detected output codes. Use of a change in fluorescence[18,19] as an output is an attractive approach because the fluorescent signal readily allows remote reading and is typically low-cost. However, reports on rotaxanes that switch between different fluorescent states (output) in response to light inputs are still rare.[18,19]

It is well known that cyclodextrins (CDs) form host–guest complexes. Many cyclodextrin-based catenanes, rotaxanes, and polyrotaxanes have been synthesized.[2,5,8,12,15,18,20–22] Pre-

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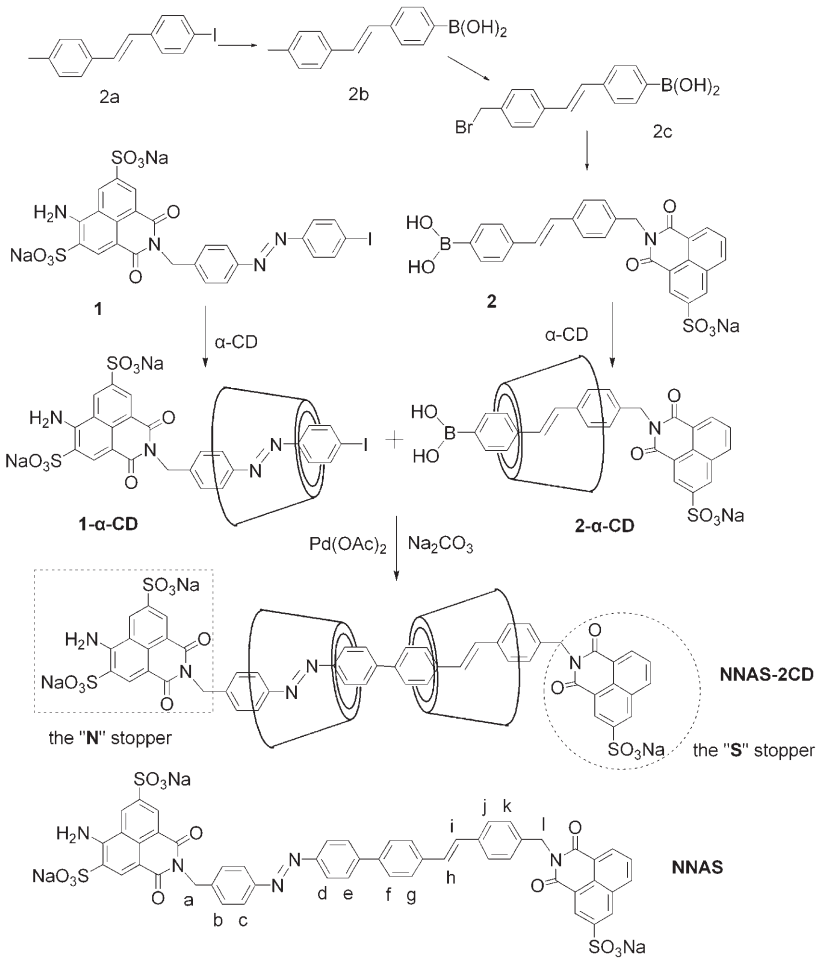
viously we have prepared two light-driven molecular shuttles comprising a stilbene unit and an azobenzene unit, respectively, and analyzed their photoisomerization phenomena in solution.[18] In this study, we designed and synthesized a [3]rotaxane **NNAS-2CD** (Scheme 1) containing two α-CD macrocycles, an azobenzene unit, a stilbene unit, and two different fluorescent naphthalimide moieties: 4-amino-1,8-naphthalimide-3,6-disulfonic disodium salt (the "**N**" stopper) and 1,8-naphthalimide-5-sulfonic sodium salt (the "**S**" stopper). The molecular shuttle **NNAS-2CD** has several key features: two different fluorescence moieties are introduced to act as "stoppers"; an azobenzene unit and a stilbene unit provide a means of changing the position of the macrocyclic CDs on the molecular thread by altering the stereostructure of the recognition site using various photochemical isomerization reactions. The great change in position of the α-CD rings can be used to create obvious changes in properties (for example, in the fluorescence spectra) of the two stoppers in a regular way. The [3]rotaxane **NNAS-2CD** is, in fact, a novel molecular shuttle with three stable states. Irradiation at 380 nm can induce isomerization of the azobenzene unit to convert ***E*-NNAS-2CD** into ***Z1*-NNAS-2CD**, and irradiation at 313 nm can induce isomerization of the stilbene unit to convert ***E*-NNAS-2CD** into ***Z2*-NNAS-2CD** (Scheme 2). The two *Z* isomers could also be shifted back to the *E* isomer reversibly by photochemical stimuli. Because of the good regulation and full reversibility of the fluorescence changes of the two stopper units in the photoisomerization, the shuttling of the CD macrocycles in [3]rotaxane **NNAS-2CD** could be characterized by the fluorescence changes. We suggest that such changes in a property (for example, fluorescence) of a rotaxane could easily address for many different types of molecular devices and biological systems that rely upon the controlled movement of multiple components to perform specific tasks at a molecular level.

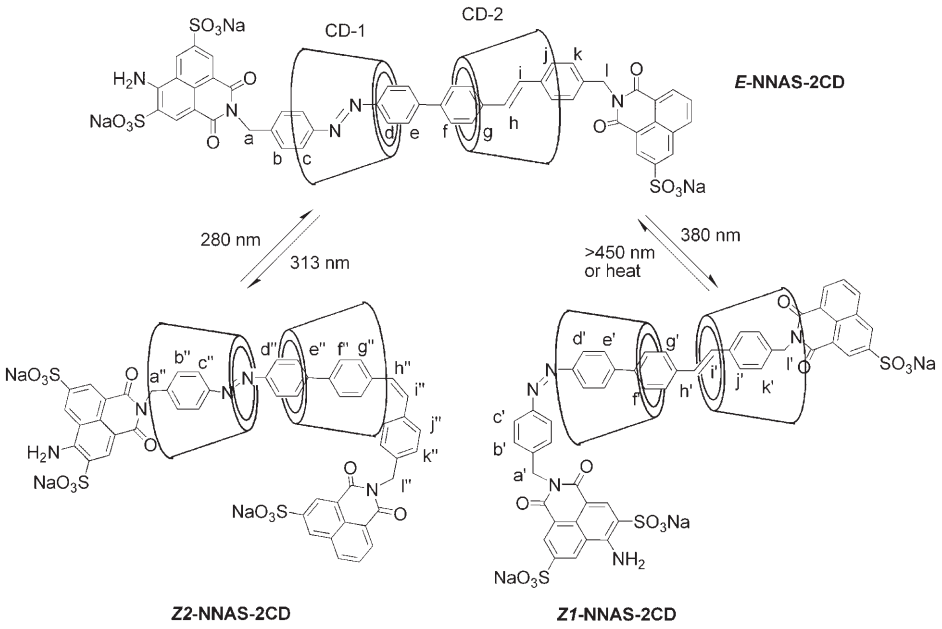
Herein, we describe the synthesis of a novel [3]rotaxane molecular shuttle **NNAS-2CD** and its photoisomerization reactions. The three stable conformations of the rotaxane were fully characterized by ^{1}H NMR and two-dimensional ^{1}H ROESY NMR spectroscopy. The light-driven shuttling motions of the α-CD rings on the molecular thread in the [3]rotaxane and the fluorescence changes of the two stoppers have been investigated.



Scheme 1. The synthetic routes to [3]rotaxane **NNAS-2CD**. The α-cyclodextrin is drawn with a wide 2,3-rim and a narrow 6-rim; **NNAS** is the free dumbbell.

Results and Discussion

Synthesis and characterization: **NNAS-2CD** consists of two α-CD macrocycles locked on to a thread that has two binding sites—an azobenzene site, and a stilbene site—trapped mechanically by two naphthalimide moieties with different fluorescence properties: 4-amino-1,8-naphthalimide-3,6-disulfonic disodium salt (the "**N**" stopper) and 1,8-naphthalimide-5-sulfonic sodium salt (the "**S**" stopper). It has been reported that cyclodextrin-based rotaxanes can be prepared by Pd(OAc)$_2$-catalyzed Suzuki coupling in the presence of CD.[5,18] First, we mixed **1** and α-CD in a 1:1 molar ratio in water to produce **1-α-CD**, and **2-α-CD** was obtained by the same method from **2** and α-CD. The structures of **1-α-CD** and **2-α-CD** were confirmed by ^{1}H NMR and two-dimensional ^{1}H ROESY NMR spectroscopy.[23] Surprisingly, the CDs in **1-α-CD** and **2-α-CD** are basically coincident in direction: in the dominant configuration the wide 2,3-rim is close to the



Scheme 2. The shuttling motions of the α-CD macrocycles under different photochemical stimuli in the [3]rotaxane **NNAS-2CD**.

stopper.[23] Then, as shown in Scheme 1, we treated **1-α-CD** with **2-α-CD** in alkaline aqueous α-CD solution, using a Pd(OAc)$_2$ catalyst, in a **1-α-CD**/**2-α-CD**/Pd(OAc)$_2$ molar ratio of 1:1:0.2, at 85 °C for 24 h, and the [3]rotaxane **NNAS-2CD** was isolated in 18% yield by chromatography (silica gel; upper layer = acetic acid/*n*-butanol/water, 1.5:3:5). In this Suzuki coupling reaction, a [2]rotaxane was also obtained in a very low yield (~2%), and the dumbbell was separated in a low yield (~1%). A large amount of dumbbell **NNAS** (yield 29.5%) can be also synthesized by treating **1** and **2** under the same conditions (but without CD) . The chemical structure of the [3]rotaxane was fully confirmed by MALDI-TOF mass spectrometry, and ^{1}H NMR and two-dimensional ROESY NMR spectroscopy.

The rotaxane obtained is indeed a [3]rotaxane, which can be confirmed and characterized by ^{1}H NMR spectra: the ratio of the integral of H$_a$ or H$_l$ in the dumbbell to the integral of H1 in the cyclodextrins is 1:6, indicating there are two cyclodextrin rings in the rotaxane. MALDI-TOF mass spectrometry[23] also supplied strong evidence in support of a [3]rotaxane. The spectrum is dominated by signals at *m*/*z* 3067.7 (100%) and 3045.7 (60%), which correspond to the [3]rotaxanes [**NNAS-2CD**+Na]$^+$ and [**NNAS-2CD**+1]$^+$, respectively.

Two-dimensional NMR spectroscopy has recently become an essential method for studying the structures of CDs and their complexes, since one can conclude that two protons are closely located in space if an NOE cross-peak is detected between the relevant proton signals in the ROESY or NOESY spectrum. The two-dimensional ROESY spectrum of **NNAS-2CD** in [D$_6$]DMSO is shown in Figure 1. The NOEs between the aromatic protons and the H3 and H5 protons on the interior of the α-CD annulus were found (from H$_b$, H$_c$, H$_j$, H$_k$, H$_h$, H$_i$ to H3, and from H$_d$, H$_e$, H$_f$, H$_g$, H$_h$, H$_i$ to H5), which indicates that the two α-CD rings are located around the azobenzene unit and the stilbene unit respectively. At the same time, the NOEs from H$_e$, H$_f$, H$_g$ to H6, from H$_c$, H$_j$, H$_k$ to OH-2,3, and from H$_e$, H$_f$ to OH-6 also prove that the chemical structure of **NNAS-2CD** was confirmed as shown in Figure 1.

Photoisomerization: Let us consider the *E*/*Z* photoisomerization of the [3]rotaxane **NNAS-2CD**. Good photoisomerization abilities have been found in azobenzene- and stilbene-based rotaxanes.[8,18] For comparison with the [3]rotaxane **NNAS-2CD** and the dumbbell **NNAS**, we irradiated **1** at 313 nm and **2** at 380 nm for 2 h (in dimethylformamide solution), respectively. There was little change in the ^{1}H NMR and the absorption spectra of **1** and **2**,[23] indicating that in the [3]rotaxane ***E*-NNAS-**

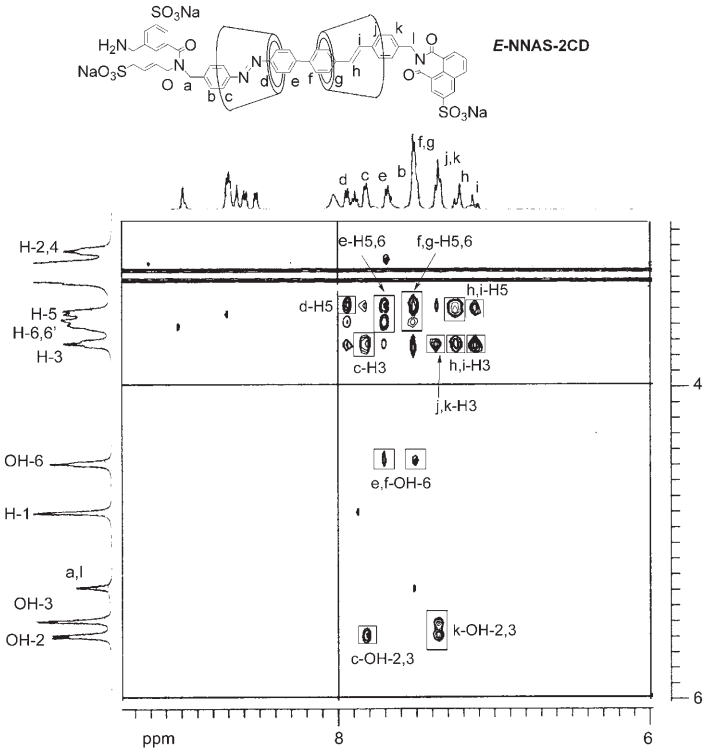


Figure 1. The two-dimensional ^{1}H ROESY NMR spectrum of **NNAS-2CD** (500 MHz in [D$_6$]DMSO at 298 K; mixing time 300 ms).

2CD photoisomerization of the azobenzene unit could not be induced by irradiation at 313 nm and photoisomerization of the stilbene unit could not be induced by irradiation at 380 nm. However, irradiation of ***E*-NNAS-2CD** at 380 nm caused photoisomerization of the azobenzene unit, which generates ***Z1*-NNAS-2CD** (Scheme 2). The photostationary equilibrium can be shifted back toward the *E* isomer by irradiation with visible light (>450 nm) or heat; irradiation of ***E*-NNAS-2CD** at 313 nm resulted in photoisomerization of the stilbene unit, which generates ***Z2*-NNAS-2CD** (Scheme 2). Then irradiation of ***Z2*-NNAS-2CD** at 280 nm shifts the system back toward its original *E* isomer. The *E*/*Z* photoisomerization reactions of [3]rotaxane **NNAS-2CD** in solution were investigated by monitoring the ^{1}H NMR spectral changes. Irradiation at 380 nm leads to two new signals of equal intensity for $H_{c'}$ and $H_{d'}$ appearing at $\delta = 6.64$ and 6.80 ppm, respectively; correspondingly, the initial peaks appear at $\delta = 7.82$ and 7.94 ppm. This is reasonable, because the signals from 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 the aromatic rings. The change in the resonance of the methylene protons ($\delta = 5.25$ ppm, $H_{a,l}$) was also profound. Before irradiation at 380 nm, the chemical shifts of the protons H_a and H_l are equal. Irradiation at 380 nm causes splitting of the proton peak into one doublet and one singlet, compared with one singlet peak before the irradiation. A new signal was found at $\delta = 5.37$ ppm ($H_{l'}$ of ***Z1*-NNAS-2CD**). This is attributed to the deshielding effect of α-CD due to the shifting of the ring away from the azobenzene unit to the biphenyl unit. New sets of NOEs (Figure 2) were found: from $H_{d'}$, $H_{e'}$, $H_{j'}$, $H_{k'}$ to H3 and H5, and from the $H_{i'}$ to H3, on the interior of the α-CD annulus; from $H_{f'}$, $H_{g'}$, $H_{h'}$, $H_{i'}$ to OH-6, on the narrow rim of α-CD; as well as from $H_{c'}$, $H_{d'}$ to OH-2,3, on the wide rim of α-CD. All these changes in NMR spectra indicate that **NNAS-2CD** underwent azobenzene photoisomerization and generated ***Z1*-NNAS-2CD**, in which the CD-1 ring shifts from the azobenzene unit to the biphenyl unit and the CD-2 ring moves close to the "**S**" stopper (Scheme 2). Integrals of the two $H_{d'}$ and H_d signals appear in a 5:3 ratio, which suggests that at the photostationary state of azobenzene isomerization (**PSS-A**), about 63% of the ***E*-NNAS-2CD** was transformed to the ***Z1*-NNAS-2CD** isomer.

Irradiation of ***E*-NNAS-2CD** at 313 nm generally results in the signals of aromatic protons of the stilbene unit shifting upfield: $H_{h''}$, $H_{i''}$ appears at $\delta = 6.6$–6.7 ppm (initially $\delta =$ 7.2–7.3 ppm), $H_{j''}$ appears at $\delta = 6.95$ ppm (initially $\delta =$ 7.38 ppm), $H_{g''}$ appears at $\delta = 7.20$ ppm (initially $\delta =$ 7.52 ppm), indicating that the stilbene unit has already undergone its characteristic photoisomerization. The resonance of the methylene protons is also split; the $H_{a''}$ signal represents a doublet at $\delta = 5.35$ ppm. Also, the coupling constant of the *cis*-stilbene protons $H_{h''}$ and $H_{i''}$ in Figure 3c (14 Hz) is smaller than that in the *trans*-stilbene protons H_h and H_i in Figure 3a (16 Hz). Reasonably, a decrease in this coupling constant serves as key evidence for the photoisomerization

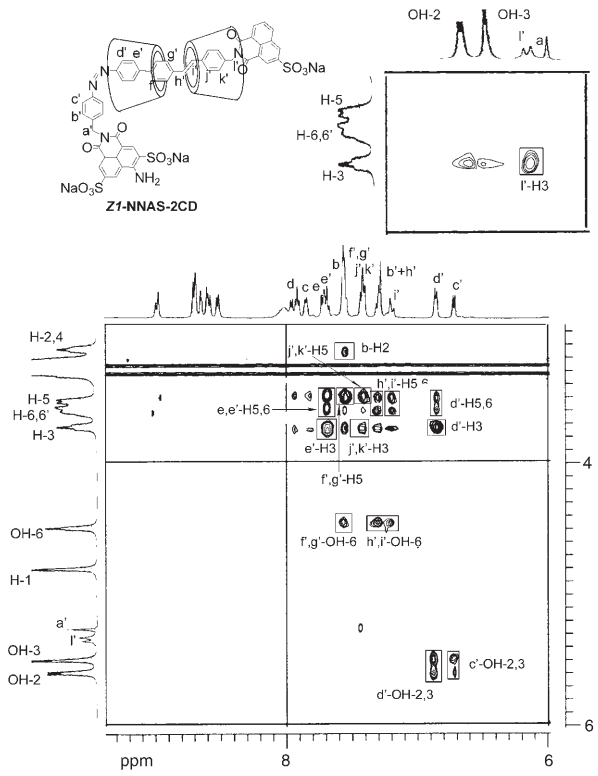


Figure 2. The two-dimensional ^{1}H ROESY NMR spectrum (500 MHz in [D_6]DMSO at 298 K; mixing time 300 ms) of **NNAS-2CD** after irradiation at 380 nm for 2 h.

of the stilbene unit. New sets of NOEs (Figure 4) from $H_{b''}$, $H_{c''}$, $H_{f''}$, $H_{g''}$ to H3, from $H_{d''}$, $H_{e''}$ to H5 and H6, and from $H_{h'}$ to H3, as well as from $H_{k''}$, $H_{h''}$, $H_{i''}$ to OH-2,3, on the wide rim of the α-CD, have been found. All these changes indicate that **NNAS-2CD** has undergone stilbene photoisomerization and has generated ***Z2*-NNAS-2CD** under irradiation at 313 nm, as shown in Scheme 2. Integrals of the two signals of $H_{h''}$ and H_h (or $H_{i''}$ and H_i) appear in a 5:4 ratio, which suggests that at the photostationary state of the stilbene isomerization (**PSS-S**) about 56% of the ***E*-NNAS-2CD** was transformed to the ***Z2*-NNAS-2CD** isomer in that case.

Luminescence properties: The absorption spectra of the [3]rotaxane and its two *Z* isomers in solution have also been investigated. Irradiation at either 380 nm or 313 nm can lead to a decrease in absorption at around 350 nm and an increase in absorption at around 280 nm, indicating that photoisomerization of the azobenzene or the stilbene unit occurs.[23,24] UV irradiation (380 nm) of ***E*-NNAS-2CD** (1.0×10^{-5} M in DMF) for 30 min causes photoisomerization from the *trans* to the *cis* configuration of the azobenzene unit, generating ***Z1*-NNAS-2CD**, which recovers to the *trans* configuration upon irradiation at 450 nm for 60 min. The change is characterized by a rise in absorption at around 270 nm ($\Delta A = 0.03$) and a decrease in absorption at 350 nm ($\Delta A = 0.06$) that is characteristic of the photoisomerization

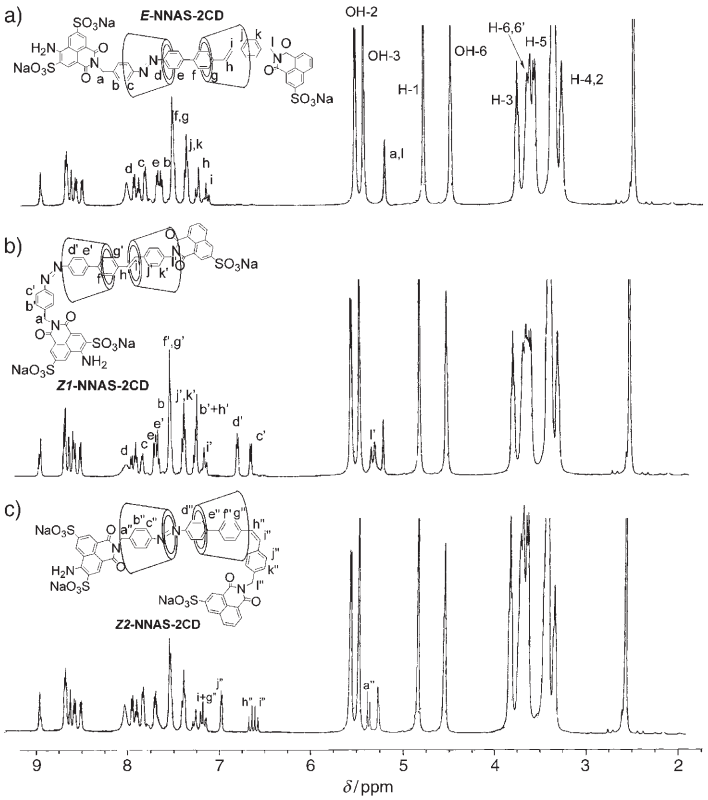


Figure 3. ^{1}H NMR spectra (500 MHz in [D$_6$]DMSO at 298 K) of **NNAS-2CD**: a) before irradiation; b) after irradiation at 380 nm for 2 h; c) after irradiation at 313 nm for 3 h. Both reactions have reached photostationary states.

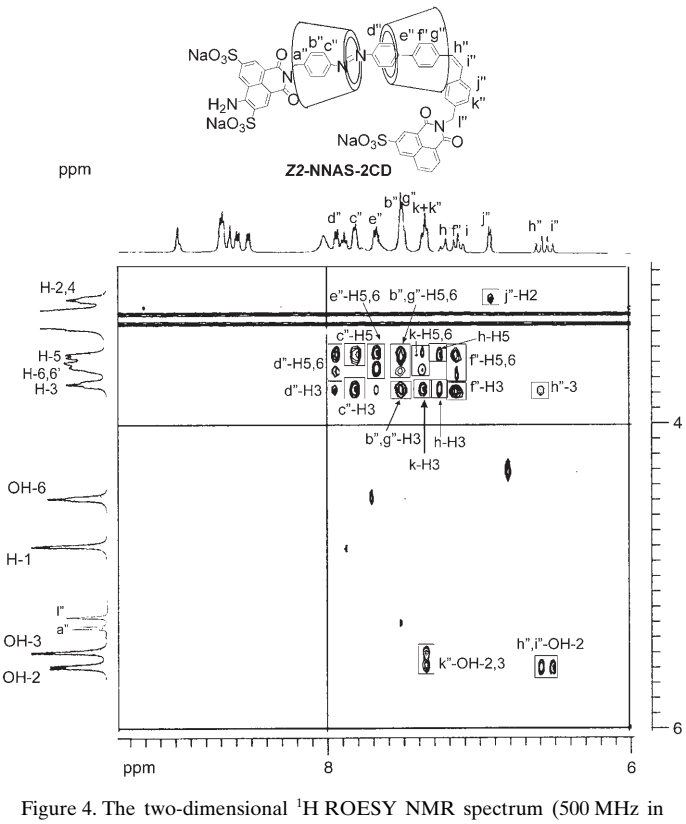


Figure 4. The two-dimensional ^{1}H ROESY NMR spectrum (500 MHz in [D$_6$]DMSO at 298 K; mixing time 300 ms) of **NNAS-2CD** after irradiation at 313 nm for 3 h.

of the azobenzene unit (see the Supporting Information). Irradiation of ***E*-NNAS-2CD** at 313 nm for 65 min causes photoisomerization from the *trans* to the *cis* configuration of the stilbene unit, generating another isomer, ***Z2*-NNAS-2CD**, which recovers to the *trans* configuration of stilbene upon irradiation at 280 nm for 2 h. The change is also characterized by a rise in absorption at around 270 nm ($\Delta A = 0.03$) and a decrease in absorption at 350 nm ($\Delta A = 0.05$). Similarly, irradiation of the dumbbell **NNAS** at 380 nm for 5 min causes an increase at around 270 nm ($\Delta A = 0.05$) and a decrease in absorption at 350 nm ($\Delta A = 0.09$), rapidly generating ***Z1*-NNAS**;[23] irradiation of the dumbbell **NNAS** at 313 nm for 15 min causes an increase at around 270 nm ($\Delta A = 0.045$) and a decrease in the absorption at 350 nm ($\Delta A = 0.08$), generating another isomer of the dumbbell ***Z2*-NNAS**.[23] The spectral changes for the dumbbell **NNAS** are more obvious than for the rotaxane **NNAS-2CD**; this indicates that the dumbbell **NNAS** undergoes photoisomerization more easily by UV irradiation. It is not surprising that the photoisomerization becomes more difficult in the presence of the α-CD ring. The maximum absorption of **NNAS-2CD** (the "**N**" stopper) at around 430 nm changes little, because it is separated from the residues by the methylene group.

Obvious changes in the fluorescence spectra have been found for the [3]rotaxane **NNAS-2CD**. Irradiation at 380 nm for 30 min results in the isomerization of the azobenzene unit, a lower intensity ratio (1.6:1) between the *E* isomer and the **PSS-A** (Figure 5) at the fluorescent emission maximum $\lambda_{max} = 520$ nm (due to the "**N**" stopper), and meanwhile an enhanced intensity ratio (0.6:1) in the fluorescence at $\lambda_{max} = 395$ nm (due to the "**S**" stopper). These changes can be reversed by irradiation at 450 nm for 60 min. By heating the **PSS-A** solution to 60 °C for 2 h, then cooling to

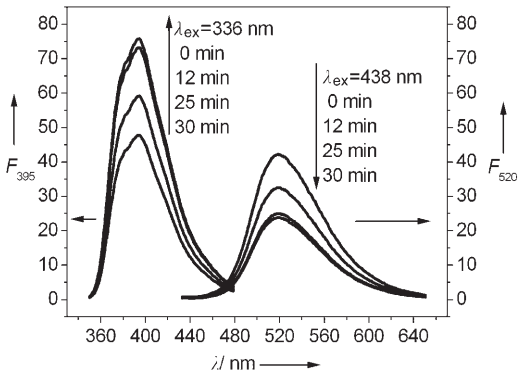


Figure 5. The fluorescence spectra of a **NNAS-2CD** solution (1.0×10^{-5} M in DMF) after irradiation at 380 nm (0–30 min). A 1.6:1 intensity ratio between the *E* isomer and the **PSS-A** is observed at the emission maximum at $\lambda_{max} = 520$ nm (due to the "**N**" stopper, $\lambda_{ex} = 438$ nm), and a 0.6:1 ratio is observed at $\lambda_{max} = 395$ nm (due to the "**S**" stopper, $\lambda_{ex} = 336$ nm).

room temperature, ***E*-NNAS-2CD** can also be recovered in the system. Contrarily, irradiation at 313 nm for 65 min causes isomerization of the stilbene unit; an enhanced ratio of 0.6:1 for the fluorescent intensity between the *E* isomer and the **PSS-S** at $\lambda_{max} = 520$ nm, and meanwhile a decreased ratio of 1.5:1 in the fluorescent intensity at the emission maximum at $\lambda_{max} = 395$ nm, are observed (Figure 6).

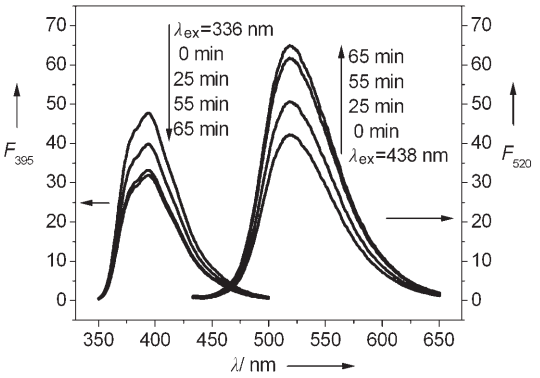


Figure 6. The fluorescence spectra of a **NNAS-2CD** solution (1.0×10^{-5} M in DMF) after irradiation at 313 nm (0–65 min). A 0.6:1 intensity ratio between the *E* isomer and the **PSS-S** is observed at the emission maximum at $\lambda_{max} = 520$ nm (due to the "**N**" stopper, $\lambda_{ex} = 438$ nm), and a 1.5:1 intensity ratio at at $\lambda_{max} = 395$ nm (due to the "**S**" stopper, $\lambda_{ex} = 336$ nm).

These changes can be reversed by irradiation at 280 nm for 2 h. The probable cause of the fluorescence changes is the rigidity of the α-CD ring. When the α-CD macrocycle stays near the fluorescent stopper, the vibration and the rotation of the bonds in the methylene group between the stopper and the recognition site are hindered, which clearly increases the fluorescence intensity of the stopper. This is confirmed by the finding of the weaker fluorescent intensity of the dumbbell **NNAS**,[23] in which the vibration and rotation are more facile without the macrocycles. Also, irradiation of the dumbbell at 380 nm and 313 nm does not induce obvious changes in the fluorescence intensity of the two stoppers in the dumbbell **NNAS**.[23] Since irradiation of the dumbbell **NNAS** at 380 nm and 313 nm can photoisomerize the azobenzene and stilbene units, the fluorescence of the two *Z* isomers obtained changes, albeit only to a very small extent, due to the changes in the configurations and the possibility of energy-transfer quenching of one stopper by the other.[23] This phenomenon is also in agreement with our previous reports.[18] In contrast, a fluorescent intensity ratio of 1:2.65 between the **PSS-A** and the **PSS-S** at the emission maximum at $\lambda_{max} = 520$ nm (due to the "**N**" stopper), and meanwhile another fluorescent signal with an intensity ratio of 2.5:1 at the emission maximum at $\lambda_{max} = 395$ nm (due to the "**S**" stopper), are observed. The fluorescence changes observed in this [3]rotaxane **NNAS-2CD** are more obvious than that in our previously reported [2]rotaxane,[18b] because of the greater rigidity of the two α-CD rings here than the single one in the [2]rotaxane. Because of the full reversibility of the photoisomerization processes, the photoinduced shuttling motions of the two α-CD rings can be repeated, and can be addressed with the reversible fluorescent output signals. By alternating irradiations at 380 nm and 450 nm, and 313 nm and 280 nm, respectively, we verified that the photochemical processes (isomerization of both the azobenzene and the stilbene) are highly reproducible over more than six cycles. As Figure 7 demonstrates, the [3]rotaxane **NNAS-2CD** has excellent recovery properties.

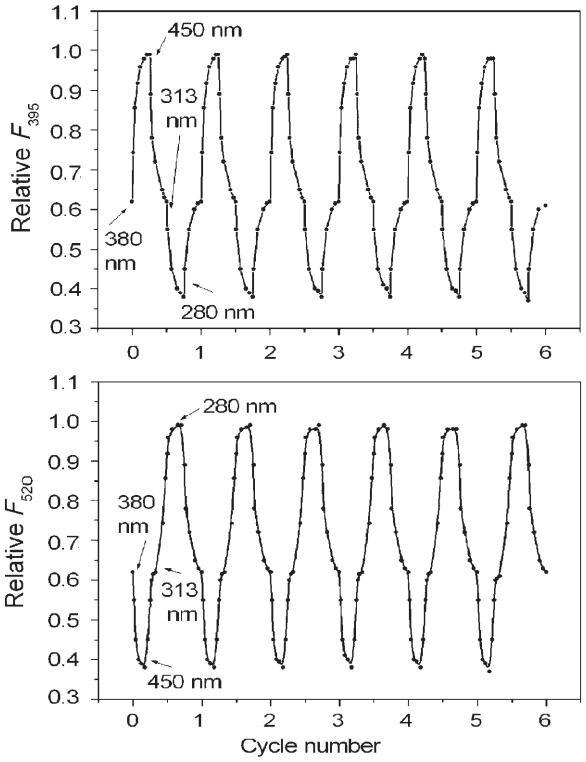


Figure 7. Changes in the fluorescence spectra of the "**S**" stopper (top, $\lambda_{ex} = 336$ nm, emission at $\lambda_{max} = 395$ nm), and the "**N**" stopper (below, $\lambda_{ex} = 438$ nm, emission at $\lambda_{max} = 520$ nm) of a **NNAS-2CD** solution (1.0×10^{-5} M in DMF) along with changes in irradiation cycle and light sources. In one cycle, 380 nm and 450 nm irradiation was first used to isomerize and recover the azobenzene unit, then 313 nm and 280 nm irradiation was used to isomerize and recover the stilbene unit. The photochemical processes are highly reproducible over more than six cycles.

The three stable states of [3]rotaxane **NNAS-2CD** can be described as the pure *E* isomer ("0" state), the **PSS-A** ("+1" state), and the **PSS-S** ("−1" state). The starting system (the "0" state) can be written with light at 380 nm and 313 nm to give the **PSS-A** ("+1" state) and the **PSS-S** ("−1" state), respectively. The transform between the "0" state and the "+1" (or "−1") state is accompanied by dual fluorescence addresses at $\lambda_{max} = 520$ nm and 395 nm. Also, the "+1" (or "−1") state can be shifted back reversibly to the "0" state with light at 450 nm (or 280 nm). Good reversibility could make it act as a molecular device such as a mul-

tistate molecular switch with entirely optical signals, or as a molecular storage medium.

Conclusion

A novel light-driven [3]rotaxane molecular shuttle, **NNAS-2CD**, has been synthesized and characterized, in which the two α-CD rings can be made to shuttle back and forth on the molecular thread that contains an azobenzene unit, a biphenyl unit, and a stilbene unit. The three stable states of this **NNAS-2CD** (that is, the *E* isomer and two *Z* isomers), are characterized by NMR experiments including two-dimensional NMR spectroscopy and dual fluorescence spectra. The shuttling movement of the α-CD rings can be addressed by the corresponding reversible fluorescence intensity changes of the two fluorescent stoppers. The output indicating the molecular shuttle movement is a fluorescence signal, which can be read easily because it allows remote sensing; thus it offers a further advantage over other spectral signals. The input is photochemical energy, which is superior to chemical or electrochemical input in terms of its cleanness and convenience. The complete reversibility exhibited by this [3]rotaxane should be emphasized; its most important feature, however, is that it demonstrates a principle that could be applied to produce molecular devices that can change any property that can be made to depend on the spatial separation of submolecular fragments. The use of stimulus-induced motion to bring individual components together to perform specific tasks that could produce an effect (for example, fluorescence changes) arguably makes such structures true mechanical molecular machines.

Experimental Section

General: H NMR spectra were measured on a Brücker AM 500 spectrometer. Elemental analysis was performed on a Perkin-Elmer 2400C instrument. Mass spectra (MS) were recorded on an MA1212 instrument using standard conditions (ESI, 70 eV), the MALDI-TOF spectrum on a 4700-Propeotics analyzer, and UV/Vis spectra on a Varian Cary 500 spectrophotometer (1 cm quartz cell) at 25 °C. Fluorescent spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer (1 cm quartz cell) at 25 °C. Photoirradiation was carried on a CHF-XM 500 W high-pressure mercury lamp with suitable filters (313 nm, 280 nm, 380 nm, half-width 30 nm, type FAL; Lambda Physics, Germany) in a sealed Ar-saturated 1 cm quartz cell. The distance between the lamp and the sample cell was 20 cm. Compound **1** and benzo[*de*]isoquinoline-1,3-dione-5-sulfonic acid sodium salt were prepared as described previously.[18b]

4-Methyl-4′-iodostilbene (2a): A solution of *p*-iodobenzyl bromide (25.0 g, 84.2 mmol) in trimethyl phosphite (50 mL, 424 mmol) was heated under reflux for 4 h. The excess phosphite was removed in vacuo, the yellow residue was dissolved in dried DMF (37 mL) and THF (37 mL), the resulting solution was cooled to 0 °C, a solution of sodium methoxide (4.6 g, 85.2 mmol) in methanol (32 mL) was added dropwise, and the mixture was stirred for 1.5 h at room temperature. Another solution of *p*-methylbenzaldehyde (10.5 g, 87.5 mmol) in DMF (70 mL) was then added dropwise and stirring was continued for another 3 h. More sodium methoxide solution (1.4 g, 26 mmol) in methanol (11 mL) was added and the resulting mixture was stirred for another 18 h, then poured into water (300 mL), The precipitate was collected by filtration, washed with water, dried, and recrystallized from methanol to give **2a** (18.1 g, 67 %) as a white solid. M.p. 209–210 °C. The product was pure enough to use in subsequent preparations.

4-(2-*p*-Tolylvinyl)phenylboronic acid (2b): Compound **2a** (17.5 g, 54.7 mmol) was lithiated with *n*-butyllithium (1.6 M, 37.0 mL, 59.2 mmol) in dry THF (180 mL) at −78 °C for 3 h. Trimethyl boronate (9.5 mL, 83 mmol) was added to the stirred suspension and the resulting mixture was allowed to warm to room temperature and stirred for another 8 h, then acidified with 10 % hydrochloric acid. After concentration, a great deal of yellow solid was precipitated, which was collected by filtration, washed with water, and dried. The resulting solid was stirred in dichloromethane (60 mL) for 1 h, filtered, and dried to give **2b** (7.1 g, 53 %) as a white solid. M.p. >250 °C; ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 8.02 (s, 2H), 7.78 (d, J = 7.7 Hz, 2H), 7.54 (d, J = 8.0 Hz 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 16.6 Hz, 1H), 7.19 (d, J = 7.7 Hz, 2H), 7.18 (d, J = 16.6 Hz, 1H), 2.31 ppm (s, 3H).

4-[2-(4-Bromomethylphenyl)vinyl]phenylboronic acid (2c): A mixture of **2b** (5.0 g, 21.0 mmol), *N*-bromosuccinimide (4.2 g, 23.6 mmol) and benzoyl peroxide (0.30 g) in dry benzene (800 mL) was stirred under reflux for 12 h, then filtered hot. The volume of the filtrate was reduced to about 150 mL under vacuum and the precipitate was collected, washed with ethanol and dried to give **2c** (4.6 g, 69 %) as an off-white powder. M.p. 210–212 °C (decomp). The product was used in subsequent preparations without purification.

4-{2-[4-(1,3-Dioxo-1*H*,3*H*-benzo[*de*]isoquinoline-5-sulfon-2-ylmethyl)-phenyl]vinyl}phenylboronic acid sodium salt (2): Sodium methoxide (3.7 g) in methane (20 mL, 8.2 mmol) was added to the solution of benzo[*de*]isoquinoline-1,3-dione-5-sulfonic acid sodium salt[18b] (2.5 g, 8.4 mmol) in DMF (20 mL). The mixture was stirred at room temperature for 4 h, then **2c** (1.3 g, 4.1 mmol) was added and stirring was continued for 8 h. The resulting solution was poured into water (100 mL), then acidified with dilute hydrochloric acid. The precipitate was filtered, washed with acetone, and dried to give **2** (1.6 g, 36 %) as a light yellow solid. M.p. >250 °C; ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 8.71 (s, 1H), 8.69 (s, 1H), 8.59 (d, J = 8.2 Hz, 1H), 8.52 (d, J = 7.3 Hz, 1H), 8.0 (s, 2H), 7.90 (dd, J_1 = 8.2 Hz, J_2 = 7.3 Hz, 1H), 7.77 (d, J = 8.1 Hz, 2H), 7.54 (m, 4H), 7.38 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 16.4 Hz, 1H), 7.19 (d, J = 16.4 Hz, 1H), 5.28 ppm (s, 2H).

1-α-CD: Compound **1** (0.15 g, 0.2 mmol), α-CD (0.20 g, 0.21 mmol) and water (20 mL) were mixed and stirred at 60 °C for 20 h, then the transparent solution was evaporated in vacuum and the solid was recrystallized from water/ethanol (1:4) to give red powder (0.3 g, 86 %). M.p. >250 °C; ^{1}H NMR (500 MHz, D$_2$O, 25 °C, TMS): δ = 9.0 (s, 1H), 8.84 (s, 1H), 8.80 (s, 1H), 7.85 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 5.27 (s, 2H), 5.0 (s, 6H), 3.87–3.56 ppm (m, 36H).

2-α-CD: A solution of **2** (0.11 g, 0.21 mmol) in DMF (5 mL) was added dropwise to the α-CD aqueous solution (0.2 g in 50 mL water). The mixture was heated to 70 °C for 40 h to give a transparent solution. Most of the solvent was evaporated in vacuum and acetone (50 mL) was added to precipitate a white solid (0.2 g, 65 %). M.p. >250 °C; ^{1}H NMR (500 MHz, D$_2$O, 25 °C, TMS): δ = 8.61 (s, 2H), 8.41 (d, J = 6.8 Hz, 1H), 8.31 (d, J = 7.8 Hz, 1H), 7.75 (dd, J_1 = 7.8 Hz, J_2 = 6.8 Hz, 1H), 7.52 (dd, J_1 = 7.2 Hz, J_2 = 8.7 Hz, 4H), 7.38 (dd, J_1 = 8.7 Hz, J_2 = 7.2 Hz, 4H), 7.26 (d, J = 16.4 Hz, 1H), 7.16 (d, J = 16.4 Hz, 1H), 5.25 (s, 2H), 5.0 (s, 6H), 3.89–3.58 ppm (m, 36H).

NNAS: Compounds **1** (0.15 g, 0.2 mmol) and **2** (0.11 g, 0.21 mmol) and Pd(OAc)$_2$ (10 mg, 0.044 mmol) were dissolved in aqueous Ar-saturated sodium carbonate solution (30 mL, 0.2 M). The mixture was stirred at 85 °C for 24 h, then cooled and acidified with acetic acid. After concentration in vacuo, the resulting dark solid was purified by column chromatography (silica gel; upper layer = acetic acid/*n*-butanol/water, 1:2:5) to give pure **NNAS** (65 mg, 29.5 %) as a yellow powder. M.p. >250 °C; ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 8.95 (s, 1H), 8.69–8.66 (m, 3H), 8.63 (s, 1H), 8.57 (d, J = 8.2 Hz, 1H), 8.50 (d, J = 7.0 Hz, 1H), 8.02 (s, 2H), 7.92 (d, J = 8.2 Hz, 2H), 7.88 (dd, J = 7.0 Hz, J = 8.2 Hz, 1H), 7.84 (d, J = 7.7 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.51 (m,

6H), 7.38 (dd, J = 8.6 Hz, 4H), 7.25 (d, J = 16.5 Hz, 1H), 7.14 (d, J = 16.5 Hz, 1H), 5.18 ppm (s, 4H); MS (70 eV, ESI): m/z (%): 1099 (65) [M^+], 1122 (100) [M^++Na]; elemental analysis: calcd (%) for $C_{52}H_{32}N_5Na_3O_{13}S_3$: C 56.78, H 2.93, N 6.37; found: C 56.76, H 2.92, N 6.39.

NNAS-2CD: Compounds **1-α-CD** (0.14 g, 0.080 mmol) and **2-α-CD** (0.12 g, 0.078 mmol) and $Pd(OAc)_2$ (3.8 mg, 0.017 mmol) were dissolved in aqueous Ar-saturated sodium carbonate solution (20 mL, 0.2 M). The mixture was stirred at 85 °C for 24 h, then cooled and acidified with acetic acid. After concentration in vacuo, the resulting dark solid was purified by column chromatography (silica gel; upper layer = acetic acid/*n*-butanol/water, 1.5:2:5) to give pure **NNAS-2CD** (43 mg, 18%) as a yellow powder. M.p. >250 °C; ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 8.95 (s, 1H), 8.69–8.65 (m, 3H), 8.62 (s, 1H), 8.58 (d, J = 8.1 Hz, 1H), 8.50 (d, J = 7.0 Hz, 1H), 8.02 (s, 2H), 7.92 (d, J = 8.1 Hz, 2H), 7.87 (dd, J = 7.0 Hz, J = 8.2 Hz, 1H), 7.83 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.51 (m, 6H), 7.38 (dd, J = 8.6 Hz, 4H), 7.25 (d, J = 16.0 Hz, 1H), 7.14 (d, J = 16.0 Hz, 1H), 5.52 (d, J = 6.6 Hz, 12H), 5.44 (s, 12H), 5.25 (s, 4H), 4.79 (s, 12H), 4.49 (s, 12H), 3.76–3.54 (m, 48H), 3.4 (m, 12H), 3.25 ppm (m, 12H); MALDI-TOF: m/z (%): 3067.7 (100) [M^++Na], 3045.7 (60) [M^++1]; elemental analysis: calcd (%) for $C_{124}H_{152}N_5Na_3O_{73}S_3\cdot 12H_2O$: C 45.66, H 5.44, N 2.15; found: C 45.68, H 5.46, N 2.17.

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[23] The Supporting Information includes the two-dimensional ^{1}H ROESY NMR spectra of **1-α-CD** and **2-α-CD**, ^{1}H NMR of dumbbell **NNAS**, absorption spectra of compounds **1**, **2**, **NNAS**, and **NNAS-2CD**, MALDI-TOF mass spectra of **NNAS-2CD**, and fluorescence spectra of dumbbell **NNAS**.

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