

Photocontrolled Molecular Assembler Based on Cucurbit[8]uril: [2+2]-Autophotocycloaddition of Styryl Dyes in the Solid State and in Water

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Three styryl dyes of the 4-pyridine series that form *syn*-head-to-tail dimeric pairs in polycrystalline films were synthesised. NMR and UV/Vis spectroscopic studies showed that this promotes stereospecific [2+2]-autophotocycloaddition (PCA) in the dimeric pairs to give *rc*tt-isomers of cyclobutane derivatives. For the dye with an *N*-ammoniopropyl substituent, this transformation was accomplished according to the single-crystal-to-single-crystal pattern. In aqueous solutions, the dyes and cucurbit[*n*]urils (CB[*n*], *n* = 7, 8) form complexes with a pseudorotaxane structure. CB[7] tends to form 1:1 complexes, and CB[8] forms 1:1 and 2:1 complexes. The structure of the termolecular complex formed by the betaine of the *N*-sulfonatopropyl styryl dye and CB[8] was determined by X-ray diffraction. The stability of the complexes

was measured by ¹H NMR titration in a D₂O/[D₃]MeCN (10:1) mixture (log *K*_{1:1} ≥ 3.2, log *K*_{2:1} ≥ 2.6). Free dyes and their complexes with CB[7] in water undergo only (*E*)/(*Z*) photoisomerisation. Termolecular complexes of all dyes with CB[8] were found to undergo effective stereospecific PCA reactions to give *rc*tt isomers of cyclobutane derivatives. The 1:1 complexes of the obtained cyclobutanes with CB[8] (log *K*_{cb} = 3.2–4.8) are less stable than those of the starting dyes with the same stoichiometry. Thus, CB[8] can play the role of a photocontrolled molecular assembler, i.e., even in the presence of 5 mol-% of CB[8], complete conversion of styryl dyes into the corresponding cyclobutane derivatives takes place upon irradiation in solution.

Introduction

The complexation properties of a relatively new class of cavitand molecules having the shape of a “barrel” with two symmetric portals – the cucurbit[*n*]urils (CB[*n*]) – have been vigorously studied over the last decade.^[1] CB[*n*] have different sizes of the hydrophobic cavity depending on the number of glycouril units (*n* = 5–8, or 10), which allows them to encapsulate one or two organic molecules of appropriate size and shape. Cucurbiturils differ from other well-known macrocyclic compounds having a 3D cavity (cyclodextrins, calix[*n*]arenes) by enhanced structural rigidity; therefore, they exhibit a higher selectivity in the formation of inclusion complexes. The relatively high partial negative charge on the donor oxygen atoms of the carbonyl groups

that constitute the CB[*n*] portals increases the stability of their adducts with positively charged ions. Owing to the properties listed above, cucurbiturils tend to form rather stable complexes with ammonium compounds^[2] and quaternary salts of nitrogen heterocycles^[3] both in water and in the solid phase.

Of particular interest for the study of the complexation properties of cucurbiturils are guest molecules, in particular, positively charged unsaturated compounds such as ammonium stilbene derivatives and viologen vinylogs.^[4] Owing to the presence of a C=C double bond, these compounds are able to undergo photoinduced changes in spatial structure upon (*E*)/(*Z*) isomerisation and [2+2]-photocycloaddition (PCA) reactions; i.e. they can mechanically move in the CB[*n*] cavity with simultaneous changes in the stability of complexes and, hence, these systems can be used to design light-controlled molecular devices and machines.^[5]

Molecular machines capable of directing chemical reactions by positioning the molecules are called *assemblers*.^[6] Ribosome is an example of a natural assembler consisting of ribonucleic acid and proteins that is capable of synthesising cell proteins from amino acids.^[6b]

Presumably, cucurbiturils could function as molecular assemblers in *mechanochemical systems*,^[6c–6h] which selectively bind a substrate and position it in the inner sphere in a particular way, i.e., they pre-organise the substrate's reac-

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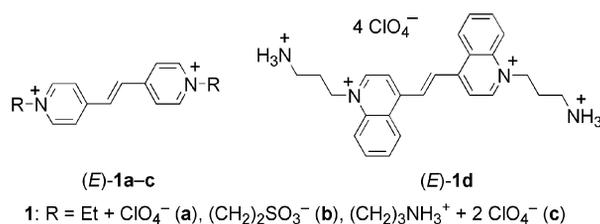
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tive sites for the desired chemical reaction, provide for energy supply and the mechanical migration of the substrate, allow chemical transformation to the products in the inner sphere, and finally release the products to the outer medium due to the lower complementarity of the assembler and the products compared to the substrate. Several types of assemblers have now been proposed; however, none have been based on CB[*n*], and generally this field is relatively unexplored.

Recently, we showed^[7] that bis(quaternary) salts of dipyrindylethylenes (*E*)-**1a,b** (Scheme 1) and CB[7] form stable 1:1 pseudorotaxane complexes in water ($\log K_{1:1} = 5.1$ and 3.5, respectively); CB[8], having a relatively larger cavity, was capable^[8] of forming highly stable complexes of different stoichiometry with *N,N'*-bis(ammonio)propyl derivatives of dihetarylethylenes (*E*)-**1c,d**. An important role in these complexes is the ability to form hydrogen bonds between the terminal ammonium groups of the guest and the oxygen atoms of CB[8] portals. On light irradiation of an aqueous solution of a mixture of (*E*)-**1d** and CB[8], reversible (*E*)/(*Z*) isomerisation of the unsaturated molecule took place to give stable complex (*Z*)-**1d**@CB[8], which was characterised by X-ray diffraction.



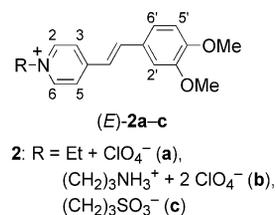
Scheme 1. Structure of viologen vinylogs **1a–d**.

We found^[9] that, unlike viologen vinylogs **1a–d**, styryl dyes with the general formula R–Het⁺–CH=CH–Ar X⁻ do not only undergo effective (*E*)/(*Z*) photoisomerisation reactions, but also stereoselective [2+2]-PCA reactions, which occur both in solution and in the solid phase. The optical characteristics of these dyes can be readily adjusted by varying the nature of the heterocyclic residue and substituents in the aryl group. The reversible PCA reaction of styryl dyes is of most interest for the design of photoswitchable molecular devices, photocontrolled molecular machines, optical molecular sensors, and reversible optical information recording systems. The resulting photoproducts – cyclobutane derivatives – are thermally stable, stable against photodegradation and do not fluoresce; the hypsochromic shift of the long-wavelength absorption maximum reaches 120 nm. For the PCA reaction to proceed in solution, the dye molecule must contain particular functional sites, such as a crown-ether fragment and a terminal SO₃⁻ or NH₃⁺ group in the *N*-substituent. These are needed for self-assembly of molecules into dimeric complexes structurally pre-organised toward the PCA.^[9a,9c] This considerably restricts the range of dyes and solvents that are suitable for effective PCA.

The problem of styryl dye pre-organisation toward the PCA reactions in solutions can be solved by using macro-

cyclic cavitands having rather large cavities. For example, the positively charged styryl dye cation seems a promising candidate for insertion into the electron-donating cucurbit[*n*]uril cavity to give complexes in which various photoprocesses can occur selectively. However, although quite a few cases of cucurbituril complexation with chromo-(fluoro)phore compounds are known to date,^[4d,10] almost no studies of complexes of CB[*n*] with styryl dyes have been reported.^[10]

In this paper, we report a ¹H NMR and UV/Vis spectroscopic study of the photochemical behaviour of a series of related (4-pyridyl)styryl dyes (*E*)-**2a–c** differing in the structure of the *N*-substituent (Scheme 2) and their complexes with CB[*n*] (*n* = 7 and 8). The complexation properties of cavitands are compared quantitatively as a function of their size and the structure of the *N*-substituents in the dyes and the respective [2+2]-photocycloaddition products: 1,2,3,4-tetrasubstituted cyclobutanes. The structures of dye (*E*)-**2b**, the *rett* isomer of the cyclobutane derivative obtained from the dye by the single-crystal-to-single-crystal pattern, and the termolecular complex {(*E*)-**2c**}₂@CB[8] were determined for the first time by X-ray diffraction.



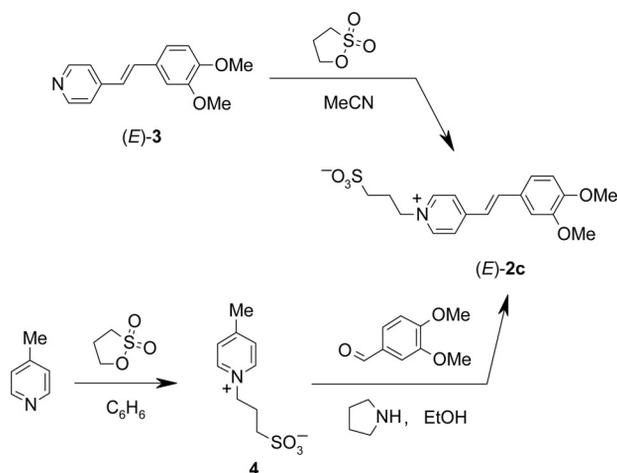
Scheme 2. Structure of styryl dyes **2a–c**.

Results and Discussion

Synthesis

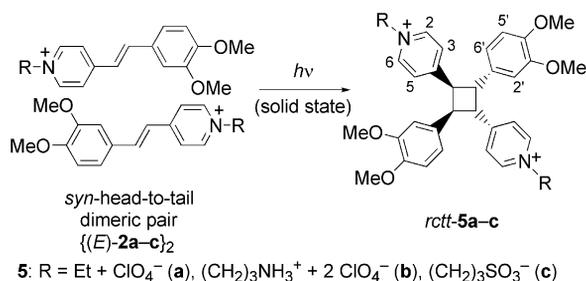
The synthesis of dyes (*E*)-**2a,b** was described previously.^[9e,11] Betaine dye **2c** was prepared by two methods: either styrylpyridine (*E*)-**3**^[12] was quaternised with 1,3-propanesultone, or the betaine of heterocyclic salt **4** was condensed with veratraldehyde in the presence of pyrrolidine as the base (Scheme 3). Salt **4** is often used in the synthesis of various dyes (see Hassner et al.^[13] for an example); however, it has been poorly described. We obtained this salt by quaternisation of 4-picoline with 1,3-propanesultone and report for the first time its characteristics. According to the spin–spin coupling constants for the ethylene protons, dye **2c** was formed in the (*E*) configuration (³*J*_{trans-CH=CH} = 16.3 Hz).

Previously, we showed^[9c,9e,9f] that polycrystalline films of (*E*)-**2a** and related styryl dyes containing electron-donating alkoxy groups in the benzene ring, undergo stereospecific PCA reaction on exposure to visible light to give centrosymmetric *rett* isomers of cyclobutane derivatives. This is caused by a structural pre-organisation of these dyes in the solid phase, specifically in single-crystals, represented by a predominant stacking motif in the molecular packing. Most

Scheme 3. Synthetic routes affording styryl dye **2c**.

often, the stacks are composed of centrosymmetric dimeric (stacking) pairs in which planar molecular cations are located one above another according to the *syn*-head-to-tail pattern. Undoubtedly, the structure of the dimeric pair is dictated by minimisation of the Coulomb repulsion of like charged fragments with the maximum secondary interaction of the p_z -orbitals of conjugated fragments. In the dimeric pairs, the ethylene bonds are antiparallel and rather closely spaced (up to 4.2 Å), which is favourable for a topochemical PCA reaction, including the single-crystal-to-single-crystal reaction, i.e., a reaction without crystal destruction.

The irradiation of polycrystalline films of dyes (*E*)-**2a–c** yielded only centrosymmetric *rc*tt isomers of cyclobutane derivatives **5a–c** (Scheme 4). This implies that *syn*-head-to-tail dimeric pairs $\{(E)\text{-}2\mathbf{a}\text{-c}\}_2$, which precede the formation of cyclobutanes with this stereochemistry, exist in the solid phase. In the case of (*E*)-**2a**, photoreaction proceeds quantitatively over a period of 110 h, whereas for (*E*)-**2b,c** this process is much slower and does not reach completion even after 230 h. Apparently, the presence of the long, bulky *N*-substituent reduces the efficiency of the photoreaction, which is in line with previous studies on PCA reactions of styryl dye films.^[9e] Yet another interpretation of the retardation of PCA may be the fact that other molecular packing motifs that do not promote PCA reactions are also encountered in polycrystalline films of (*E*)-**2b,c**. Cyclobutanes

Scheme 4. Synthetic route to cyclobutanes *rc*tt-**5a–c** in the solid state.

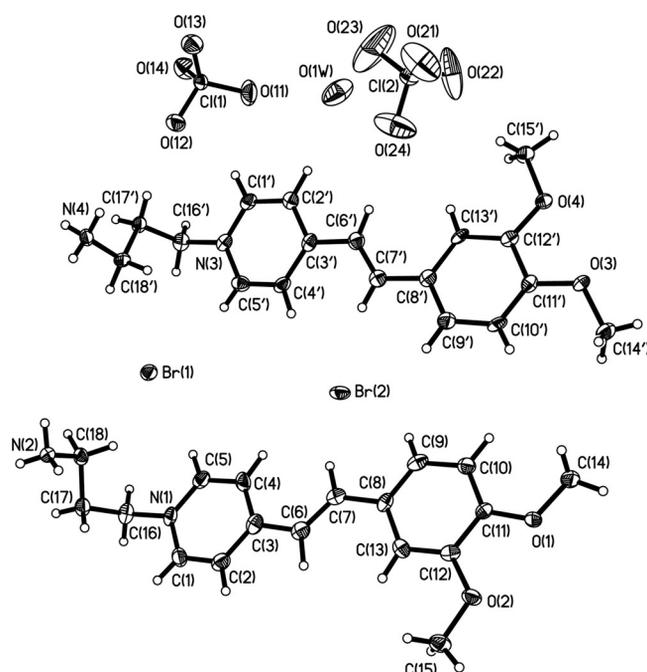
*rc*tt-**5b,c** were isolated from reaction mixtures in 85–86% yields by fractional crystallisation.

The structures of all of the obtained compounds were confirmed by ¹H and ¹³C NMR spectroscopy, spectrophotometry, and by elemental analysis.

X-ray Diffraction Studies of Dye **2b** and Cyclobutane **5b**

Dye (*E*)-**2b** was prepared as single crystals by slow crystallisation of the mother liquor formed after the exchange of bromide anions with perchlorate anions on treatment of the dibromide dye with perchloric acid.^[11] The resulting crystalline compound was a mixed salt containing an equal ratio of bromide and perchlorate anions. Apparently, only with this combination of anions can sufficiently large single crystals of this dye, that are suitable for X-ray diffraction analysis, be grown.

The structure of (*E*)-**2b** is shown in Figure 1. The unit cell comprises two independent dye dications, two perchlorate and two bromide anions, and a solvation water molecule O(1W) with an occupation of 0.25. For more convenient comparison of the geometric parameters of organic cations, rather than following IUPAC rules, the same numbering of like atoms is used. The chromophore fragments of both independent cations are nearly planar, which attests to a high degree of π -conjugation. Indeed, the dihedral angles between the pyridine and benzene ring planes are 6.3 and 14.8°. Both dye cations have (*E*) configuration of the ethylene fragment. The ethylene bonds are substantially localised; the bond lengths in the C_(Py)–C=C–C_(Ar) fragments are distributed as follows: 1.468(7), 1.335(7), 1.466(7) and 1.448(7), 1.340(7), 1.470(7) Å. The oxygen atoms O(1), O(2), O(3) and O(4) are efficiently conjugated with the ben-

Figure 1. Structure of dye (*E*)-**2b**. Thermal ellipsoids are drawn at the 50% probability level.

zene rings, as indicated by the values of bond angles at these atoms [116.9(4)–117.7(4)°], which are close to the perfect value of 120° for the sp^2 -hybrid state.

Highly skewed stacks composed of centrosymmetric dimeric pairs of the *syn*-head-to-tail type were found in the crystal for both independent cations (Figure 2); this is the most commonly found packing motif of styryl dyes.^[9e] The ammonium groups in the dimeric pairs are positioned near the methoxy groups of neighbouring cations in such a way that one hydrogen atom of the NH_3^+ group forms a bifurcate hydrogen bond with two oxygen atoms. The N(2)–H···O(1A), N(2)–H···O(2A), N(4)–H···O(3A) and N(4)–H···O(4A) distances are in the range of 2.08–2.37 Å, the angles at the H atoms are 122–152°, which implies relatively weak hydrogen bonds. In the dimeric pairs, the chromophore fragments occur in parallel planes at about 3.5 Å distances, their ethylene bonds being antiparallel and approaching each other to a distance of 4.00 Å [C(6)···C(7A) and C(7)···C(6A)] and 3.68 Å [C(6')···C(7'A) and C(7')···C(6'A)], whereas the distances between the ethylene bonds of the dimeric pairs neighbouring in the stacks are increased to 7.53 Å (both). Undoubtedly, this dye packing facilitates the solid-phase PCA reaction, giving the *rectt* isomer of the cyclobutane derivative, as was shown previously^[9c–9f] for (*E*)-**2a** and the related styryl dyes.

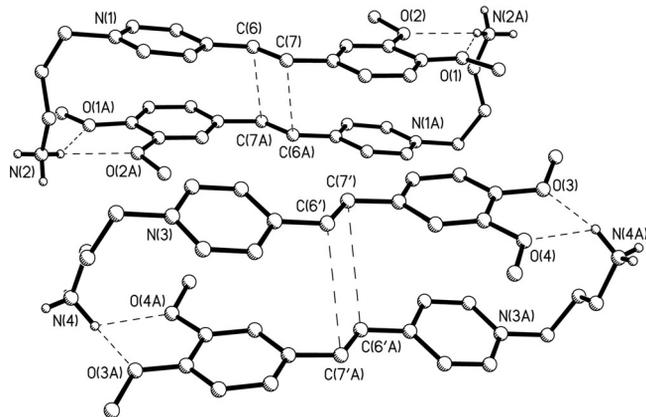


Figure 2. Structure of the dimeric pairs of independent cations of dye (*E*)-**2b**. Most of the hydrogen atoms are omitted for clarity. Hydrogen bonds and distances between ethylene bonds are drawn with dashed lines. The additional letter "A" indicates that atoms are at $(1-x, 1-y, 1-z)$ and $(1-x, 1-y, 2-z)$.

Indeed, visible-light irradiation of crystals of (*E*)-**2b** for 20 h resulted in complete transformation of the dye into centrosymmetric cyclobutane derivative *rectt*-**5b** according to the single-crystal-to-single-crystal type. The PCA reaction took place in both independent dimeric pairs, and, hence, two independent cyclobutane tetracations were formed (Figure 3). The PCA was accompanied by release of crystallisation water molecules and by only a 3.8% decrease in the crystal volume. The centres of the cyclobutane rings coincide with the symmetry centres of the crystal, which pre-determines an ideally planar conformation of these rings. A similar planar conformation of cyclobutane rings was observed in our previous study^[9c,9f] for the crystals of all cen-

trosymmetric *rectt* isomers of cyclobutane derivatives obtained from styryl dyes and their synthetic precursors, namely, neutral styrylheterocycles. The dihedral angle between the planes of the N(1) C_5 pyridine ring and the *cis*-positioned benzene ring, and a similar angle between the N(3) C_5 pyridine ring plane and *cis*-benzene ring, are 30.1 and 32.1°, respectively. Thus, in both cyclobutane tetracations, two *cis* substituents in the cyclobutane ring are proximate in space, and the ammonium group of one of them forms a bifurcate hydrogen bond with oxygen atoms of the methoxy groups, which is similar to the situation in the precursor dimeric pairs. Characteristics of the hydrogen bonds are as follows: the lengths, N(2)–H···O(1A), N(2)–H···O(2A), N(4)–H···O(3A) and N(4)–H···O(4A), occur in the range of 2.19–2.34 Å, and the angles at the H atoms are 123–164°.

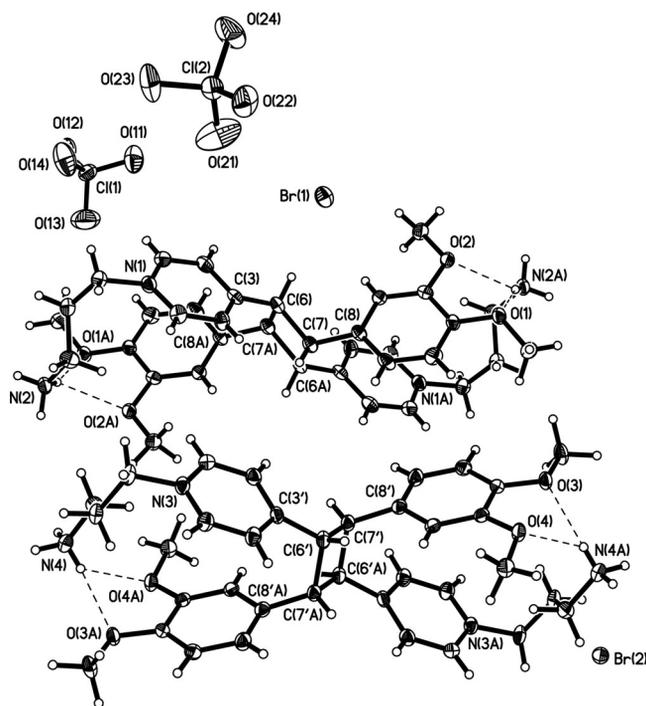
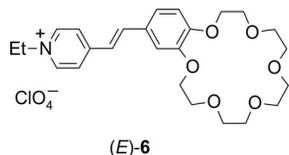


Figure 3. Structure of cyclobutane *rectt*-**5b**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen bonds are depicted with dashed lines. The additional letter "A" indicates that atoms are at $(1-x, 1-y, 1-z)$ and $(1-x, 1-y, 2-z)$.

UV/Vis and 1H NMR Spectroscopic Studies

The ability of dyes (*E*)-**2a–c** to form inclusion complexes with CB[*n*] in water was studied by spectral methods. Free compounds (*E*)-**2a**, (*E*)-**2b** and (*E*)-**2c** in water have an intense long-wavelength absorption band (LAB) with maxima at 385, 389 and 381 nm, respectively ($\epsilon = 29600, 30500$ and $28300 \text{ M}^{-1} \text{ cm}^{-1}$). Visible-light irradiation of dye solutions with concentrations of ca. $5 \times 10^{-5} \text{ M}$ resulted in a gradual decrease in the LAB intensity down to 76–83% of the initial value. Clearly, this reflects (*E*)/(*Z*) isomerisation of the dye and relatively slow (over 1 h) development of the photo-stationary state. A similar behaviour was observed pre-

viously^[9c] for a solution of a related crown-ether styryl dye (*E*)-**6** (see Scheme 5) in MeCN, where the photostationary equilibrium was attained much faster (<10 min), other factors being the same, and resulted in a much more pronounced decrease in LAB intensity (to 64% of the initial value). Evidently, this difference in the behaviour of dyes (*E*)-**2a–c** and (*E*)-**6** is caused by the solvent nature, as also indicated by the hypsochromic shift of the LAB maximum of the dyes (*E*)-**2a** and (*E*)-**6** (in MeCN, 397 and 399 nm, respectively) and by a decrease in the extinction by ca. 25% when changing the solvent from MeCN^[9c,9e] to water.^[14]



Scheme 5. Structure of dye **6**.

The visible-light irradiation of ca. 1×10^{-3} M solutions of dyes (*E*)-**2a–c** in a D₂O/[D₃]MeCN mixture (10:1) resulted, after 2–5 h, in the appearance of second sets of signals in the ¹H NMR spectra, indicating the presence of (*Z*)-**2a–c**, with typical spin–spin coupling constants for the ethylene protons ($^3J_{cis-CH=CH} = 12.0\text{--}12.1$ Hz). The relative amount of (*Z*) isomers in the mixtures varied from 31 to 41%, as indicated by comparison of the integral intensities of signals of like protons of the two geometric isomers. Long-term storage of the irradiated samples in the dark at room temperature resulted in very slow decrease in the relative amount of (*Z*) isomers (to 25–33% in 45 d), which is indicative of a low rate of thermal (*Z*) → (*E*) isomerisation under these conditions.

Cucurbit[*n*]urils do not contain long conjugated chromophore fragments; therefore, even their saturated solutions absorb above 250 nm only very slightly.^[7,15] Mixing of (*E*)-**2a–c** with either CB[7] or CB[8] leads to a considerable bathochromic shift of the LAB maximum and to its broadening and decrease in intensity (for example, see Figure 4). Apparently, this is due to the formation of inclusion complexes of CB[*n*] with the dyes in which the local solvation of the guest molecule differs from its solvation by water molecules. Complexation with CB[7] induces much greater shifts of the LAB maximum than with CB[8] ($\Delta\lambda_{\text{max}}$ up to 34 and 15 nm, respectively); this is attributable to tighter arrangement of molecules (*E*)-**2a–c** in the smaller cavity and, hence, their better shielding from the aqueous medium by the cavitand walls. An increase in the cucurbituril content in (*E*)-**2a–c**/CB[*n*] mixtures with respect to the equimolar ratio results in only minor changes in the form and position of the LAB (especially for CB[8]).

¹H NMR spectroscopic studies of the complexation of (*E*)-**2a–c** with CB[*n*] provided more information. The spectral behaviour of the components differs substantially when they are mixed in different ratios. For example, in the system (*E*)-**2a**/CB[7], one set of rather narrow signals was present for each of the components at any component ratio,

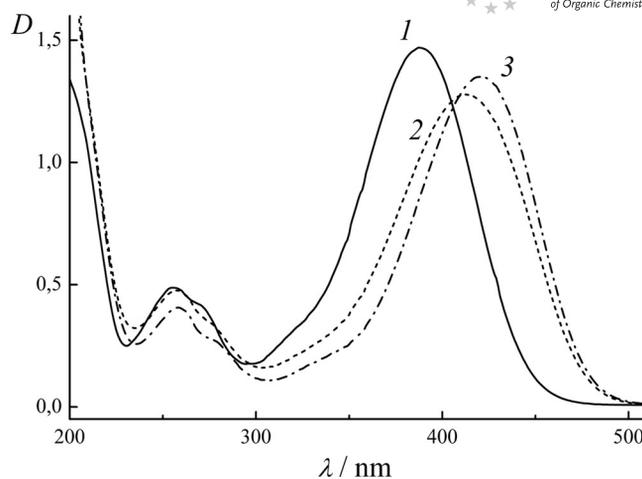


Figure 4. Absorption spectra in water at room temp.: (1) dye (*E*)-**2b** (4.85×10^{-5} M, 1 cm quartz cell) and its mixtures with CB[7] in (2) 1:1 and (3) 1:2 ratios.

which points to fast exchange on the ¹H NMR time scale. Conversely, the spectrum of (*E*)-**2c**/CB[7] always exhibited two sets of narrow proton signals for betaine (*E*)-**2c** and two sets of signals for CB[7] (see Figure 5). This spectral pattern attests to the formation of inclusion complex (*E*)-**2c**@CB[7], which undergoes slow exchange with free components. A similar spectral behaviour was observed previously^[7] for the complexation of dibetaine (*E*)-**1b** with CB[7]. Apparently, the presence of negatively charged bulky sulfonate groups in the guest molecule hampers the decomposition of the supramolecular complex (*E*)-**2c**@CB[7] to the starting components and thus increases its kinetic stability. Note that the presence of two sets of signals for each of the components contained in an equimolar ratio attests to the relatively low stability constant of the 1:1 complex, which was confirmed by investigating the quantitative characteristics of (*E*)-**2c** complexation with CB[7] (see below). The spectral behaviour of the system (*E*)-**2b**/CB[7] was more complicated than that of systems based on dyes (*E*)-

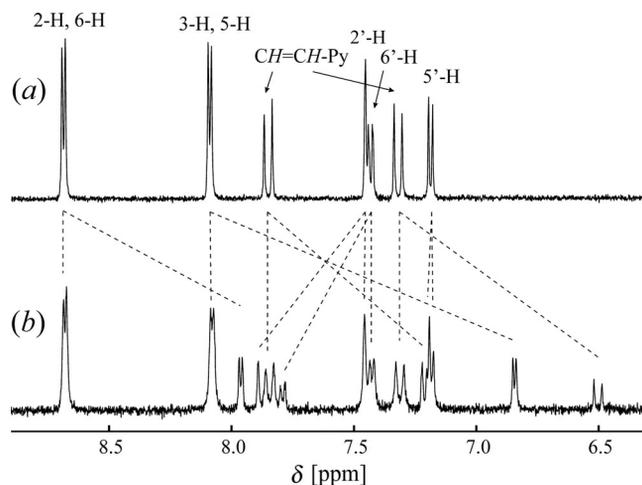


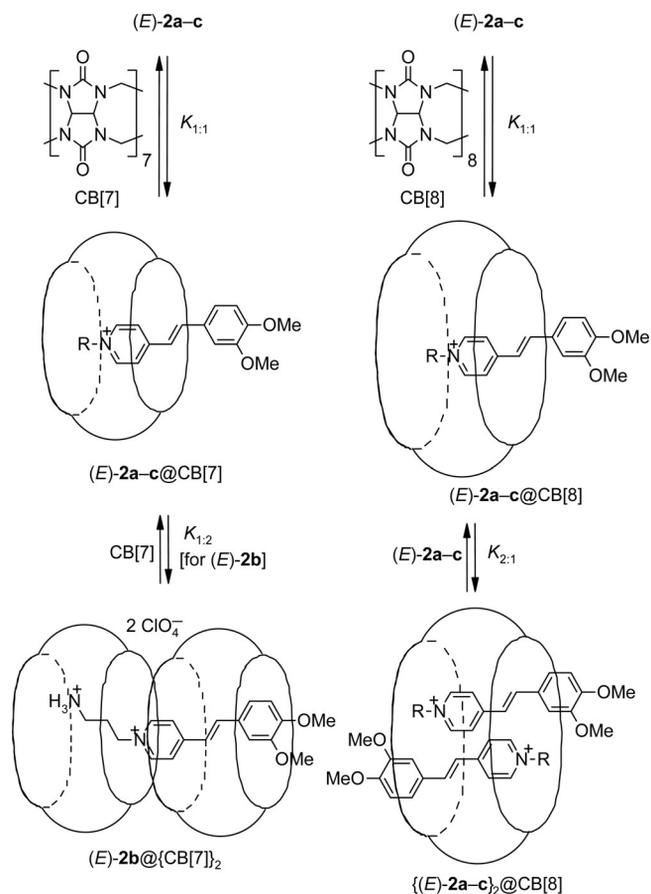
Figure 5. The ¹H NMR spectra (region of the aromatic protons) in D₂O/[D₃]MeCN (10:1) at 30 °C: (a) dye (*E*)-**2c** (1×10^{-3} M) and (b) its 1:1 mixture with CB[7].

2a,c. At a 1:2 component molar ratio of [(*E*)-**2b**]/(CB[7]) and at higher contents of CB[7], each system component was responsible for one set of narrow signals, whereas an increase in the relative content of (*E*)-**2b** resulted in pronounced broadening of most of dye signals. This result points indirectly to the formation of a more intricate composition of the supramolecular complexes and to their higher stability with the dye containing an ammonium group in the *N*-substituent compared to other styryl dyes.

In the case of mixtures of dyes (*E*)-**2a–c** with CB[8], broadening of the proton signals of guest molecules was more pronounced than for the CB[7] systems; this may be indicative of a more complicated equilibrium, i.e., formation of complexes having a different composition for CB[8] and relatively slow exchange on the ¹H NMR time scale between these complexes. Note that in the system (*E*)-**2c**/CB[8], study of the complexation was complicated by low solubility of the complexes, resulting in salting-out in the presence of excess dye.

Figure 5 shows the changes in the positions of the ¹H NMR signals of the aromatic and ethylene protons of dye (*E*)-**2c** following mixing with CB[7] in an equimolar ratio. It can be readily seen that the signals of the new set considerably differ in the direction and the magnitude of their shift with respect to analogous signals of free (*E*)-**2c**. The signals of both the pyridine residue and the ethylene bond undergo upfield shifts ($\Delta\delta_{\text{H}}$ of up to -1.24 ppm), whereas signals of the 2'-H and 6'-H protons of the benzene ring are shifted downfield ($\Delta\delta_{\text{H}}$ up to 0.44 ppm). This means that the CB[7] walls shield the protons of the CH=CHPy fragment to the highest extent, and, hence, the cavita nd is predominantly arranged in the complex above the positively charged region of the dye molecule. Following the migration away from the geometric centre of the CH=CHPy fragment, the protons of molecule (*E*)-**2c** become less shielded, and the signals of the peripheral CH₂SO₃⁻ group of the *N*-substituent and the 2'-H and 6'-H protons show a downfield shift, probably due to the deshielding action of the carbonyl groups of the host molecule portals. The signals of the most remote protons – 5'-H of the benzene ring and the methoxy protons – are relatively insensitive to complex formation. This variation of the magnitude and direction of $\Delta\delta_{\text{H}}$ attests to the formation of a pseudorotaxane structure of complex (*E*)-**2c**@CB[7] where the guest molecule runs through the macrocycle cavity, and its terminal fragments are outside the cavity of CB[7] (Scheme 6). The obtained NMR spectroscopic data lead to the same conclusion concerning the structures of other supramolecular complexes, although in the case of CB[8] complexes, interpretation of the spectral changes is complicated by substantial broadening of the dye signals. Nevertheless, evidence for this particular structure of complex {(*E*)-**2c**}₂@CB[8] was obtained by X-ray diffraction (see below).

Quantitative determination of the stability constants of the complexes of dyes (*E*)-**2a–c** with CB[*n*] was performed by ¹H NMR titration in a D₂O/[D₃]MeCN mixture (10:1) at 30 °C. The dependence of the variation of chemical shifts ($\Delta\delta_{\text{H}}$) of the dye and cucurbituril protons on the ratio of

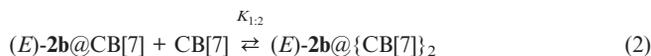


Scheme 6. Complex formation of dyes **2a–c** with CB[*n*].

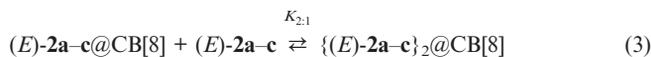
their concentrations for CB[7] systems was adequately described by a model taking into account one equilibrium [Equation (1)].



where $K_{1,1}$ is the stability constant of complexes (*E*)-**2a–c**@CB[*n*] [M^{-1}]. In the case of dye (*E*)-**2b** and CB[7], it was necessary to take into account both Equations (1) and (2).



where $K_{1,2}$ is the stability constant of complex (*E*)-**2b**@CB[7]₂ [M^{-1}]. For CB[8]-based systems, good results were provided by simultaneously taking into account Equations (1) and (3).



where $K_{2,1}$ is the stability constant of complexes {(*E*)-**2a–c**}₂@CB[8] [M^{-1}]. In the case of slow exchange on the ¹H NMR time scale, averaged positions of like signals were calculated taking into account their integral intensities. The stability constants thus found are summarised in Table 1.

It can be seen from Table 1 that CB[7] forms only 1:1 complexes with monocationic and betaine styryl dyes (*E*)-**2a,c**. Evidently, the relatively small size of the cavity of this cavita nd predetermines its ability to accommodate one

Table 1. Stability constants of complexes of CB[n] with dyes (*E*)-**2a–c** and cyclobutanes *rctt*-**5a–c**.^[a]

| Dye | CB[7] | | log $K_{1:1}^{[b]}$ | CB[8] | | Cyclobutane |
|-------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|-------------------------|
| | log $K_{1:1}^{[b]}$ | log $K_{1:2}^{[c]}$ | | log $K_{1:1}^{[b]}$ | log $K_{2:1}^{[d]}$ | |
| (<i>E</i>)- 2a | 4.1 | | 4.9 | 4.1 | 4.3 | <i>rctt</i> - 5a |
| (<i>E</i>)- 2b | >5 | >5 | ca. 5.0 | 4.4 | 4.8 | <i>rctt</i> - 5b |
| (<i>E</i>)- 2c | 3.2 | | 4.0 | 2.6 | 3.2 | <i>rctt</i> - 5c |

[a] ¹H NMR titration in D₂O/[D₃]MeCN (10:1) at 30 °C. The formation constants are measured to within approximately ±30%. [b] $K_{1:1} = [(E-2@CB[n])/((E-2)·[CB[n]])]$ [M⁻¹] is the formation constant for a 1:1 complex. [c] $K_{1:2} = [(E-2@{CB[7]}_2)/([CB[7]]·[(E-2@CB[7])])]$ [M⁻¹] is the formation constant for a 1:2 (dye)/(CB[7]) complex. [d] $K_{2:1} = [{(E-2)}_2@CB[8]/([CB[8]]·[(E-2)·(E-2@CB[8])])]$ [M⁻¹] is the formation constant for a 2:1 (dye)/(CB[8]) complex. [e] $K_{cb} = [rctt-5@CB[8]/([rctt-5]·[CB[8]])]$ [M⁻¹] is the formation constant for a 1:1 (cyclobutane)/(CB[8]) complex.

guest molecule inside. The dicationic dye (*E*)-**2b** was also able to form a termolecular complex (*E*)-**2b**@{CB[7]}₂, in which two macrocyclic molecules are probably threaded simultaneously onto a relatively long guest (Scheme 6). The stability of the 1:1 complexes increases considerably in the sequence (*E*)-**2c** < (*E*)-**2a** < (*E*)-**2b**, which correlates with the increase in the effective positive charge of the dye molecule on passing from the betaine to the dication structure. In the case of (*E*)-**2b**, an additional contribution to the stability of the supramolecular complex comes from hydrogen bonding between the terminal ammonium group of the dye and the donor oxygen atoms of the CB[7] portals, as has been found previously^[8] for the complexes (*E*)-**1c,d**@CB[8]. Determining the stability constants of the complexes of (*E*)-**2b** with CB[7] was precluded by their very high values, which exceeded the upper limit of the ¹H NMR titration method (log $K > 5$). Cucurbit[8]uril forms two types of complexes, 1:1 and 2:1, with all dyes; the stability sequences for both types of complex as a function of dye structure are similar to those of the CB[7] complexes. The 1:1 CB[8]-based complexes proved to be somewhat more stable than analogous complexes of CB[7] ($\Delta\log K_{1:1}$ up to 0.8) and than the 2:1 complexes of CB[8] ($\Delta\log K_{1:1/2:1} = 0.6–1.4$). This can be attributed to (1) looser arrangement of the guest in the larger cavity of CB[8] in 1:1 complexes, which simultaneously reduces the free space needed to dispose the second guest molecule in the 2:1 complex and (2) the Coulomb repulsion of the molecular cations in the CB[8]-based termolecular complexes. That is, by varying the terminal functional group within the *N*-substituent of the dye molecule, one can finely control the strength of its binding to cavitands.

Complex $\{(E-2c)_2@CB[8]\}$ was obtained in the solid state by precipitation upon mixing of aqueous solutions of the components in a 2:1 ratio; its stoichiometry was confirmed by elemental analysis (see Exp. Sect.).

X-ray Diffraction Study of Complex $\{(E-2c)_2@CB[8]\}$

We were able to prepare single crystals of the 2:1 complex of dye (*E*)-**2c** and cucurbit[8]uril. The structure of the independent components of the complex is presented in Figure 6. The geometric centre of the molecule CB[8] coincides with the centre of symmetry of the crystal. The CB[8] portals are distorted toward an oval: the shortest and longest distances between the opposing oxygen atoms, O(3)⋯O(7A)

and O(1)⋯O(5A), being 9.37 and 10.45 Å, respectively. Certainly, this distortion is a result of accommodating two dye molecules in the host cavity.

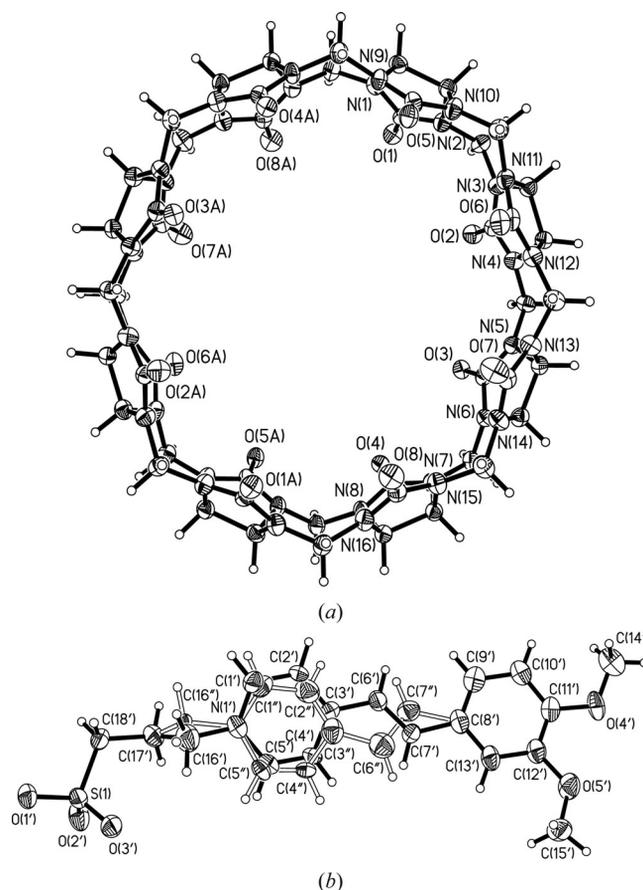


Figure 6. Structure of independent components of crystal $\{2c\}_2@CB[8]·21.25H_2O$: (a) host molecule of CB[8] and (b) guest molecule of dye (*E*)-**2c**, which is disordered over two *s-trans* conformations. The minor conformer is drawn with hollow lines. Thermal ellipsoids are drawn at the 40% probability level. The additional letter “A” indicates that atoms are at $(-x, 1-y, -z)$.

The chromophore fragment of (*E*)-**2c** exists in the (*E*) configuration and is disordered over two positions corresponding to two *s-trans* conformers in a 0.78:0.22 ratio. As in dye (*E*)-**2b**, the chromophore fragments of both *s*-conformers are nearly planar: the dihedral angles between the pyridine and benzene ring planes are 19.3 and 13.7°, respectively, in the major and minor conformers. The ethylene bonds in the conformers are localised: the bond lengths in

the $C_{(Py)}-C=C-C_{(Ar)}$ fragments are 1.461(13), 1.357(14), 1.490(12) and 1.52(6), 1.34(6), 1.53(4) Å. The oxygen atoms O(4') and O(5') are effectively conjugated with the benzene ring, as indicated by the values for the angles at these atoms, 115.0(6) and 119.1(5)°, which are typical of an sp^2 -hybrid state.

Figure 7 shows the arrangement of the major components of the complex $\{(E)\text{-}2\mathbf{c}\}_2@CB[8]$. A centrosymmetric dimeric pair of dye molecules formed according to the *syn*-head-to-tail pattern resides in the cucurbituril cavity. Only the pyridine ring and the ethylene bond of each dye molecule are located directly in the cavity; the sulfonatopropyl and dimethoxyphenyl substituents protrude on both sides of the torus-like cavitand. Apparently, this arrangement of the parts of the dye with respect to the cucurbituril walls is due to the favourable interaction of the electron-donating CB[8] cavity, with the electron-withdrawing pyridine ring bearing the greater part of the positive charge. Thus, this complex is a pseudorotaxane sandwich structure. In the dimeric pair, the chromophore fragments are located in parallel planes about 3.7 Å apart. Their ethylene bonds are antiparallel; however, since the region of stacking interactions covers only the vinylpyridine fragments of the dyes, the C=C bonds are too remote from each other (the distance is 5.21 Å for both pairs of conformers) for solid-phase PCA to occur. In solution, the mobility of the dye molecules in 2:1 complexes is clearly high enough, thus enabling the PCA reaction to take place (see below).

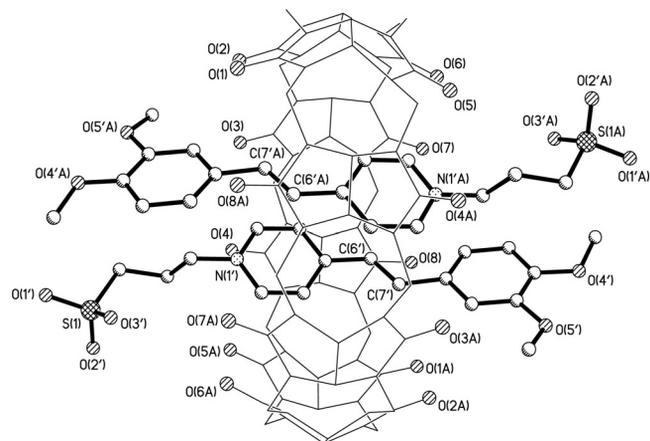


Figure 7. Arrangement of components in complex $\{2\mathbf{c}\}_2@CB[8]\cdot 21.25H_2O$. The additional letter "A" indicates that atoms are at $(-x, 1-y, -z)$. Atoms of minor *s-trans* conformer of $(E)\text{-}2\mathbf{c}$, hydrogen atoms, and solvation water molecules are omitted for clarity.

The unit cell was also found to contain 13 independent solvation water molecules with either full or partial site occupations. The considerable disorder of the solvation shell and the dye molecule decreases appreciably the quality of the $\{(E)\text{-}2\mathbf{c}\}_2@CB[8]$ crystal. Although the hydrogen atoms of the water molecules could not be localised, the fact that they are located approximately 2.5–2.9 Å from the oxygen atoms of CB[8], sulfonate groups and from each other, indicates unambiguously that the crystal contains a network of numerous hydrogen bonds.

Photochemical Study of Complexes of the Styryl Dyes with CB[n]

Visible-light irradiation of approximately 5×10^{-5} M aqueous solutions of equimolar mixtures of dyes $(E)\text{-}2\mathbf{a-c}$ and CB[7], resulted in a relatively fast (over 10 min) decrease in the LAB intensity up to 47% of the initial value. Subsequent irradiation did not result in changes in the spectral characteristics of the mixtures, which proves that the photostationary $(E)/(Z)$ equilibrium had been attained. This is the expected behaviour of CB[7]-based systems for which the formation of only 1:1 and 1:2 complexes has been observed (see above).

A different situation was observed on irradiation of solutions of $(E)\text{-}2\mathbf{a-c}$ and CB[8] mixtures in 2:1 molar ratio. In all cases, the LAB intensity decreased to nearly zero at 400 nm (e.g., Figure 8). This means that the chromophore conjugation chain in dyes $(E)\text{-}2\mathbf{a-c}$ has been destroyed as a result of effective PCA reaction taking place in termolecular complexes $\{(E)\text{-}2\mathbf{a-c}\}_2@CB[8]$ to give complexes of cyclobutane derivatives *rcbt*- $5\mathbf{a-c}@CB[8]$ (Scheme 7). Measurement of the kinetics of disappearance of the long-wavelength absorption showed equal reactivities for dyes $(E)\text{-}2\mathbf{a,c}$ and somewhat slower consumption of dye $(E)\text{-}2\mathbf{b}$, other

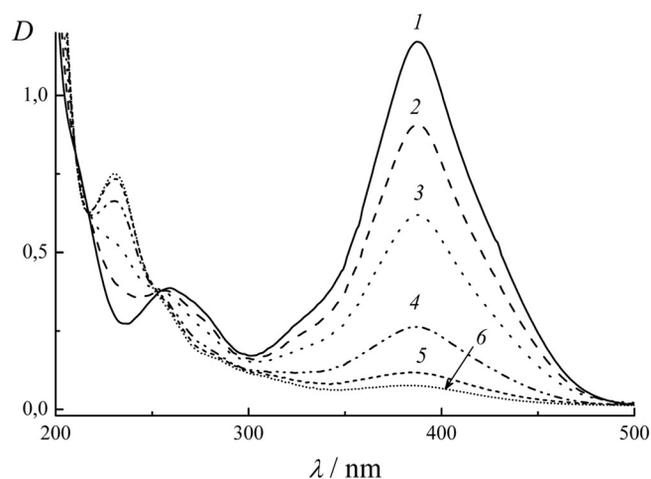
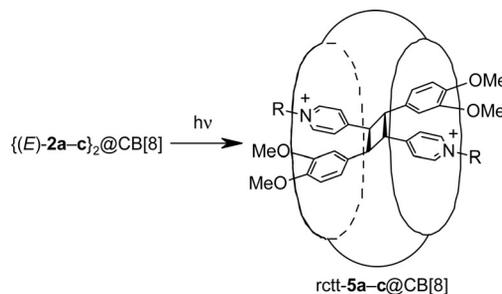


Figure 8. Absorption spectra of mixtures of $(E)\text{-}2\mathbf{c}$ (4.88×10^{-5} M) and CB[8] (2.44×10^{-5} M, 1-cm quartz cell) in water, after irradiation for: (1) 0, (2) 200, (3) 500, (4) 1100, (5) 2300, and (6) 4700 s (light from a 60 W incandescent lamp; distance from the light source 10 cm).



Scheme 7. Synthetic route to cyclobutanes *rcbt*- $5\mathbf{a-c}$ in aqueous solution.

factors being the same. In all cases, after exposure for 100 min, the subsequent spectral changes were negligible.

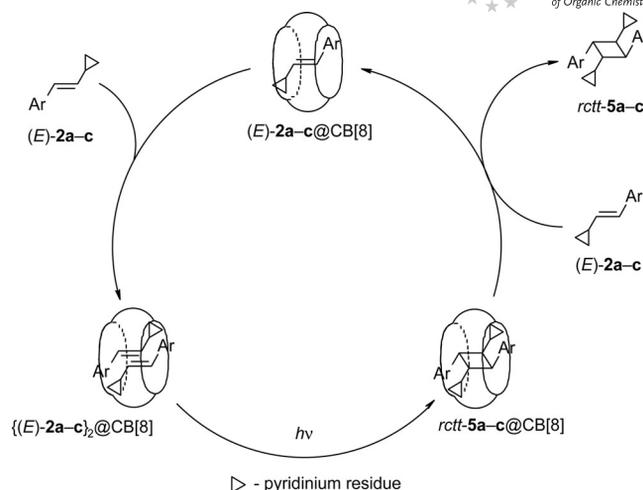
The structure of **5a–c** obtained in solution was identical to the structure of *rc*tt isomers of cyclobutanes formed upon irradiation of polycrystalline films of dyes (*E*)-**2a–c**; this was confirmed by ¹H NMR spectroscopic data. Quantitative determination of the stability constants of the complexes formed by cyclobutanes *rc*tt-**5a–c** and CB[8] was performed by ¹H NMR titration in a D₂O/[D₃]MeCN mixture (10:1) at 30 °C. The change in the proton chemical shifts of cyclobutane and cucurbituril following variation of their concentration ratio was adequately described in this case by a model including only one equilibrium [Equation (4)].



where K_{cb} is the stability constant of the complexes *rc*tt-**5a–c**@CB[8] [M⁻¹]. The stability constants found in this way are summarised in Table 1.

The order of increasing stability of the complexes *rc*tt-**5a–c**@CB[8] is similar to the order of the starting dyes, which confirms once again the conclusion that the most stable complexes are formed by compounds bearing the maximum possible positive charge and capable of hydrogen bonding with the cavitand portals. It is noteworthy that the stability of bimolecular complexes (*E*)-**2a–c**@CB[8] is much higher than that of bimolecular complexes *rc*tt-**5a–c**@CB[8] ($\Delta \log K_{1:1/cb}$ up to 0.8). This may be caused by the larger size of the cyclobutane derivative compared with the preceding *syn*-head-to-tail dimeric pair of the styryl dye. Thus, the competition between the dye and its photoproduct for complexation with CB[8] in solution should result in the predominant formation of dye complexes, in particular, the termolecular complexes $\{(E)\text{-}2\text{a-c}\}_2\text{@CB}[8]$ pre-organised toward PCA. This conclusion means that it is possible to use catalytic amounts of CB[8] to perform the stereospecific conversion of the styryl dye into *rc*tt-cyclobutane in aqueous solution. Indeed, irradiation experiments with solutions of (*E*)-**2a–c** in the presence of 5 mol-% of CB[8] demonstrated complete transformation of the dye into *rc*tt-**5a–c** (NMR spectroscopic monitoring).

The whole functioning cycle of this photocontrolled molecular assembler, based on CB[8] in solution, is shown in Scheme 8. In the presence of excess dye, complexes (*E*)-**2a–c**@CB[8] are able to incorporate a second dye molecule, and are assembled as dimeric pairs $\{(E)\text{-}2\text{a-c}\}_2\text{@CB}[8]$ in the cavity as a result of pre-organisation. Upon light irradiation at the absorption maxima, the PCA reaction can be carried out in these pairs if necessary. The efficiency of binding of the cyclobutane thus formed by the cavitand as *rc*tt-**5a–c**@CB[8] is considerably lower than that of the starting dyes (*E*)-**2a–c**; this facilitates translocation of the reaction product outside the CB[8] cavity. This release is followed by occupation of the cavity by a new dye molecule. The subsequent formation of further complexes (*E*)-**2a–c**@CB[8] completes the functioning cycle of the photocontrolled molecular assembler and makes it ready for the next one.



Scheme 8. Working cycle of photocontrolled molecular assembler giving cyclobutanes *rc*tt-**5a–c** from styryl dyes **2a–c**.

Conclusions

The stereospecific [2+2]-autophotocycloaddition of styryl dyes can be carried out both in their polycrystalline films, in which the *syn*-head-to-tail organisation of dye molecules into dimeric pairs is controlled by the stacked molecular packing, and in aqueous solution in the presence of cucurbit[8]uril, whose cavity can accommodate a *syn*-head-to-tail dimeric pair of the dye molecules to give a stable pseudorotaxane complex. The stability of 1:1 complexes of the cyclobutanes thus formed with CB[8] was found to be lower than that of the complexes of the starting dyes of the same stoichiometry. This was used to design the first light-induced molecular assembler based on CB[8], which ensures stereospecific transformation of styryl dyes into cyclobutane derivatives in aqueous medium. This type of self-assembly of styryl dyes can be used to produce photocontrolled molecular devices and machines, including photocontrolled assemblers, and to design information recording and storage systems at the molecular level.

Experimental Section

General: Melting points were measured with a Mel-Temp II apparatus in capillaries. ¹H and ¹³C NMR spectra were recorded with a Bruker DRX500 instrument in [D₆]DMSO and D₂O/[D₃]MeCN (10:1) at 30 °C by using the solvent as internal reference ($\delta_{\text{H}} = 2.50$ and 4.70 ppm, respectively; $\delta_{\text{C}} = 39.43$ ppm for [D₆]DMSO); ¹H-¹H COSY and ROESY spectra and ¹H-¹³C COSY (HSQC and HMBC) spectra were used to assign the proton and carbon signals (see Schemes 2 and 4 for atom numbering). IR spectra were measured with a Bruker ISF-113V spectrometer. Absorption spectra were recorded in distilled water (HPLC-grade, Aldrich) at room temp. by using 1 cm quartz cells with a UV-3101PC spectrophotometer (Shimadzu) in the range of 200–600 nm, with an increment of 0.5 nm. All solutions were prepared under red light and kept in the dark to avoid photoreactions. Elemental analyses were performed at the microanalytical laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds (Moscow, Russian Federa-

tion); the samples for elemental analyses were dried in vacuo at 80 °C.

Preparations: 4-Picoline, 1,3-propanesultone and veratraldehyde were used as received (Aldrich). Styrylpyridine (*E*)-**3** was obtained according to a published procedure.^[12]

Dye (E)-2a: Obtained according to the published procedure.^[9e] M.p. 224–226 °C (decomp.). ¹H NMR (500 MHz, [D₆]DMSO): δ = 1.53 (t, ³J = 7.3 Hz, 3 H, CH₃CH₂), 3.83 (s, 3 H, 4'-CH₃O), 3.85 (s, 3 H, 3'-CH₃O), 4.51 (q, ³J = 7.3 Hz, 2 H, CH₂), 7.08 (d, ³J = 8.3 Hz, 1 H, 5'-H), 7.30 (dd, ³J = 8.3, ⁴J = 1.8 Hz, 1 H, 6'-H), 7.38 (br. s, 1 H, 2'-H), 7.40 (d, ³J = 16.5 Hz, 1 H, CH=CHPy), 7.96 (d, ³J = 16.5 Hz, 1 H, CH=CHPy), 8.16 (d, ³J = 6.7 Hz, 2 H, 3-H, 5-H), 8.90 (d, ³J = 6.7 Hz, 2 H, 2-H, 6-H) ppm. ¹³C NMR (125 MHz, [D₆]DMSO): δ = 15.90 (CH₃CH₂), 54.96 (CH₂N), 55.48 (OCH₃), 55.52 (OCH₃), 109.95 (2'-C), 111.68 (5'-C), 120.67 (CH=CHPy), 122.98 (6'-C), 123.14 (3-C, 5-C), 127.88 (1'-C), 141.00 (CH=CHPy), 143.62 (2-C, 6-C), 148.99 (3'-C), 151.07 (4'-C), 153.08 (4-C) ppm.

Dye (E)-2b: Obtained according to the published procedure.^[11] M.p. 224–226 °C. ¹H NMR (500 MHz, [D₆]DMSO): δ = 2.19 (m, 2 H, CH₂CH₂N), 2.86 (m, 2 H, CH₂NH₃), 3.84 (s, 3 H, 4'-CH₃O), 3.86 (s, 3 H, 3'-CH₃O), 4.55 (t, ³J = 7.0 Hz, 2 H, CH₂N), 7.09 (d, ³J = 8.4 Hz, 1 H, 5'-H), 7.31 (dd, ³J = 8.4, ⁴J = 1.6 Hz, 1 H, 6'-H), 7.40 (d, ⁴J = 1.6 Hz, 1 H, 2'-H), 7.45 (d, ³J = 16.2 Hz, 1 H, CH=CHPy), 7.78 (br. s, 3 H, NH₃), 8.00 (d, ³J = 16.2 Hz, 1 H, CH=CHPy), 8.21 (d, ³J = 6.8 Hz, 2 H, 3-H, 5-H), 8.89 (d, ³J = 6.8 Hz, 2 H, 2-H, 6-H) ppm. ¹³C NMR (125 MHz, [D₆]DMSO): δ = 28.35 (CH₂CH₂NH₃), 35.64 (CH₂NH₃), 55.56 (2 OCH₃), 56.48 (CH₂N), 110.02 (2'-C), 111.72 (5'-C), 120.70 (CH=CHPy), 123.15 (6'-C), 123.32 (3-C, 5-C), 127.89 (1'-C), 141.39 (CH=CHPy), 143.94 (2-C, 6-C), 149.02 (3'-C), 151.17 (4'-C), 153.48 (4-C) ppm.

Betaine 4: A mixture of 4-picoline (1.36 mL, 14.0 mmol), 1,3-propanesultone (2.60 g, 21.3 mmol) and benzene (7 mL) was heated at reflux for 30 h. The precipitate formed was filtered, washed with hot benzene, then with acetone, and recrystallized from EtOH to give compound **4** (2.40 g, 80%) as a white powder; m.p. 205–207 °C. ¹H NMR (500 MHz, [D₆]DMSO): δ = 2.20 (m, 2 H, CH₂CH₂N), 2.40 (t, ³J = 7.3 Hz, 2 H, CH₂SO₃), 2.60 (s, 3 H, CH₃), 4.66 (t, ³J = 6.7 Hz, 2 H, CH₂N), 7.96 (d, ³J = 6.7 Hz, 2 H, 3-H, 5-H), 8.90 (d, ³J = 6.7 Hz, 2 H, 2-H, 6-H) ppm. C₉H₁₃NO₃S (215.27): calcd. C 50.21, H 6.09, N 6.51, S 14.90; found C 50.14, H 6.10, N 6.54, S 15.13.

Dye (E)-2c

Method 1: A mixture of compound (*E*)-**3** (138 mg, 0.57 mmol), 1,3-propanesultone (105 mg, 0.86 mmol) and anhydrous MeCN (3 mL) was kept at room temp. in dark for 50 h. The precipitate formed was filtered, washed with CH₂Cl₂ (3 × 5 mL), and dried in air to give dye (*E*)-**2c** (157 mg, 76%) as a yellow powder; m.p. 282–284 °C (decomp.).

Method 2: A mixture of compound **4** (0.65 g, 3.0 mmol), veratraldehyde (0.50 g, 3.0 mmol), pyrrolidine (1 drop) and abs. EtOH (5 mL) was heated at reflux in the dark for 4 h. After cooling to room temp., the precipitate formed was filtered, washed with abs. EtOH, then with acetone, and dried in air to give dye (*E*)-**2c** (0.25 g) as a yellow powder. The mother solution was cooled to –10 °C, and the precipitate formed was filtered, washed with cold abs. EtOH, and dried in air to give an additional amount of dye (*E*)-**2c** (0.35 g, overall yield 55%); m.p. 284–287 °C (decomp.). ¹H NMR (500 MHz, [D₆]DMSO): δ = 2.22 (quint, ³J = 7.0 Hz, 2 H, CH₂CH₂N), 2.44 (t, ³J = 7.0 Hz, 2 H, CH₂SO₃), 3.83 (s, 3 H, 4'-CH₃O), 3.85 (s, 3 H, 3'-CH₃O), 4.62 (t, ³J = 7.0 Hz, 2 H, CH₂N),

7.07 (d, ³J = 8.2 Hz, 1 H, 5'-H), 7.29 (dd, ³J = 8.2, ⁴J = 1.8 Hz, 1 H, 6'-H), 7.39 (d, ⁴J = 1.8 Hz, 1 H, 2'-H), 7.40 (d, ³J = 16.3 Hz, 1 H, CH=CHPy), 7.95 (d, ³J = 16.3 Hz, 1 H, CH=CHPy), 8.15 (d, ³J = 6.8 Hz, 2 H, 3-H, 5-H), 8.90 (d, ³J = 6.8 Hz, 2 H, 2-H, 6-H) ppm. ¹³C NMR (125 MHz, [D₆]DMSO/D₂O, 2:1): δ = 27.37 (CH₂CH₂N), 48.04 (CH₂SO₃), 56.58 (OCH₃), 56.65 (OCH₃), 59.45 (CH₂N), 110.95 (2'-C), 112.71 (5'-C), 121.80 (CH=CHPy), 124.34 (6'-C), 124.52 (3-C, 5-C), 129.00 (1'-C), 142.10 (CH=CHPy), 144.53 (2-C, 6-C), 149.75 (3'-C), 151.86 (4'-C), 154.51 (4-C) ppm. C₁₈H₂₁NO₅S (363.43): calcd. C 59.49, H 5.82, N 3.85; found C 59.21, H 5.71, N 3.84.

Cyclobutane rctt-5a: A solution of dye (*E*)-**2a** (41.5 mg, 112 μmol) in MeCN (1 mL) was kept in a Petri dish (*d* = 10 cm) for concentration to give a thin polycrystalline film of the compound. This film was irradiated with light from a 60 W incandescent lamp (110 h; distance from the light source 15 cm) to give *rctt*-**5a** (quantitative yield) as a yellowish powder; m.p. 156–159 °C (ref.^[9e] 155–158 °C). ¹H NMR (500 MHz, [D₆]DMSO): δ = 1.42 (t, ³J = 7.3 Hz, 6 H, 2 CH₃CH₂), 3.66 (s, 6 H, 2 4'-CH₃O), 3.68 (s, 6 H, 2 3'-CH₃O), 4.50 (q, ³J = 7.3 Hz, 4 H, 2 CH₂), 4.81 (dd, ³J = 9.8, ³J = 7.5 Hz, 2 H, 2 CHAr), 4.90 (dd, ³J = 9.8, ³J = 7.5 Hz, 2 H, 2 CHPy), 6.78 (s, 4 H, 2 5'-H, 2 6'-H), 6.80 (s, 2 H, 2 2'-H), 7.95 (d, ³J = 6.7 Hz, 4 H, 2 3-H, 2 5-H), 8.87 (d, ³J = 6.7 Hz, 4 H, 2 2-H, 2 6-H) ppm. ¹³C NMR (125 MHz, [D₆]DMSO): δ = 16.15 (2 CH₃CH₂), 45.00 (2 CHAr), 45.97 (2 CHPy), 55.30 (2 4'-OCH₃), 55.46 (2 CH₂N, 2 3'-OCH₃), 111.41 (2 5'-C), 112.04 (2 2'-C), 119.72 (2 6'-C), 126.97 (2 3-C, 2 5-C), 129.93 (2 1'-C), 143.18 (2 2-C, 2 6-C), 147.62 (2 4'-C), 148.42 (2 3'-C), 160.05 (2 4-C) ppm.

Cyclobutane rctt-5b: A solution of dye (*E*)-**2b** (49.8 mg, 100 μmol) in a mixture of MeCN (1 mL) and water (0.2 mL) was kept in a Petri dish (*d* = 10 cm) for concentration to give a thin polycrystalline film of the compound. This film was irradiated with light from a 60 W incandescent lamp (230 h; distance from the light source 15 cm). According to ¹H NMR analysis, the dye/cyclobutane molar ratio was 1.2:1 (conversion 64%) after 65 h and 1:4.3 (conversion 90%) after 230 h. The resulting substance was dissolved in a mixture of MeCN (3 mL) and water (0.2 mL), and this solution was slowly saturated with benzene and dioxane (1:1) at room temp. by vapour diffusion methods for 2 weeks. The glassy precipitate formed was decanted and dried in vacuo at 80 °C to give *rctt*-**5b** (hydrate, 44.7 mg; 86%) as a dark-yellow powder; m.p. >175 °C (decomp.). ¹H NMR (500 MHz, [D₆]DMSO): δ = 2.06 (m, 4 H, 2 CH₂CH₂N), 2.76 (m, 4 H, 2 CH₂NH₃), 3.65 (s, 6 H, 2 4'-CH₃O), 3.68 (s, 6 H, 2 3'-CH₃O), 4.52 (t, ³J = 7.3 Hz, 4 H, 2 CH₂N), 4.82 (dd, ³J = 9.3, ³J = 7.7 Hz, 2 H, 2 CHAr), 4.90 (dd, ³J = 9.3, ³J = 7.7 Hz, 2 H, 2 CHPy), 6.77 (s, 4 H, 2 5'-H, 2 6'-H), 6.82 (s, 2 H, 2 2'-H), 7.69 (br. s, 6 H, 2 NH₃), 8.00 (d, ³J = 6.7 Hz, 4 H, 2 3-H, 2 5-H), 8.84 (d, ³J = 6.7 Hz, 4 H, 2 2-H, 2 6-H) ppm. ¹³C NMR (125 MHz, [D₆]DMSO): δ = 28.60 (2 CH₂CH₂NH₃), 35.64 (2 CH₂NH₃), 45.13 (2 CHAr), 46.15 (2 CHPy), 55.38 (2 4'-OCH₃), 55.54 (2 3'-OCH₃), 57.05 (2 CH₂N), 111.36 (2 5'-C), 112.01 (2 2'-C), 119.79 (2 6'-C), 127.27 (2 3-C, 2 5-C), 129.93 (2 1'-C), 143.56 (2 2-C, 2 6-C), 147.67 (2 4'-C), 148.46 (2 3'-C), 160.61 (2 4-C) ppm. C₃₆H₄₈Cl₄N₄O₂₀·2.5H₂O (1043.63): calcd. C 41.43, H 5.12, N 5.37; found C 41.13, H 4.76, N 5.65.

Cyclobutane rctt-5c: A solution of dye (*E*)-**2c** (50.0 mg, 138 μmol) in a mixture of MeCN (1 mL) and water (0.5 mL) was kept in a Petri dish (*d* = 10 cm) for concentration to give a thin polycrystalline film of the compound. This film was irradiated with light from a 60 W incandescent lamp (115 h; distance from the light source 15 cm). According to ¹H NMR analysis, the dye/cyclobutane molar ratio was 1:2.1 (conversion 82%) after 50 h and 1:4.4 (conversion

90%) after 115 h. The resulting substance was dissolved in a mixture of MeCN (3 mL) and water (1 mL), and this solution was slowly saturated with dioxane at room temp. by vapour diffusion methods for 2 weeks. The glassy precipitate formed was decanted and dried in vacuo at 80 °C to give *rectt*-**5c** (hydrate, 44.9 mg; 85%) as a dark-yellow powder; m.p. >190 °C (decomp.). ¹H NMR (500 MHz, [D₆]DMSO): δ = 2.10 (m, 4 H, 2 CH₂CH₂N), 2.67 (t, ³J = 7.4 Hz, 4 H, 2 CH₂SO₃), 3.66 (s, 6 H, 2 4'-CH₃O), 3.69 (s, 6 H, 2 3'-CH₃O), 4.60 (t, ³J = 6.7 Hz, 4 H, 2 CH₂N), 4.81 (dd, ³J = 10.3, ³J = 7.8 Hz, 2 H, 2 CHAr), 4.89 (dd, ³J = 10.3, ³J = 7.8 Hz, 2 H, 2 CHPy), 6.72 (dd, ³J = 8.4, ⁴J = 1.7 Hz, 2 H, 2 6'-H), 6.76 (d, ³J = 8.4 Hz, 2 H, 2 5'-H), 6.86 (d, ⁴J = 1.7 Hz, 2 H, 2 2'-H), 7.94 (d, ³J = 6.7 Hz, 4 H, 2 3-H, 2 5-H), 8.87 (d, ³J = 6.7 Hz, 4 H, 2 2-H, 2 6-H) ppm. ¹³C NMR (125 MHz, [D₆]DMSO): δ = 27.21 (2 CH₂CH₂N), 44.98 (2 CHAr), 46.04 (2 CHPy), 46.55 (2 CH₂SO₃), 55.32 (2 4'-OCH₃), 55.57 (2 3'-OCH₃), 58.59 (2 CH₂N), 111.38 (2 5'-C), 112.33 (2 2'-C), 119.69 (2 6'-C), 126.99 (2 3-C, 2 5-C), 129.89 (2 1'-C), 143.59 (2 2-C, 2 6-C), 147.66 (2 4'-C), 148.40 (2 3'-C), 160.22 (2 4-C) ppm. C₃₆H₄₂N₂O₁₀S₂·2H₂O (762.89): calcd. C 56.68, H 6.08, N 3.67; found C 56.65, H 6.01, N 3.55.

Complex between Dye (E)-2c** and CB[8]:** A mixture of dye (*E*)-**2c** (5.8 mg, 16.0 μmol) and CB[8]·20H₂O (12.1 mg, 7.2 μmol) in water (15 mL) was heated at reflux in the dark for 1 h, then concentrated to ca. 5 mL, and cooled to 5 °C. The crystals formed were decanted and dried in vacuo at 80 °C to give {(*E*)-**2c**}₂@CB[8] complex (hydrate, 12.9 mg, 84%) as a yellow powder; m.p. >400 °C (decomp.). IR (KBr): ν̄ = 1736 (br., C=O) cm⁻¹. C₄₈H₄₈N₃₂O₁₆·2C₁₈H₂₁NO₅S₅·5H₂O (2146.04): calcd. C 47.01, H 4.70, N 22.19; found C 46.89, H 4.61, N 22.24.

¹H NMR Titration: The titration experiments were performed in D₂O/[D₃]MeCN (10:1) solutions at (30 ± 1) °C. The concentration of CB[7] was approximately 1 × 10⁻³ M, and the real concentrations of CB[8] [(0.3–5.2) × 10⁻⁴ M] were calculated as described previously.^[8] The concentration of **2** and **5** in the solution was gradually increased starting from zero. The highest **2**(**5**)/CB[*n*] real concentration ratios were ca. 3–90. The proton chemical shifts were measured as a function of the **2**(**5**)/CB[*n*] ratio. The Δδ_H values were measured with an accuracy of 0.001 ppm. In the case of slow exchange on the ¹H NMR time scale, the average chemical shifts were calculated taking into account the integral intensities of corresponding signals, and the complex formation constants were then calculated by using the HYPNMR program.^[16]

Photolysis of Aqueous Solutions: The irradiation of aqueous solutions of free dyes **2a–c** (ca. 5 × 10⁻⁵ M, V = 3 mL, 1 cm quartz cell) or their mixtures with CB[*n*] {approximately (5–10) × 10⁻⁵ M for CB[7] and (2.5–10) × 10⁻⁵ M for CB[8]} was performed with light from a 60 W incandescent lamp (distance from the light source 10 cm) for a period of 0–3 h. The course of photolysis was monitored by spectrophotometric methods. For ¹H NMR studies, the D₂O/[D₃]MeCN (10:1) solutions of free dyes **2a–c** (1 × 10⁻³ M, V = 0.55 mL, standard NMR tube) were irradiated with light from a 60 W incandescent lamp (distance from the light source 15 cm) for 2–5 h, and then the ¹H NMR spectra were recorded. The aqueous solutions of mixtures of dyes **2a–c** (3.8 × 10⁻⁴ M, V = 10 mL, glass bottle) and CB[*n*] (1 equiv. of CB[7] or 0.05–0.5 equiv. of CB[8]) were irradiated with light from a 60 W incandescent lamp (distance from the light source 15 cm) with stirring for 20 h. After the irradiation was finished, an aliquot (2–3 mL) of the solution was concentrated in vacuo at room temp., and the solid residue was dissolved in [D₆]DMSO to measure ¹H NMR spectrum.

X-ray Crystallography: Crystals of **2b** were obtained by slow saturation of an MeCN solution with benzene by vapour diffusion meth-

ods in the dark. The crystals of the complex formed by **2c** and CB[8] were obtained as described above. Single crystals of all compounds were coated with perfluorinated oil and mounted on a Bruker SMART-CCD diffractometer (graphite-monochromatized Mo-K_α radiation, λ = 0.71073 Å, ω-scan mode) under a stream of cold nitrogen [T = 120.0(2) K]. All the calculations were performed by using the SHELXTL-Plus software.^[17] CCDC-748331 (**2b**·0.125H₂O), -748333 (*rectt*-**5b**), and -748332 ({**2c**}₂@CB[8]·21.25H₂O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for **2b·0.125H₂O:** A set of experimental reflections for **2b** were measured by using a yellow single crystal of dimensions 0.26 × 0.14 × 0.06 mm. Absorption correction was applied by using the SADABS method. The structure was solved by direct methods and refined with anisotropic thermal parameters. All hydrogen atoms were located in the difference Fourier synthesis but for further refinement, their geometrically calculated positions were used. All hydrogen atoms were refined with an isotropic approximation. The hydrogen atoms of solvation water molecules were not located. C₁₈H_{24.25}BrClN₂O_{6.13}, M = 482.00, triclinic, space group P $\bar{1}$ (No. 2), a = 9.0420(13), b = 14.539(2), c = 16.857(2) Å, α = 71.242(3), β = 87.881(3), γ = 84.445(3)°, V = 2088.5(5) Å³, Z = 4, μ = 2.133 mm⁻¹ (min/max transmission = 0.3709/0.7544), ρ_{calcd.} = 1.533 g cm⁻³, 2θ_{max} = 58.0°, 12607 reflections measured, 9719 unique (R_{int} = 0.0279), R₁ = 0.0648 [6541 reflections with I > 2σ(I)], wR₂ = 0.1559 (all data), goodness-of-fit on F² = 1.046, 705 parameters, min/max residual electron density = -1.406/1.886 e⁻ Å⁻³.

Crystal Data for *rectt*-5b**:** A single crystal of **2b** was subjected to irradiation with visible light from a standard incandescent lamp (60 W, distance from the light source ca. 10 cm) over a period of 20 h to form *rectt*-**5b**. After irradiation, the single crystal became light-yellow. A set of experimental reflections for *rectt*-**5b** was measured with the same diffractometer. Absorption correction was applied by using the SADABS method. The structure was solved and refined as described above. The solvation water molecule was released during irradiation. C₃₆H₄₈Br₂Cl₂N₄O₁₂, M = 959.50, triclinic, space group P $\bar{1}$ (No. 2), a = 8.4303(3), b = 14.7742(6), c = 16.9805(7) Å, α = 71.8470(10), β = 89.1700(10), γ = 88.3270(10)°, V = 2008.78(14) Å³, Z = 2, μ = 2.217 mm⁻¹ (min/max transmission = 0.5964/0.8785), ρ_{calcd.} = 1.586 g cm⁻³, 2θ_{max} = 58.0°, 17722 reflections measured, 10510 unique (R_{int} = 0.0382), R₁ = 0.0452 [7021 reflections with I > 2σ(I)], wR₂ = 0.1103 (all data), goodness-of-fit on F² = 0.951, 697 parameters, min/max residual electron density = -0.587/1.337 e⁻ Å⁻³.

Crystal Data for {2c**}₂@CB[8]·21.25H₂O:** Structure {**2c**}₂@CB[8] was solved by direct methods and refined in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms were fixed at calculated positions and refined by using the riding model. The strongest peaks in the residual-electron density map were assigned to solvation water molecules with full or partial site occupation factors. Hydrogen atoms of the water molecules were not located. The difference Fourier map contained many electron density peaks at distances from other atoms corresponding to van der Waals contacts. However, structure refinement with additional oxygen atoms attributed to these peaks gave unacceptable values for their thermal parameters. C₈₄H_{132.50}N₃₄O_{47.25}S₂, M = 2438.86, monoclinic, space group P2₁/c (No. 14), a = 14.3170(14), b = 19.7222(18), c = 19.9897(18) Å, β = 105.533(2)°, V = 5438.2(9) Å³, Z = 2, μ = 0.159 mm⁻¹ (no absorption correction was applied), ρ_{calcd.} = 1.489 g cm⁻³, 2θ_{max} = 58.0°, 54587 reflections

measured, 14447 unique ($R_{\text{int}} = 0.1301$), $R_1 = 0.1205$ [6404 reflections with $I > 2\sigma(I)$], $wR_2 = 0.3795$ (all data), goodness-of-fit on $F^2 = 1.101$, 850 parameters, min/max residual electron density = $-0.640/0.971 \text{ e}^- \text{ \AA}^{-3}$.

Supporting Information (see footnote on the first page of this article): Selected bond lengths and angles for **2b**·0.125H₂O, **rcct-5b**, and **{2c}₂@CB[8]**·21.25H₂O (Tables S1–S3).

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