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Photocontrol over Cucurbit[8]uril Complexes: Stoichiometry and Supramolecular Polymers

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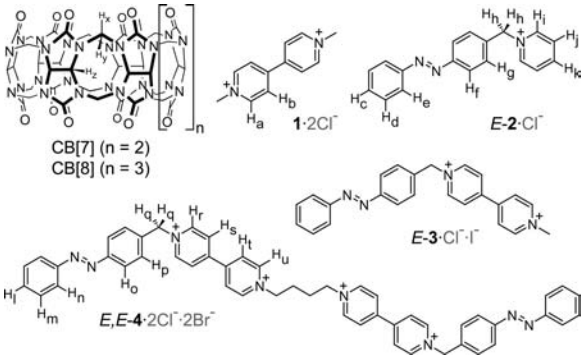
S *Supporting Information*

ABSTRACT: Herein we report the photocontrol of cucurbit[8]uril (CB[8])-mediated supramolecular polymerization of azobenzene-containing monomers. The CB[8] polymers were characterized both in solution and in the solid state. These host−guest complexes can be reversibly switched between highly thermostable photostationary states. Moreover, a remarkable stabilization of *Z*-azobenzene was achieved by CB[8] complexation, allowing for structural characterization in the solid state.

External control of self-assembling systems has attracted considerable interest across many scientific disciplines.[1] In supramolecular chemistry, an important focus is the use of light to harness reversible control over the state of host−guest complexes, as it does not require additional components and triggering can be easily achieved in a completely remote manner where and when required. The photoinduced isomerization of azobenzene compounds has been the molecular basis for a range of such photosensitive materials and self-assembling systems.[2] Thus, the inclusion of azobenzene compounds as guests in different macrocyclic host molecules, including cyclodextrins, calixarenes, pillararenes, and more recently cucurbit[*n*]urils (CB[*n*]; the structures of CB[7] and CB[8] are shown in Chart 1), can give rise to photosensitive host−guest complexes.[3]

Chart 1. Structures and Labeling of the Studied Compounds



The photocontrolled molecular recognition of hosts with azobenzenes has been used to develop hydrogels, micelles, molecular shuttles, ion channels, and drug-delivery vehicles.[4] With regard to the combination of azobenzenes and CB[*n*], Isaacs and co-workers demonstrated that CB[7] can promote the *E* → *Z* isomerization of 4,4′-diaminoazobenzene in aqueous solution at pH 3−6, as the high binding energy of the complex overcompensates for the thermodynamic cost of populating the *Z* form.[5] This system was cleverly used to construct an indicator displacement assay for a series of biologically relevant amines. We recently described the stimuli-responsive properties of a noncovalent complex based upon CB[8]-mediated heteroternary complexation with 1,1′-dimethyl-4,4′-bipyridinium dication (**1**) and an uncharged azobenzene derivative.[3d] In that case, the extended *E*-azobenzene was able to act as a second guest for a CB[8]·**1** binary complex, leading to the formation of a 1:1:1 heteroternary complex. Conversely, the photogenerated bent-shaped *Z* isomer was geometrically unfavorable for binding inside the CB[8] cavity in the presence of **1**.

Here we describe a new photoinduced complexation/decomplexation process to control the binding stoichiometry of a series of CB[8] complexes in a fully reversible manner. Kim and co-workers demonstrated the growth of a CB[8] oligo(pseudorotaxane) from a metallic surface.[6a] More recently, Zhang and co-workers reported a series of naphthalene- and anthracene-containing monomers that polymerized in the presence of CB[8].[6b] Herein we demonstrate for the first time the formation of CB[8] supramolecular polymers from guest monomers bearing azobenzene moieties both in solution and in the solid state. We also report the photocontrol of CB[8]-mediated supramolecular polymerization by means of photoinduced *E*−*Z* isomerization of the azobenzene moieties.

We selected **1** and 1-[*p*-(phenylazo)benzyl)]pyridinium chloride (*E*-**2**) (Chart 1) as model first and second guest molecules for the investigation of the photoresponsive properties of CB[8] complexes. Doubly charged guest **1** first binds to CB[8] in a 1:1 ratio to form the CB[8]·**1** complex with a binding constant (K_1) on the order of 10^5 M^{-1} (Scheme 1b).[7] In general, *E* isomers of azobenzene compounds are extended organic

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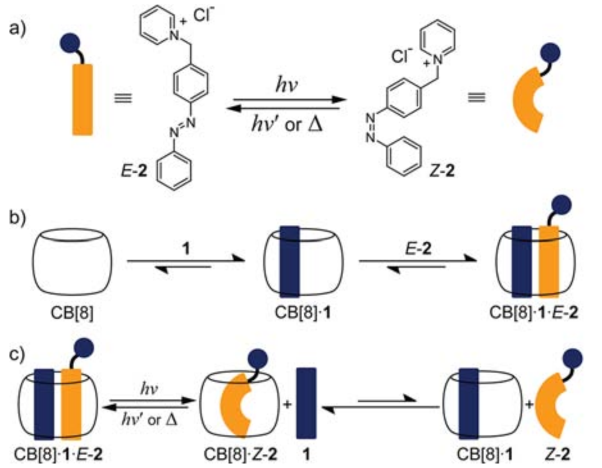
Scheme 1. (a) Isomerization of 2; (b) Stepwise Formation of CB[8]·1·*E*-2; (c) Isomerization of 2 in the Presence of CB[8] and 1 and Equilibrium after UV Irradiation of CB[8]·1·*E*-2



structures that can form CB[8] ternary complexes with complementary 4,4′-bipyridinium derivatives.[3d] The CB[8]·**1** complex can accommodate one *E*-**2** molecule in a second binding event, which was initially investigated by UV−vis spectroscopy. A relative decrease in intensity as well as a slight hypsochromic shift of the main absorption band of the azobenzene chromophore ($\pi-\pi^*$ transition at ∼320 nm) were detected when *E*-**2** was added to a solution of CB[8]·**1** in a 1:1 ratio [Figure S1 in the Supporting Information (SI)]. The band associated with the n−π^* transition at ∼430 nm was also decreased and broadened. These changes are due to intermolecular interactions and/or changes in the polarity of the chromophore environment and indicate the formation of a CB[8]·**1**·*E*-**2** ternary complex.

To further confirm the formation of the ternary complex, ^{1}H NMR titration experiments were performed in D_2O by gradually increasing the concentration of *E*-**2** while the concentration of CB[8]·**1** was kept constant (Figure S2). The signals for the protons in **1** and *E*-**2** were shifted upfield and broadened, except for those of H_i and H_j of *E*-**2**, which were slightly shifted downfield (Figures 1 and S2). These changes indicated the formation of a ternary complex with fast exchange on the NMR time scale. The association strength of *E*-**2** and CB[8]·**1** was obtained by isothermal titration calorimetry (ITC). Titration of *E*-**2** into an aqueous solution of CB[8]·**1** resulted in an exothermic isotherm; fitting to a 1:1 complexation model (Figure S3) gave a K_2 value of $(2.6 \pm 0.4) \times 10^4$ M^{-1} after correction for the heats of dilution.

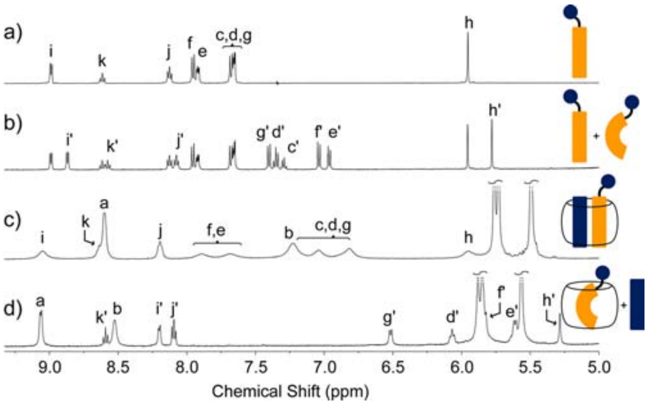


Figure 1. Partial ^{1}H NMR spectra (500 MHz, D_2O, 298 K) of (a, b) **2** before (a) and after (b) UV irradiation with an E:Z ratio ∼0.40:0.60 and (c, d) CB[8]·**1**·*E*-**2** before (c) and after (d) UV irradiation with an E:Z ratio ∼0.05:0.95. See Chart 1 for proton labeling. Signals corresponding to protons of the *Z*-**2** isomer are indicated with apostrophes. For clarity, only the *Z*-**2** signals are labeled in (b).

In general, upon irradiation with UV light, the *E* isomer of an azobenzene compound can be transformed into the *Z* isomer, which can revert back to the *E* state through either a thermal or photoinduced process (Scheme 1a). The photoisomerization properties of **2** in the absence and presence of CB[8]·**1** were investigated by UV−vis spectroscopy. The main band associated with *E*-**2** decreased upon UV irradiation, and two new bands appeared at ∼290 and ∼425 nm (Figure S12). These bands were related to *Z*-**2**, and the changes in the UV−vis spectrum can be ascribed to a decrease in the *E*:*Z* ratio after irradiation. The lifetime of the *Z* isomer was found to be on the order of several days, similar to those of other cationic azobenzene derivatives.[4d] Figure 1a,b shows partial ^{1}H NMR spectra of pure *E*-**2** before and after UV exposure. The set of upfield peaks in the NMR spectrum of an irradiated sample of *E*-**2** (Figure 1b) corresponds to the *Z* isomer. The photostationary state of the *Z* isomer (PSS_Z) of **2** was observed at an *E*:*Z* ratio of 20:80. Subsequent irradiation of *Z*-**2** with visible light ($\lambda > 420$ nm) resulted in a PSS with the *E* form as the predominant isomer (∼90%).

When a solution of CB[8]·**1**·*E*-**2** was exposed to UV light, the band corresponding to the $\pi-\pi^*$ transition strongly decreased, whereas the n−π^* band became narrower and shifted to lower wavelength (Figure S12). The changes in the UV−vis spectrum indicated the efficient *E* → *Z* photoisomerization of **2**, and the presence of two isosbestic points at 273 and 397 nm established that the system involves a clean two-state equilibrium. However, the differences between **2** alone and CB[8]·**1**·*E*-**2** after UV irradiation certainly suggested different molecular environments of *Z*-**2** in the presence and absence of CB[8] and **1**. In an effort to elucidate the type of interactions between CB[8], **1**, and *Z*-**2**, we recorded the ^{1}H NMR spectrum of an equimolar mixture of these three molecules after irradiation with UV light (Figure 1d). The spectrum is composed of a significant number of relatively sharp resonances in comparison to that of CB[8]·**1**·*E*-**2** (Figure 1c). After UV irradiation, the signals corresponding to protons H_j and H_k of the azobenzene guest remained almost unchanged, whereas those corresponding to protons H_{c-i} were significantly shifted upfield relative to those for *Z*-**2** alone. Conversely, the signals corresponding to protons H_a and H_b of **1** were shifted downfield. These changes suggested that *Z*-**2** was included inside the CB[8] cavity, whereas **1** may have resided outside the host cavity. The exclusion of **1** after UV irradiation of CB[8]·**1**·*E*-**2** was clearly evidenced by a series of diffusion-ordered NMR spectroscopy (DOSY) experiments. Before irradiation, the NMR signals of CB[8], **1**, and *E*-**2** shared a single diffusion coefficient ($D = [2.72 \pm 0.07] \times 10^{-10}$ m^2 s^{-1}) as they diffused together as one entity (Figure S4). After UV irradiation, the *D* values of two species were clearly separated, as **1** ($D = [7.94 \pm 0.50] \times 10^{-10}$ m^{2}s^{-1}) and the larger species CB[8]·*Z*-**2** ($D = [2.88 \pm 0.08] \times 10^{-10}$ m^2 s^{-1}) diffused independently (Figure S5). According to the Stokes−Einstein equation ($D = k_BT/6\pi\eta r$), the hydrodynamic radius of a molecular species (r) is inversely proportional to *D* in a medium of viscosity η (k_B is Boltzmann's constant and *T* is the absolute temperature).[8] Thus, a comparison of the sizes of two molecular species on the basis of their *D* values is valid, assuming that they have a spherical hydrodynamic shape and are at the same temperature.

We formulate the structures resulting after UV irradiation primarily as a mixture of uncomplexed **1** and CB[8]·*Z*-**2** (Scheme 1c). This result can be rationalized most simply by assuming that *Z*-**2** fully occupies the CB[8] cavity with a binding constant much higher than K_1. A series of ITC experiments allowed us to confirm this hypothesis. When a solution of CB[8] was titrated with *Z*-**2**, an exothermic isotherm was obtained, and fitting suggested a binding constant of up to $(1.0 \pm 0.4) \times 10^7$ M^{-1} (Figure S3). In comparison, the binding constant for preformed CB[8]·*Z*-**2** and **1** was too small to be measured by ITC.

The interactions between CB[8], **1**, and **2** greatly influence the photoswitchable behavior. First, the conversion of **2** after UV irradiation of CB[8]·**1**·*E*-**2** was determined to be >95% at PSS$_Z$. The higher conversion is likely related to the lack of spectral overlap of the two isomers, thus allowing for selective excitation at 360 nm. The photoinduced *E* → *Z* process is slower for CB[8]·**1**·*E*-**2** than for *E*-**2** alone (Figure S13). The CB[8]·*Z*-**2** complex also shows a slower thermal *Z* → *E* isomerization than *Z*-**2** alone, which could be attributed to a higher stability of the binary complex. Indeed, the high stability of CB[8]·*Z*-**2** allowed for structural characterization in the solid state, which is quite uncommon for both *Z*-azobenzene compounds and CB[8] inclusion complexes. Pale-yellow single crystals of CB[8]·*Z*-**2** were grown by slow evaporation of an aqueous solution of CB[8]·**1**·*E*-**2** after UV irradiation. Figure 2 shows the X-ray crystal structure of CB[8]·*Z*-**2**. The *Z*-azobenzene moiety of the guest is locked inside the CB[8] cavity, while the pyridinium group remains at the carbonyl portal area. The complexed CB[8] exhibits an ellipsoidal deformation characterized by the major and minor axes at the equator (major, 14.1 Å; minor, 12.0 Å) and the carbonyl portal (major, 10.8 Å; minor, 8.7 Å).

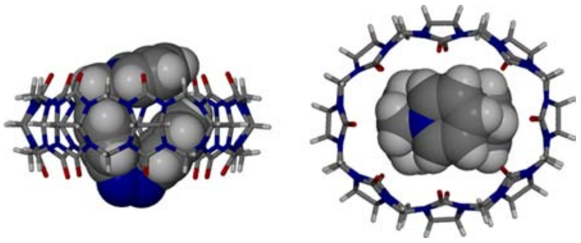


Figure 2. Side and top views of CB[8]·*Z*-**2**. Only the largest component of *Z*-**2** disorder is shown. C, gray; N, blue; O, red; H, white.

Guest molecule *E*-**3** can be regarded as an AB-type monomer, with A and B representing bipyridinium- and azobenzene-type first and second CB[8]-binding motifs (Chart 1). A theoretical equilibrium between a 2:2 complex and a linear supramolecular polymer can be expected for a 1:1 mixture of CB[8] and *E*-**3** (Scheme S2 in the SI). Comparison of the ^{1}H NMR spectra for *E*-**3** in the absence and presence of CB[8] revealed that most of the proton resonances of the guest were shifted upfield (Figure S21), suggesting the formation of a host−guest inclusion complex. Since the integration of the resonances was consistent with either 2:2 or *n*:*n* (supramolecular polymer) stoichiometry, the absolute stoichiometry was further investigated by DOSY, which gave $D = (2.16 \pm 0.03) \times 10^{-10}$ m^2 s^{-1} for a sample prepared from equimolar amounts of CB[8] and *E*-**3** (Figure S6). This value is 79% of that for CB[8]·**1**·*E*-**2**, meaning that the heteroternary complex is approximately half the size of the CB[8] complex with *E*-**3**.[9] Therefore, the absolute stoichiometry of the latter is CB[8]$_2$·*E*-**3**$_2$ on the basis of the DOSY results. The molecular size of the complex was further investigated by small-angle neutron scattering (SANS) and static light scattering (SLS). Surprisingly, large structures with a radius of gyration (R_g) of ~35 nm were detected by SANS (Figure S19). A similar R_g of ~40 nm was obtained when the same mixture was analyzed by SLS. These results give a more complete description of the equilibrium between the 2:2 and *n*:*n* complexes that exists when CB[8] and *E*-**3** are mixed in a 1:1 ratio. The larger structures detected by SANS and SLS are probably related to "short-lived" solution-phase supramolecular polymers (*n*:*n* complexes), which can be detected only by static techniques. We were also successful in characterizing the structure of the CB[8]$_n$·*E*-**3**$_n$ supramolecular polymer in the solid state by synchrotron X-ray diffraction measurements (Figure 3). The *E*-**3** guest molecules clearly form a polymeric structure through pseudorotaxane interdigitation of CB[8] host molecules. To the best of our knowledge, this crystal structure represents the first of its kind for a linear CB[8]-mediated polymer.

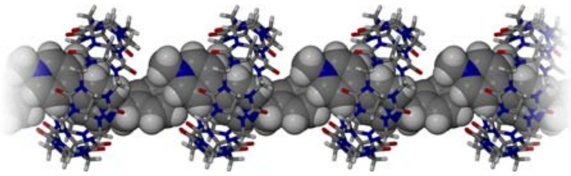


Figure 3. Side view of CB[8]$_n$·*E*-**3**$_n$. Colors as in Figure 2.

The photoswitchable behavior of CB[8]·**3** and its effect on the host−guest complex stoichiometry was investigated by UV−vis and ^{1}H and DOSY NMR spectroscopies. A decrease in the intensity of the π−π* absorption band as well as a large blue shift of the n−π* band were detected after the photoinduced *E* → *Z* isomerization of **3** in the presence of CB[8] (Figure S11). This parallels the results observed for CB[8]·**1**·*E*-**2**. The changes in the ^{1}H NMR spectrum after UV exposure were also consistent with those detected for the heteroternary complex and suggested the formation of a 1:1 CB[8]·*Z*-**3** complex with CB[8] tightly bound to the azobenzene moiety of *Z*-**3** (Figure S21). DOSY experiments yielded *D* values for two different species after UV irradiation: the 2:2 complex CB[8]$_2$·*E*-**3**$_2$ ($D = [2.16 \pm 0.03] \times 10^{-10}$ m^2 s^{-1}) and the 1:1 complex CB[8]·*Z*-**3** ($D = [2.82 \pm 0.05] \times 10^{-10}$ m^2 s^{-1}), which is roughly half the size of CB[8]$_2$·*E*-**3**$_2$ (Figures S7 and S8). A drastic size reduction from ~35 to ~1 nm was also observed by both SLS and SANS, indicating that the host−guest complex after UV irradiation can be adequately described as a 1:1 CB[8]·*Z*-**3** complex. Thus, depolymerization was indeed achieved after UV irradiation.

A 2:1 mixture of CB[8] and the guest molecule *E*,*E*-**4** could yield only linear supramolecular polymers, as the formation of complexes with lower absolute stoichiometry would be prevented by the design of **4**.[6b] The ^{1}H NMR spectrum of this mixture contained a set of broad and ill-defined signals presumably corresponding to polymeric species (Figure 4a). The molecular size of the complexes could not be determined by either DOSY (because of the absence of well-defined spectra) or SANS (on account of the limited *q* range of the setup to which we had access). Thus, the size determination relied only on SLS experiments, which gave $R_g \approx 60$ nm for a 2:1 mixture of CB[8] and *E*,*E*-**4**. This larger R_g relative to that obtained by SLS for an equimolar mixture of CB[8] and *E*-**3** is likely due to both the larger size of **4** and stronger association between the repeating units of the supramolecular polymer. A control experiment was performed wherein CB[7] (Chart 1) instead of CB[8] was mixed

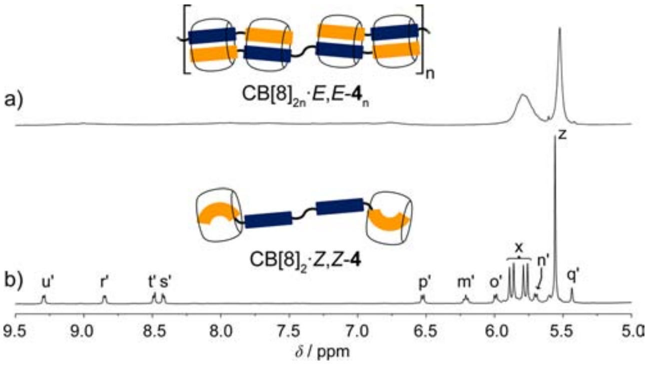


Figure 4. Partial ^{1}H NMR spectra (500 MHz, D_2O, 298 K) of a 1:2 mixture of **4** and CB[8] before (a) and after (b) UV irradiation. See Chart 1 for proton labeling.

with *E*,*E*-**4** in a 2:1 ratio. The cavity of CB[7] is large enough to encapsulate only one guest, so supramolecular polymerization cannot occur. The ^{1}H NMR spectrum contained a set of sharp resonances as is typically associated with well-defined species rather than supramolecular polymers. DOSY analysis gave a D value of $(2.13 \pm 0.03) \times 10^{-10}$ m^2 s^{-1} (Figure S9), consistent with a three-component CB[7]$_2$·*E*,*E*-**4** complex.

The optical properties and photoswitchable behavior of guest molecule **4** in the presence and absence of CB[8] showed features analogous to those previously described for **3**, as they have similar chromophore moieties and CB[8] binding domains (Figure S11). The ^{1}H NMR spectrum of a 2:1 mixture of CB[8] and **4** after UV irradiation consisted of a number of sharp and dispersed signals, indicative of a host−guest complex with a single, well-defined stoichiometry (Figure 4b). Much stronger evidence for the low absolute stoichiometry of the CB[8] complex of *Z*,*Z*-**4** was provided by DOSY, which gave $D = (1.83 \pm 0.07) \times 10^{-10}$ m^2 s^{-1} (Figure S10). The reduction in the size of the complexes was also confirmed by SLS, which gave $R_g < 5$ nm. Thus, the stoichiometry after irradiation can be rationally described as CB[8]$_2$·*Z*,*Z*-**4**, with the CB[8] cavities fully occupied by the azobenzene binding domains, evidencing that depolymerization was achieved after UV irradiation.

In summary, we have displayed control over the stoichiometry of a series of CB[8] complexes through photoirradiation. The *E*−*Z* isomerism of azobenzene-containing guest molecules for CB[8] is modified in the presence of the macrocycle. A remarkable stabilization of the *Z*-azobenzene moieties of guests **2**−**4** was achieved by CB[8] complexation. Host−guest complexes that can be remotely switched between highly thermostable photostationary states in aqueous media are valuable molecular systems in biological and materials sciences and are also of interest in information storage technologies and for the construction of molecular machinery.[10] Furthermore, we have shown that guests **3** and **4** in the presence of CB[8] can form supramolecular polymers, which were characterized both in solution and, for the first time, in the solid state and whose structures can be externally controlled by light irradiation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Procedures and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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