Photocontrol of Molecular Association attained by Azobenzene-modified Cyclodextrin

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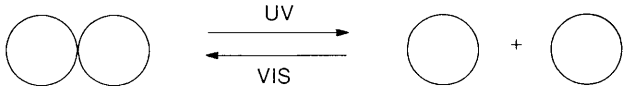
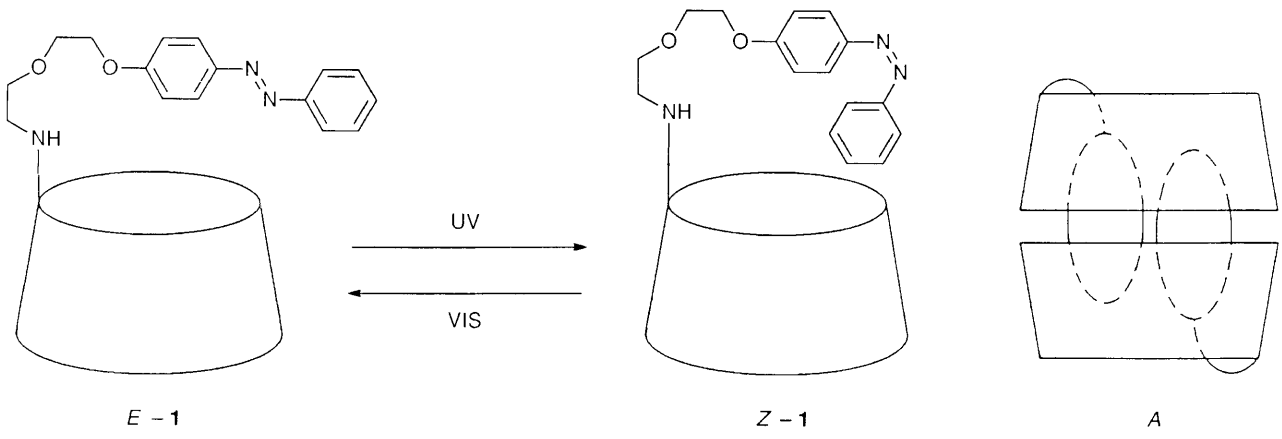
Interconversion between the monomer and the dimer of azobenzene-appended β-cyclodextrin **1** can be regulated by light in an on-off fashion.

Photocontrol of host–guest complexation has recently been achieved with crown ethers,[1,2] cyclodextrins[3,4] and other hosts,[5,6] each possessing at least one photochromic moiety. However, photoregulation of association or dissociation of molecular species as shown in Scheme 1 has never been



Scheme 1



E - **1** *Z* - **1** *A*

reported. We report here that azobenzene-modified cyclodextrin **1** forms an association dimer, which dissociates into monomers by UV irradiation and returns to its original form by visible light irradiation.

Cyclodextrins are cyclooligomers of α-D-glucose, named as α, β and γ for hexa-, hepta- and octa-mers, respectively. They can accommodate a variety of organic compounds in aqueous solution [7] and their binding behaviour has been shown to be modified by incorporating aliphatic[8] or aromatic[9] units into the original frameworks. We have prepared some photoreactive cyclodextrin derivatives to achieve photocontrol of complexation,[10] and, as an extension of the work, azobenzene-appended β-cyclodextrin **1** has recently been synthesized by reaction of 6-deoxy-6-iodo-β-cyclodextrin and 1-amino-5-(4-phenylazophenoxy)-3-oxapentane in *N*,*N*-dimethylformamide at 70 °C. The product was identified by ^{1}H NMR, UV, IR and elemental analysis.

The absorption spectrum of *E*-**1** in aqueous solution (1.96×10^{-5} mol dm^{-3}) at pH 6.7 exhibits a strong peak at 345 nm and a broad peak above 400 nm associated with azobenzene π–π* and n–π* transitions, respectively. Irradiation by UV light ($310 < \lambda < 390$ nm) converts *E*-**1** into *Z*-**1**, markedly decreasing the absorption of the π–π* band and slightly enhancing the n–π* band (420 nm) with isosbestic points at 298 and 408 nm. The circular dichroism (CD) spectrum of the solution of *E*-**1** (1.96×10^{-5} mol dm^{-3}) exhibits positive peaks at 345 and 420 nm associated with π–π* and n–π* transitions, respectively. The positive CD band of the π–π* transition indicates that the azobenzene moiety is included in the cavity of *E*-**1** with the orientation parallel to the cyclodextrin axis,[11] and consequently *E*-**1** exists as an intramolecular self-complexation form.[12] The molecular ellipticities [θ] of these bands, however, are greatly affected by the concentration of **1**; with increasing concentration of **1**, the π–π* CD band increases whereas the n–π* one decreases until the sign of the band becomes negative (Fig. 1). This results suggests that association of *E*-**1** takes place in concentrated solutions. Since the intensity of the π–π* band is much larger for the associated form than for the monomer, the azobenzene moicty is likely to be more deeply inserted in the β-cyclodextrin cavity of the dimer.

It was reported that a β-cyclodextrin derivative bearing a pendant naphthalene forms an association dimer (*A*).[13] The *E*-azobenzene moiety of **1** has a molecular shape which is more suited to be bound by two cyclodextrin units, and consequently **1** may also exist as such an associated form. Since secondary hydroxy groups of cyclodextrins become alkoxide anions above pH 12, the association dimer of *E*-**1** would be dissociated into the monomers under the alkaline conditions due to the electronic repulsion between the charged faces of two β-cyclodextrin units. From this viewpoint, we have undertaken a pH titration for the [θ] value of

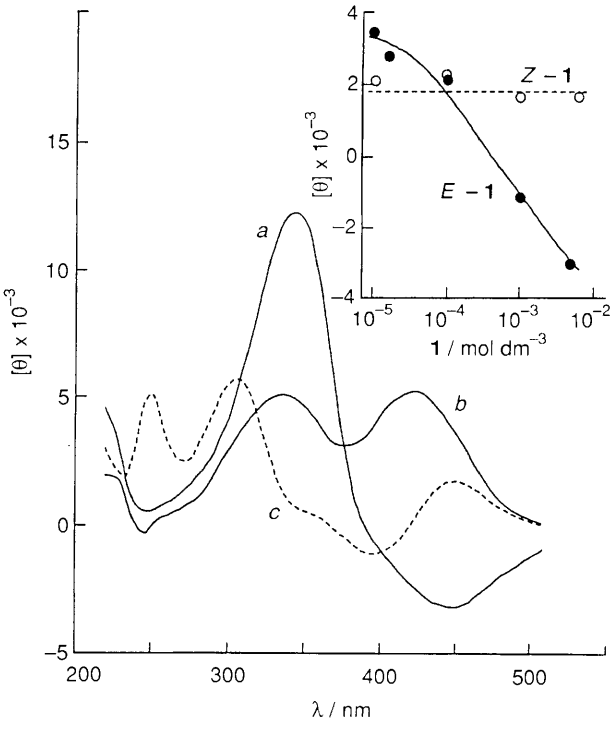


Fig. 1 The CD spectra of *E*-**1** (*a*, 4.91×10^{-3} mol dm^{-3}; *b*, 1.96×10^{-5} mol dm^{-3} and *Z*-**1** (*c*, 4.91×10^{-3} mol dm^{-3}) in aqueous solution at pH 6.7. The spectrum of *Z*-**1** in solution (1.96×10^{-5} mol dm^{-3}) is the same as *c* and is not shown here. The plots of [θ] (450 nm) against the concentration of **1** are shown in the upper-right corner.

E-**1** and observed an abrupt decrease in [θ] around pH 12.5 when pH of the solution was raised. This result confirms that *E*-**1** exists as the association dimer *A*, where the wider open sections of two cyclodextrin units are faced towards each other. The dimer may be formed by association of two species of the intramolecular self-complexation form, similar to that of pyrene-appended γ-cyclodextrin.[14] Although the association constant for the dimerization of *E*-**1** was not correctly obtained from the analysis of the concentration dependency of [θ] owing to the limited solubility of **1**, it was roughly estimated to be smaller than 10^4 mol^{-1} dm^3.

The CD spectrum of *Z*-**1** in aqueous solution (1.96×10^{-5} mol dm^{-3}) at pH 6.7 exhibits peaks at 245, 300 and 445 nm and a weak trough around 395 nm. This spectral pattern is similar to that reported for the *Z*-azobenzene–β-cyclodextrin complex.[11] In contrast to *E*-**1**, the molecular ellipticities as well as

the spectral pattern of *Z*-**1** are not affected by the concentration of **1** (Fig. 1). The results suggest that *Z*-**1** does not form such an association dimer as *A*. This property of *Z*-**1** may arise from the fact that the nonplanar azobenzene moiety of *Z*-**1** is not favourable for dimer formation. Since visible light (> 400 nm) immediately converts *Z*-**1** into the original *E*-**1**, it is possible to regulate the interconversion between the monomer and the dimer in an on-off fashion.

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