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Self-assembly of a (benzothiazolyl)ethenylbenzocrown ether into a sandwich complex and stereoselective [2+2] photocycloaddition

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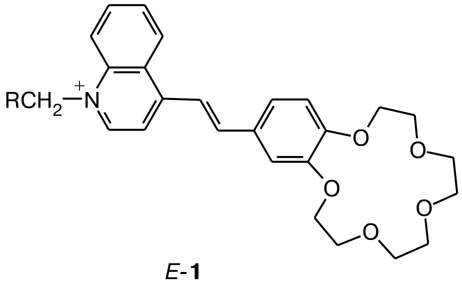
In the presence of Ba^{2+} ions, (benzothiazolyl)ethenylbenzocrown ether forms the stable sandwich complex $2L \cdot Ba^{2+}$ with an unusual structure, in which the benzothiazole fragments are arranged one above the other. Irradiation of the sandwich complex with visible light induces stereoselective [2+2] cycloaddition giving rise to two "head-to-head" isomers of biscrown-cyclobutane. The addition of dibasic dicarboxylic acids that additionally stabilize the sandwich complex in a favorable conformation affects the isomer ratio of the cyclobutanes formed. The conformational equilibria for the sandwich complex and cyclobutanes were studied by ^1H NMR spectroscopy.

Key words: hetarylphenylethylenes, (benzothiazolyl)ethenylbenzocrown ether, complexation, barium, sandwich complexes, cycloaddition, cyclobutanes, dicarboxylic acids.

Self-assembling multicomponent structures[1—4] containing photosensitive fragments[5—9] underlie the simplest photoswitchable molecular devices.[10—13] Crown-containing derivatives of azobenzene[5] and anthracene,[14] spiropyrans, and spironaphthoxazines[15] were studied as photosensitive ligands necessary for the design of such molecular devices. A unique combination of the required characteristics is inherent in crown-containing unsaturated compounds, since they are rather easily accessible by synthesis,[16] provide highly efficient molecular photoswitching,[17] have multiphotochromic properties, *i.e.*, can undergo different types of photochemical transformations depending on their structures,[18] and are prone to spontaneous self-organization to form various supramolecular assemblies.[19] Styryl dyes of the quinoline series *E*-**1** provide an example.

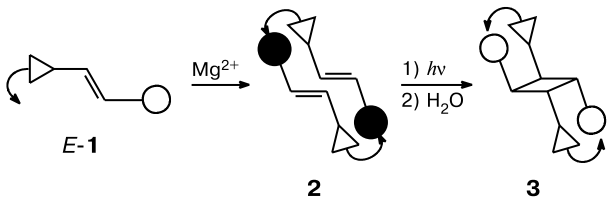


E-**1**

R = $(CH_2)_nSO_3^-$; *n* = 1—3

In the presence of Mg^{2+} ions, these compounds form dimeric complexes **2** with a parallel arrangement of the molecules (*syn*-"head-to-tail") through intermolecular interactions between the sulfo group of one molecule and the Mg^{2+} ion located in the crown-ether cavity of the other molecule (Scheme 1). Photoirradiation of solutions of dimeric complex **2** induces stereospecific [2+2] photocycloaddition giving rise to the only cyclobutane derivative **3** (see Scheme 1).[20] The photochemical reaction is

Scheme 1



○ is a benzocrown ether fragment; ● is a benzocrown ether fragment with Mg^{2+}; ▷ is a heterocyclic fragment; ↷ is $(CH_2)_nSO_3^-$; *n* = 1—3

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reversible, which allows disassembly of the resulting receptor molecules as well.

In the presence of Mg^{2+} ions, styryl dyes, in which quinoline is replaced by benzothiazole, were demonstrated[13] to form dimeric complexes with a cross arrangement of the molecules (*anti*-"head-to-tail") and the corresponding cyclobutanes. In this case, self-assembly of supramolecular complexes from two styryl dye molecules and two metal cations is a convenient tool for controlling regio- and stereoselectivity of photocycloaddition.

Complexation of crown-containing unsaturated compounds with metal cations with a large ionic radius giving rise to sandwich complexes can provide a new approach to the control. In certain cases, the formation of more stable complexes and higher selectivity with respect to the metal ions as compared with the complexation involving one macrocyclic fragment would be expected due to a cooperative effect of two crown-ether fragments. Sandwich complexes have attracted also particular attention because unsaturated ligands in these complexes can be arranged in a "head-to-head" fashion, *i.e.*, they are preorganized for the formation of the corresponding cyclobutanes in photocycloaddition reactions.

Hetarylphenylethylenes are known to be involved in photocycloaddition both in the crystalline state and in solution.[21—26] Generally, the reactions in solution occur with low quantum yields and low stereoselectivity. In most studies known to date, the structures of the resulting cyclobutanes have not been determined, or the isomers have not been isolated in the individual state. However, the photocycloaddition of benzoxazolylphenylethylene in an acidic medium occurs stereoselectively to give cyclobutanes, in which substituents are arranged in a "head-to-tail" fashion.[27] The factors responsible for high stereoselectivity of the process remain unclear.

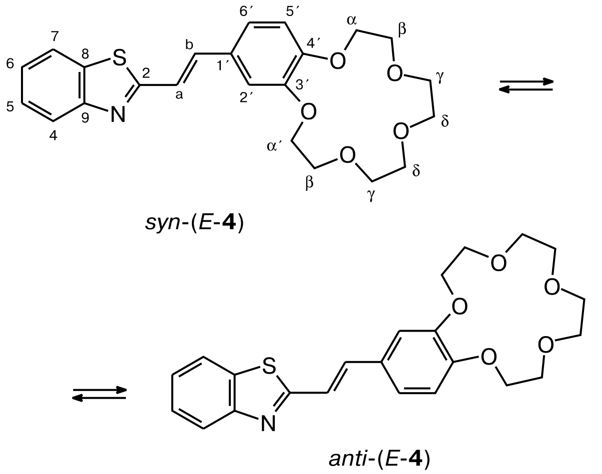
In the present study, we examined the influence of the size of the metal cation and of the addition of dibasic acids on the formation of sandwich complexes and the efficiency and stereoselectivity of photocycloaddition using (benzothiazolyl)ethenylbenzocrown ether **4** as an example.

Results and Discussion

Complexation

The synthesis of compound **4** has been described by us earlier.[28] The coupling constants for the protons of the ethylene fragment ($^3J_{Ha,Hb}$ = 16.2 Hz) in the ^1H NMR spectrum of a solution of **4** in $MeCN-d_3$ suggest that this compound exists as the *E* isomer. Earlier, it has been demonstrated[29] that **4** exists as a mixture of *syn* and *anti* conformers both in the crystalline state and in a solution in $MeCN-d_3$. These conformers differ in the orientation of the crown-ether fragment of the molecule relative to the C=C bond of the vinyl fragment (Scheme 2).

Scheme 2



The addition of magnesium or barium perchlorate to solutions of *E*-**4** in MeCN causes substantial hypsochromic shifts of the long-wavelength absorption band (see, for example, Fig. 1), which is indicative of interactions between the cations of these metals and the crown-ether fragment of the compound.[30] The stability constants of the complexes were determined by spectrophotometric titration taking into account the following two schemes of complex formation:

$$L + M^{2+} \overset{K_1}{\rightleftarrows} L \cdot M^{2+}, \quad (1)$$

$$2\,L + M^{2+} \overset{K_2}{\rightleftarrows} 2L \cdot M^{2+}, \quad (2)$$

where L is *E*-**4**, M^{2+} is the metal cation, and K_1 and K_2 are the stability constants of the corresponding complexes. It was found that ligand **4** forms the *E*-**4**$\cdot Mg^{2+}$ complex with $Mg(ClO_4)_2$ and two types of complexes, *viz.*, *E*-**4**$\cdot Ba^{2+}$ and 2(*E*-**4**)$\cdot Ba^{2+}$, with $Ba(ClO_4)_2$ (Table 1).

The structures of the complexes were studied by ^1H NMR spectroscopy. Upon the addition of Mg^{2+} ions to a solution of *E*-**4** in $MeCN-d_3$, the signals for all protons of the ligand are shifted downfield, which is characteristic of guest—host complexation of crown compounds.[31] The most substantial changes are observed for the methylene groups of the crown-ether fragment

Table 1. Stability constants of the complexes of ligands **4**, **6a**, and **6b** with $Ba(ClO_4)_2$ in MeCN (20 °C) and complexation conditions

Ligand	$\log K_{11}$	$\log K_{21}$	Ionic strength, $I \cdot 10^4$/mol L^{-1}
4	4.74±0.045	10.76±0.02	0—8
6a	7.69±0.04	—	0—5
6b	7.21±0.04	—	0—5

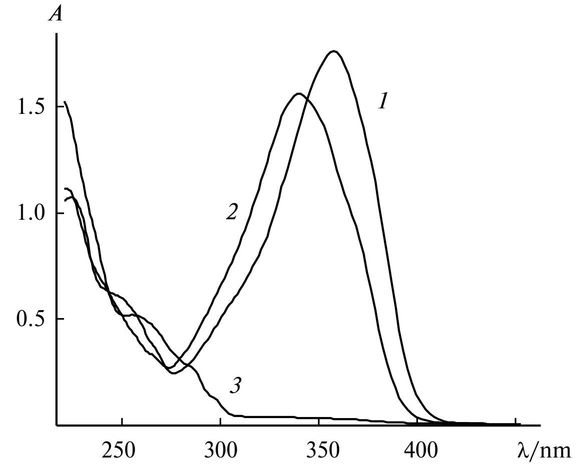


Fig. 1. UV-Vis absorption spectra of ligand *E*-**4** ($C_{E\text{-}\mathbf{4}} = 5 \cdot 10^{-5}$ mol L^{-1}) (*1*); the 2(*E*-**4**) • Ba^{2+} complex ($C_{2(E\text{-}\mathbf{4})\cdot\text{Ba}^{2+}} = 2.5 \cdot 10^{-5}$ mol L^{-1}) (*2*); and the **6a,b** • Ba^{2+} cycloadduct in MeCN (C = $2.5 \cdot 10^{-5}$ mol L^{-1}) (*3*) at 20 °C.

($\Delta\delta_H$ 0.34—0.42), the protons H(2´), H(5´), and H(6´) of the benzene ring ($\Delta\delta_H$ 0.22—0.24), and the proton H$_a$ of the ethylene fragment, which is sensitive to changes in the electron density on the oxygen atom in the *para* position with respect to this fragment (Table 2). This indicates that the metal cation is located in the cavity of the macroheterocycle and is efficiently bound to the oxygen atoms (Scheme 3). The electron-withdrawing effect of the Mg^{2+} cation located in the cavity of the crown-ether fragment notably decreases along the conjugation chain of *E*-**4**, and $\Delta\delta_H$ for other protons are at most 0.05 ppm.

In the ^{13}C NMR spectrum of the *E*-**4** • Mg^{2+} complex, the signals for all methylene groups are shifted upfield ($\Delta\delta_C$ varies from −2.24 to −2.77), which is typical of complexation of crown ethers.[32] There is no general tendency for changes in the chemical shifts of the carbon atoms of the conjugated fragment in the *E*-**4** • Mg^{2+} complex (Table 3). The signals for the C(3´) and C(4´) atoms of the benzene ring are most substantially shifted upfield

Table 2. Chemical shifts for the protons of ligand **4** and its complexes with Mg(ClO$_4$)$_2$ and Ba(ClO$_4$)$_2$^{a}

Compound	*E*-**4** : M^{2+} ^{b}	δ_H ($\Delta\delta_M$)^c												
		H(4)	H(5)	H(6)	H(7)	H$_a$	H$_b$	H(2´)	H(5´)	H(6´)	H$_\alpha$	H$_{\alpha'}$	H$_\beta$	H$_{\gamma,\delta}$
E-**4**		7.96	7.52	7.42	7.98	7.37	7.57	7.31	7.00	7.25	4.21	4.18	3.86	3.70
E-**4** • Mg^{2+}	1 : 2	8.00	7.55	7.47	8.01	7.50	7.62	7.55	7.24	7.47	4.63	4.52	4.20	4.04
		(0.04)	(0.03)	(0.05)	(0.03)	(0.13)	(0.05)	(0.24)	(0.24)	(0.22)	(0.42)	(0.34)	(0.34)	(0.34)
E-**4** • Ba^{2+}	1 : 350	7.95	7.50	7.41	7.96	7.42	7.56	7.47	7.17	7.39	4.46	4.41	3.94	3.89
		(−0.01)	(−0.02)	(−0.01)	(−0.02)	(0.05)	(−0.01)	(0.16)	(0.17)	(0.14)	(0.25)	(0.23)	(0.08)	(0.19)
2(*E*-**4**) • Ba^{2+}	2 : 1	7.77	7.42	7.33	7.74	7.30	7.43	7.01	7.01	7.31	4.32	4.19	3.95	3.95
		(−0.19)	(−0.10)	(−0.09)	(−0.24)	(−0.07)	(−0.14)	(−0.30)	(0.01)	(0.06)	(0.11)	(0.01)	(0.09)	(0.25)

^{a} Conditions for recording ^{1}H NMR spectra and complex formation: solutions in MeCN-d$_3$, 60 °C, $C_4 = 2 \cdot 10^{-3}$ mol L^{-1}.
^{b} The molar ratio of the starting complexation reagents.
^{c} $\Delta\delta_M = \delta_{\text{complex}} - \delta_{\text{ligand}}$ (M = Mg or Ba).

Scheme 3

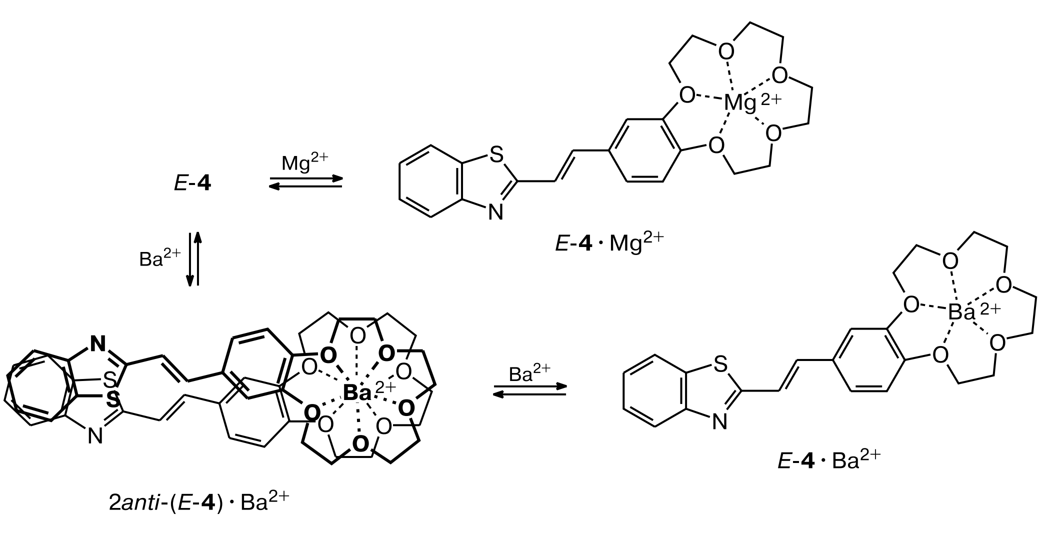


Table 3. Chemical shifts for the carbon atoms of ligand **4** and its complexes with $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$[a]

Compound	*E*-**4** : M^{2+} [b]	δ_C $(\Delta\delta_M)$[c]									
		C(2)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C_a	C_b	C(1′)
E-**4**		168.45	123.87	127.57	126.49	122.98	135.84	155.53	121.59	138.81	130.48
E-**4**·Mg^{2+}	1 : 1	167.95	123.89	127.72	126.80	123.07	135.83	155.14	124.87	137.25	132.81
		(−0.50)	(0.02)	(0.15)	(0.31)	(0.09)	(−0.01)	(−0.39)	(3.28)	(−1.56)	(2.33)
2(*E*-**4**)·Ba^{2+}	2 : 1	167.61	123.78	127.39	126.47	122.76	135.73	155.15	124.91	137.05	132.82
		(−0.84)	(−0.09)	(−0.18)	(−0.02)	(−0.22)	(−0.11)	(−0.38)	(3.32)	(−1.76)	(2.34)
		C(2′)	C(3′)	C(4′)	C(5′)	C(6′)	C_α	$C_{\alpha'}$	C_β		$C_{\gamma,\delta}$
E-**4**		114.36	150.95	152.23	115.67	123.29	70.74	70.51	70.51, 70.61		71.50, 71.56, 72.05, 72.05
E-**4**·Mg^{2+}	1 : 1	111.60	145.37	145.68	113.68	123.54	67.97	67.97	68.28, 68.36		69.04, 69.04, 69.90, 69.90
		(−2.76)	(−5.58)	(−6.55)	(−1.99)	(0.25)	(−2.77)	(−2.54)	(~−2.24)		(~−2.32)
2(*E*-**4**)·Ba^{2+}	2 : 1	114.94	147.91	148.43	116.53	123.39	70.78	70.99	70.42, 70.49		69.55, 69.59, 69.74, 69.82
		(0.58)	(−3.04)	(−3.80)	(0.86)	(0.10)	(0.04)	(0.48)	(~−0.11)		(~−2.12)

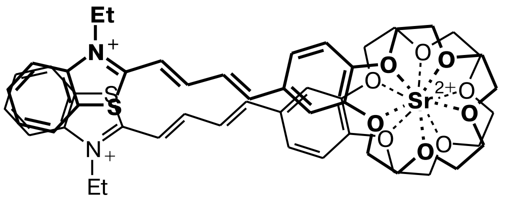
[a] Conditions for recording ^{13}C and complex formation: solutions in MeCN-d_3, 60 °C, $C_4 = 0.14$ mol L^{-1}.

[b] The molar ratio of the starting complexation reagents.

[c] $\Delta\delta_M = \delta_{complex} - \delta_{ligand}$ (M = Mg or Ba).

($\Delta\delta_C$ varies from −5.58 to −6.55), smaller shifts are observed for the C(2′), C(5′), and C_b atoms, and the signals for the C(1′) and C_a atoms are noticeably shifted downfield. Apparently, $\Delta\delta_C$ for the sp^2-hybridized carbon atoms are determined primarily by a decrease in the contribution of a charge-separated resonance structure in the *E*-**4**·Mg^{2+} complex. This occurs because the lone pair of the oxygen atom in the *para* position with respect to the ethylene group is no longer involved in conjugation with the π-system of the benzene ring and is instead coordinated to the metal cation, which causes the electron density redistribution throughout the conjugated system, the density on odd and even atoms, starting from C(4′), being increased and decreased, respectively.

Interaction of *E*-**4** with Ba^{2+} ions is accompanied by changes in the ^1H NMR spectrum, which differ from those observed for the complex with Mg^{2+}. For the L : Ba^{2+} concentration ratio of 2 : 1, the ^1H NMR spectrum recorded at room temperature represents a set of strongly broadened signals, which are difficult to reliably interpret. An increase in the temperature to 60 °C leads to substantial narrowing of the lines and allows unambiguous assignment of the signals for the protons (see Table 2). As compared with the *E*-**4**·Mg^{2+} complex, the downfield shifts $\Delta\delta_H$ for the α-, α′-, and β-CH_2O groups and the protons H(5′) and H(6′) are small, whereas the signals for the proton H(2′) and the protons of the ethylene fragment and the benzothiazole moiety are shifted upfield. Earlier,[19] we have already described an analogous spectral behavior of 15-crown-5-containing butadienyl dye **5** upon the formation of a complex with Sr^{2+} ions, in which two ligands are coordinated to one metal cation. A sandwich structure was assigned to this complex based on the characteristic changes in the positions of the signals. In this complex, the chromophore systems of the dye are stacked due to intermolecular π,π interactions, the *anti* conformation of compound **5** being the major one.



2*anti*-(*E*,*E*-**5**)·Sr^{2+}

In the case of complexation of *E*-**4** with Ba^{2+} ions, the observed spectral changes also suggest the formation of a 2 : 1 sandwich complex, in which molecules **4** are held by stacking interactions. This arrangement of two molecules **4** should give rise to mutual anisotropic effects on some of the protons because they fall in the shielding regions of the conjugated π systems. As can be seen from Table 2, the most substantial upfield shifts are observed for the protons H(2′), H_b, H(4), and H(7), suggesting that the complex has the structure 2*anti*-(*E*-**4**)·Ba^{2+} (see Scheme 3). It should be emphasized that this is a major, but not the only, structure of the sandwich complex. Strong broadening of the lines at room temperature suggests that there is an equilibrium between several complexes, which undergo slow (on the ^1H NMR time scale) interconversions.

More complex changes in the chemical shifts are observed in the ^{13}C NMR spectrum of the sandwich complex 2*anti*-(*E*-**4**) • Ba^{2+} as compared with those observed for the complexation with Mg^{2+} ions (see Table 3). The values of $\Delta\delta_C$ for the γ- and δ-CH_2O groups of the crown ether are on the whole similar to those observed for *E*-**4** • Mg^{2+}, whereas the changes in the chemical shifts of the α-, α´-, and β-CH_2O groups are, apparently, determined by a substantial conformational rearrangement of the macroheterocycle relative to the benzene ring, which is required for binding of a large cation. Analysis of $\Delta\delta_C$ for the sp^2-hybridized carbon atoms shows that the upfield $\Delta\delta_C$ for C(3´) and C(4´) are as small as –3.04 and –3.80, respectively, whereas the C(2´) and C(5´) atoms are characterized, on the contrary, by upfield shifts. The electron density redistribution over all atoms of the conjugated system of *E*-**4** in the 2*anti*-(*E*-**4**) • Ba^{2+} complex differs only slightly from that in the *E*-**4** • Mg^{2+} complex, because other carbon atoms in these complexes have rather similar δ_C. The sensitivity of the ^{13}C nuclei to anisotropic effects is low as compared with the ^1H nuclei, and shielding of the carbon atoms of the benzothiazole fragment and C_b is manifested as upfield shifts of their signals up to 0.34 ppm (for C(2)) as compared with those observed for the magnesium complex.

An increase in the Ba^{2+} : ligand ratio to 350 : 1 leads to changes in δ_H, which are similar to those observed for complexation with Mg^{2+} cations. The signals for the protons of the benzocrown-ether fragment and the proton H_a are shifted downfield relative to the free ligand (see Table 2). Evidently, a large excess of Ba^{2+} ions causes a shift of the equilibrium toward the *E*-**4** • Ba^{2+} complex. Taking into account the equilibrium constants for the 1 : 1 and 2 : 1 complexes (see Table 1), 89% of the ligand exist in this state. The smaller values of $\Delta\delta_H$ for *E*-**4** • Ba^{2+} as compared with *E*-**4** • Mg^{2+} are apparently associated with a lower positive charge density on the larger barium ion and, consequently, the smaller electron-withdrawing effect of this ion on the protons of the ligand in the complex.

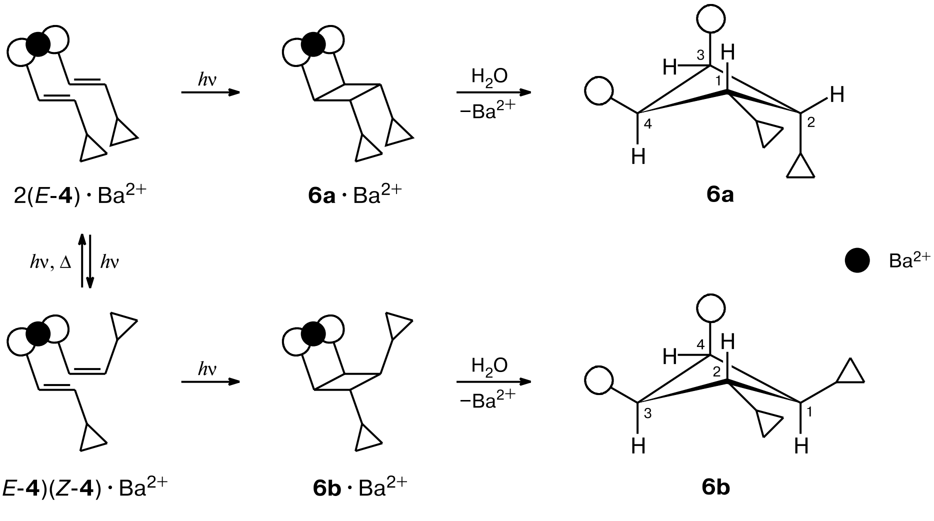
[2+2] Photocycloaddition

Self-assembly of compound **4** into a sandwich complex in the presence of Ba^{2+} cations leads to a decrease in the distance between the unsaturated fragments, which is favorable for photocycloaddition. One would expect the formation of "head-to-head" cyclobutanes in accordance with the orientation of the double bonds of **4** in the complex.

Irradiation of solutions of the *E*-**4** • Mg^{2+} and 2(*E*-**4**) • Ba^{2+} complexes in MeCN at λ = 365 nm with intensity $I = 7.8 \cdot 10^{-9}$ Einstein s^{-1} cm^{-2} causes rapid changes in their absorption spectra. Photostationary states due to reversible *E—Z* photoisomerization are attained within approximately 1 min.**30** Upon further irradiation for several hours, the absorption spectrum of the Mg complex remains unchanged. For the 2(*E*-**4**) • Ba^{2+} complex, rather fast changes in the absorption spectrum characteristic of photocycloaddition are observed once the *E—Z* photostationary state is attained (see Fig. 1).**33** The quantum yield of photocycloaddition of *E*-**4** (φ), calculated from the kinetics of consumption of the dye, is high and is 0.13±0.015 ($C_{[2(E\text{-}4)\cdot Ba^{2+}]} = 2.5 \cdot 10^{-5}$ mol L^{-1} in MeCN, $I_0 = 4.4 \cdot 10^{-9}$ Einstein s^{-1} cm^{-2}).

The structures of photocycloaddition products of the 2(*E*-**4**) • Ba^{2+} complex were studied by NMR spectroscopy. The ^1H NMR spectrum in MeCN-d_3 at 25 °C has a set of strongly broadened lines, which are impossible to interpret. Apparently, these products form aggregates in the presence of Ba^{2+} ions. To decompose these aggregates, we gradually added D_2O to the solution under study. When the D_2O concentration in the mixture became as

Scheme 4



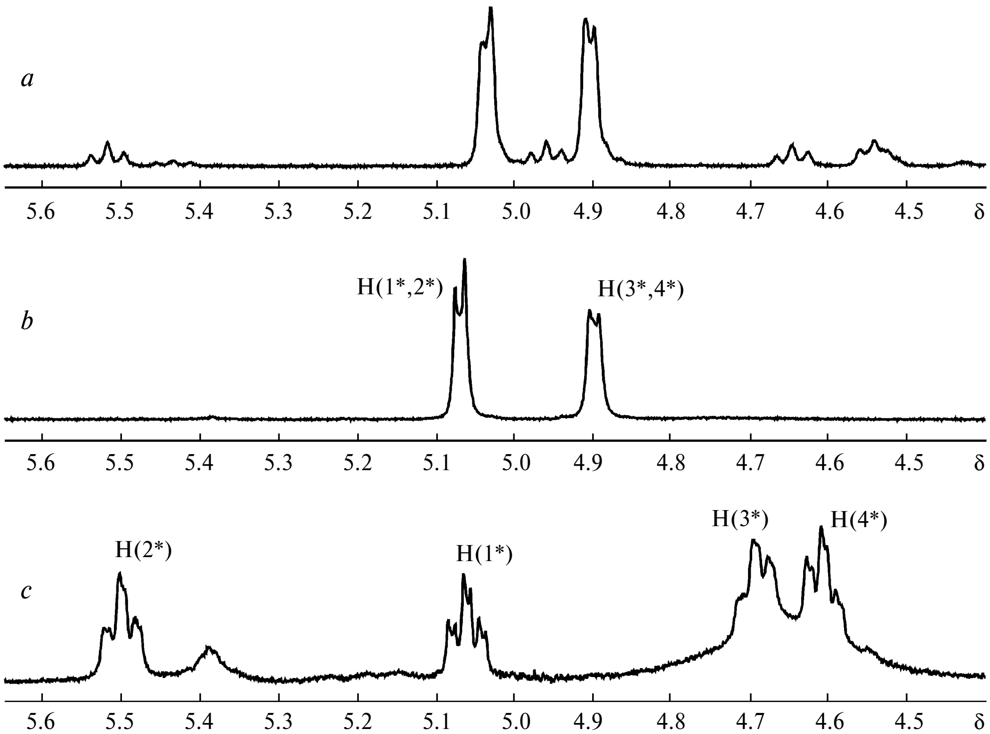


Fig. 2. ^{1}H NMR spectra of the reaction mixture (*a*) and compounds **6a** (*b*) and **6b** (*c*) separated by HPLC (region of cyclobutane protons; in MeCN-d_3 for individual cyclobutanes **6a** and **6b** and in MeCN-d_3—D_2O (6.7 : 1) for a mixture of isomers, 45 °C).

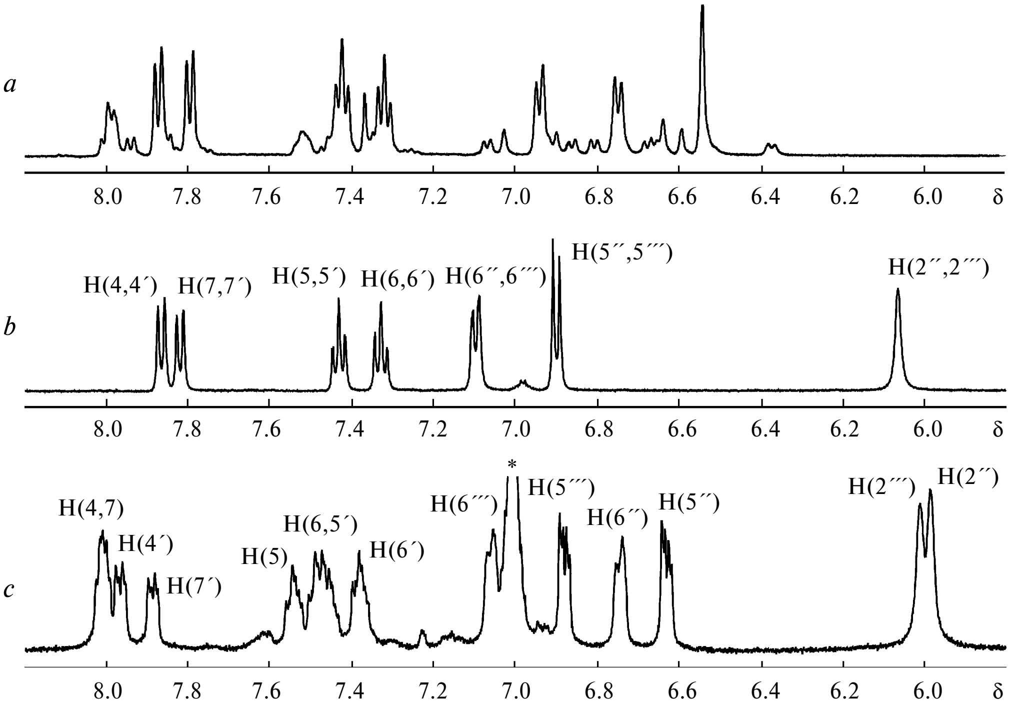


Fig. 3. ^{1}H NMR spectra of the reaction mixture (*a*) and compounds **6a** (*b*) and **6b** (*c*) separated by HPLC (region of aromatic protons, in MeCN-d_3 for individual cyclobutanes **6a** and **6b** and in MeCN-d_3—D_2O (6.7 : 1) for a mixture of isomers, 45 °C). An impurity with an unknown structure is marked with an asterisk.

high as 13% (v/v), the spectral pattern became more simple. The fragments of the spectrum of the reaction mixture, recorded at 45 °C to improve resolution, are shown in Figs 2, *a* and 3, *a*. These spectral regions contain signals for the protons at δ 4.0—5.0, whereas signals for the protons of the ethylene double bond are absent. The analysis of this spectrum and 2D COSY and NOESY spectra show that two major photocycloaddition products, *viz.*, isomeric crown-containing cyclobutanes **6a** and **6b**, are formed in the ratio of 78 : 22 (Scheme 4).

Individual cyclobutanes **6a** and **6b** were isolated by HPLC.

Fragments of the ^{1}H NMR spectra of compounds **6a** and **6b** are presented in Figs 2, *b*, *c* and 3, *b*, *c*. The ^{1}H NMR spectrum of the cyclobutane fragment of the minor isomer **6b** corresponds to the ABCD-type system and is characterized by the coupling constants $^3J_{\mathrm{H(1^*),H(2^*)}} = 9.9$ Hz, $^3J_{\mathrm{H(1^*),H(4^*)}} = 9.7$ Hz, $^3J_{\mathrm{H(2^*),H(3^*)}} = 9.7$ Hz, and $^3J_{\mathrm{H(3^*),H(4^*)}} = 9.5$ Hz, which were obtained by computer optimization of the lines in a theoretical spectrum against the experimental data (Fig. 4).

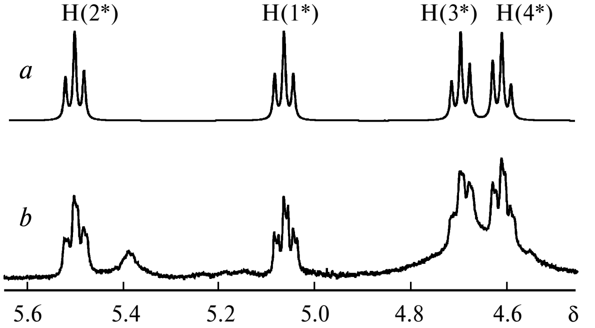
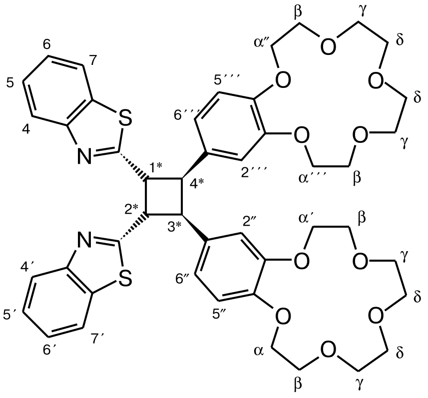
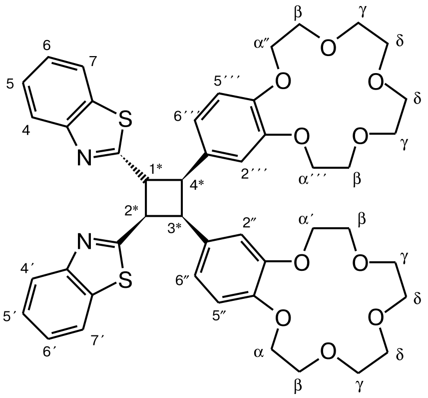


Fig. 4. Theoretical ABCD (*a*, for the major conformer) and experimental (*b*) ^{1}H NMR spectra of the cyclobutane protons in **6b** (MeCN-d_3, 45 °C).

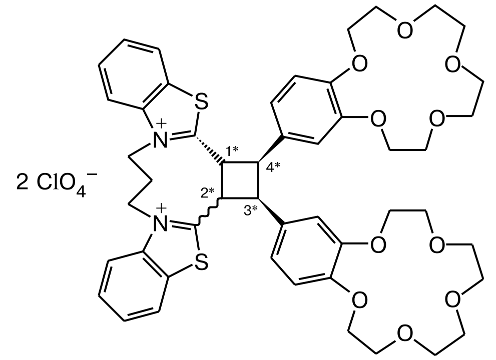


6a



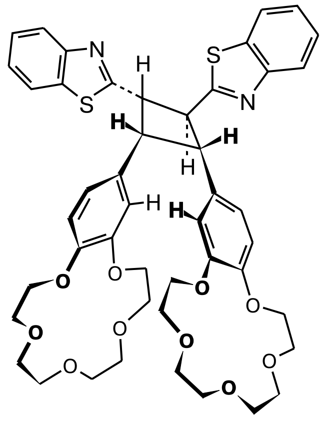
6b

It should be noted that the spectrum of compound **6b** is analogous to that of one of isomeric cyclobutanes **7a,b** prepared by the photocycloaddition reaction from a bisstyryl dye, in which the benzothiazolium fragments are linked by the trimethylene spacer.[34] The experimental coupling constants for isomer **7b** ($^3J_{\mathrm{H(1^*),H(2^*)}} = 10.2$ Hz, $^3J_{\mathrm{H(1^*),H(4^*)}} = 10.8$ Hz, $^3J_{\mathrm{H(2^*),H(3^*)}} = 8.8$ Hz, $^3J_{\mathrm{H(3^*),H(4^*)}} = 10.0$ Hz) (lit. data[34]) and the theoretical vicinal coupling constants calculated for the same isomer of 1,2,3,4-tetraphenylcyclobutane[35] are similar to the experimental coupling constants for **6b**.

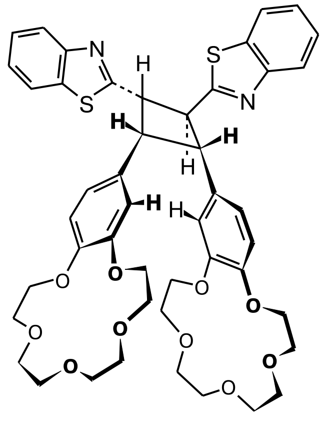


7a,b

Hence, as in the case of compound **7b**,[34] the structure of cyclobutane formed upon the reaction of *E*-**4** with *Z*-**4** (see Scheme 4) was assigned to compound **6b**. The structure **6b** was additionally confirmed by the presence of a NOE signal between the protons H(2*) and H(4*), which suggests that these protons are on the same side of the cyclobutane ring. Compound **6b** exists as a mixture of two conformers in a ratio of 53 : 47, which is reflected in the doubling or broadening of the majority of lines in the ^{1}H NMR spectrum (see Figs 2, *c* and 3, *c*). The fact that the coupling constants of the cyclobutane protons are virtually identical for both conformers suggests that they do not appear as a result of inversion of the cyclobutane ring. In addition, changes in the ratio of the axial and equatorial substituents in the cyclobutane ring due to inversion are energetically very unfavorable, which predetermines the existence of cyclobutane **6b** in one major conformation. It is of note that the signals for the protons H(2″) and H(2‴) of the benzene rings in **6b** appear at unusually high field (at approximately δ 6.0, see Fig. 3, *c*) relative to the starting *E*-**4**. Apparently, these protons are in the shielding cone of the adjacent benzene ring, *i.e.*, the benzocrown-ether fragments in **6b** are in spatial proximity and are arranged one above the other. The *cis* arrangement of the benzocrown-ether fragments in the cyclobutane ring predetermined by the structure of the sandwich complex 2(*E*-**4**)•Ba^{2+} suggests two possible mutual orientations of these fragments (**A** and **B**). Therefore, doubling of the majority of the signals observed in the spectrum is apparently associated with the existence of two conformers of **6b** (**A** and **B**), whose interconversions are slow (on the ^1H NMR time scale) for steric reasons.



A



B

Conformers of cyclobutane derivative **6b**

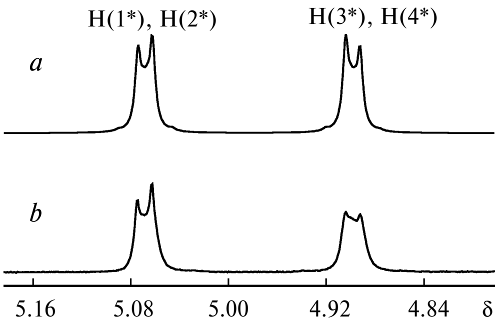


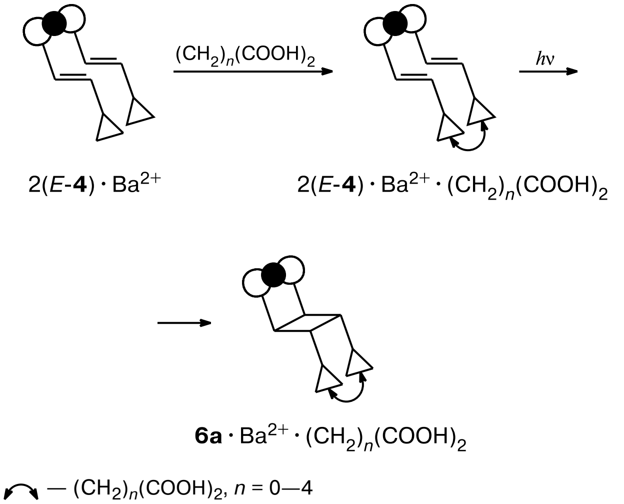
Fig. 5. Theoretical AA′BB′ (*a*) and experimental (*b*) ^1H NMR spectra of the cyclobutane protons in **6a** ($MeCN-d_3$, 45 °C).

The ^1H NMR spectrum of the cyclobutane fragment of the major product **6a** formed in the photocycloaddition reaction of 2(*E*-**4**)•Ba^{2+} corresponds to a symmetrical AA′BB′ spin system with the following vicinal coupling constants: $^3J_{H(1^*),H(4^*)} = {}^3J_{H(2^*),H(3^*)} = 5.9$ Hz and $^3J_{H(1^*),H(2^*)} = {}^3J_{H(3^*),H(4^*)} = 5.1-5.2$ Hz, which were obtained by computer optimization of the lines in a theoretical spectrum against the experimental data (Fig. 5). The spectrum of compound **6a** is similar to that of the related cyclobutane **7a**,[34] but the coupling constants for **7a** are somewhat larger: $^3J_{H(1^*),H(4^*)} = {}^3J_{H(2^*),H(3^*)} =$ 6.7 Hz and $^3J_{H(1^*),H(2^*)} = {}^3J_{H(3^*),H(4^*)} = 8.5$ Hz. Analogously to **7a**, the structure of cyclobutane produced by the reaction of two *E*-**4** molecules (see Scheme 4) was assigned to compound **6a**. The difference in the coupling constants is apparently associated with the difference in the endocyclic dihedral angles in cyclobutanes **6a** and **7a** and is attributed to the presence of the additional strongly strained ring in structure **7a**. The signals for the protons H(2″) and H(2‴) of the benzene rings in pure **6a**, as in **6b**, are observed at very high field (see Fig. 3, *b*). Moreover, the positions of the protons for the benzene rings in the spectra of pure **6a,b** differ substantially from those observed in the spectrum of the reaction mixture (see Fig. 3). Apparently, the addition of a small amount of water to the reaction mixture obtained upon the photocycloaddition leads to dissociation of aggregates due to cleavage of weak intermolecular bonds but does not cause noticeable dissociation of the stable **6a,b**•Ba^{2+} complexes.

The photoreaction performed in the presence of dicarboxylic acids affords isomer **6a** in substantially higher yield. The ratio of isomers **6a** and **6b** in the reaction mixture was found to depend on the length of the polymethylene chain in the dicarboxylic acid. The observed effect is presumably associated with coordination of two benzothiazole fragments of *E*-**4** to one molecule of the acid through two hydrogen bonds. This apparently leads to an increase in the equilibrium concentration of the sandwich complex 2(*E*-**4**)•Ba^{2+} in a conformation in which the orientation of the double bonds is favorable for photocycloaddition (Scheme 5).

The most substantial change in the ratio of cyclobutanes **6a,b** from 3.4 : 1 to 11.2 : 1 in favor of **6a** is observed in the presence of adipic acid. The nature of the observed effects will be analyzed in more detail in future investigations.

Scheme 5



We studied complexation of cyclobutanes **6a,b** with the Ba^{2+} ion by competitive ligand titration with a $Ba(ClO_4)_2$ solution (see Experimental). The reaction scheme for this system includes three equations:

$$L + Ba^{2+} \underset{}{\overset{K_1}{\rightleftarrows}} L\cdot Ba^{2+}, \tag{3}$$

$$L' + Ba^{2+} \overset{K_{1c}}{\rightleftarrows} L'\cdot Ba^{2+}, \tag{4}$$

$$2\,L' + Ba^{2+} \overset{K_{2c}}{\rightleftarrows} 2L'\cdot Ba^{2+}, \tag{5}$$

where L is ligand **6a** or **6b**, L´ is the competitive ligand *E*-**4**, and K_1, K_{1c}, and K_{2c} are the stability constants of the corresponding complexes.

The stability constants of complexes of **4** with the Ba^{2+} ion were first determined by titration with a solution of a metal salt. The stability constants for two isomers of cyclobutanes **6a** and **6b** were high and have similar values (see Table 1). Apparently, this can be attributed to the cooperative effect and the *cis* arrangement of two crown ether fragments in both isomeric cyclobutanes.

To summarize, by the example of (benzothiazolyl)ethenylbenzocrown ether **4**, we discovered the previously unknown spontaneous self-assembly giving rise to a sandwich complex. Photoirradiation of this complex induces intermolecular stereoselective [2+2] cycloaddition to form two isomeric cyclobutanes. The use of this type of preorganization may provide an additional way to control regio- and stereoselectivity of photocycloaddition of crown-containing unsaturated compounds. The above-considered transformations show the potentiality of using hetarylphenylethylenes as building blocks for the design of photoswitchable molecular devices.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer (500.13 and 125.76 MHz, respectively) in MeCN-d_3 using signals of the solvent as the internal standard (δ_H 1.96 and δ_C 118.10, respectively). Two-dimensional homonuclear $^1H-^1H$ COSY and NOESY spectra and heteronuclear $^1H-^{13}C$ COSY spectra were used to assign the signals for protons and carbon atoms. The subspectrum of the cyclobutane moiety (see Figs 4 and 5) was analyzed using the CALM iteration program, which is a version of the UEALTR program adapted to PC.**[36]** The calculations were characterized by the rms deviation of 0.1 Hz. The MALDI mass spectra were obtained on a Vision 2000 MALDI-TOF mass spectrometer (Finnigan, USA) equipped with a UV laser (337 nm; pulse duration, 3 nm; maximum pulse energy, 250 μJ) using 2,5-dihydroxybenzoic acid as the matrix. Elemental analysis was carried out in the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences (Moscow). The melting points were measured on a Mel-Temp II instrument.

The course of the reactions was monitored by TLC on DC-Alufolien Aluminiumoxid 60 F_{254} neutral (Typ E) and Kieselgel 60 F_{254} (Merck) plates. Studies by HPLC were carried out on a Waters-600 high-pressure chromatograph. The chromatographic conditions are as follows: detection at 290 nm, Diasorb-130-C_{16}T (7 μm, 250×4 mm) column, a 4 : 1 MeCN—H_2O mixture as the eluent, elution rate, 1 mL min^{-1}, sample volume, 100 μL.

The UV-Vis absorption spectra were recorded at 20±1 °C on a Specord M40 spectrophotometer coupled to a computer.

The photocycloaddition products of the $2(E\text{-}\mathbf{4})\cdot Ba^{2+}$ complex were prepared by irradiating a solution of the complex in acetonitrile using a DRK-120 mercury lamp. The line with a wavelength of 365 nm was isolated using UFS-6 + BS-7 glass light filters from a standard kit of optical stained glasses. The light intensity was measured using a ferrioxalate actinometer.

The quantum yield of photocycloaddition for the $2(E\text{-}\mathbf{4})\cdot Ba^{2+}$ complex was determined from the data on the consumption of the complex depending on the time of irradiation at 365 nm. The light intensity was $I_0 = 4.4\cdot10^{-9}$ Einstein s^{-1} cm^{-2}. The consumption of the complex was evaluated as follows. After irradiation for a certain period of time (0—1920 s), perchloric acid was added to a solution of the complex up to the concentration of $8\cdot10^{-4}$ mol L^{-1}. The addition of the acid led to protonation of the complex, as a result of which the complex was no longer able to form a cycloadduct upon irradiation. The resulting solution was again irradiated at 365 nm for 4 min until a photostationary mixture of the *trans* and *cis* isomers of ligand **4** and its barium complexes was formed. The consumption of the complex was calculated from the change in the absorbance of the long-wavelength absorption maximum of the photostationary mixture at 423 nm where the absorption of the cycloadduct is absent. The quantum yield was determined from the data on the consumption of the complex in the initial step of irradiation.

The complexation of ligand *E*-**4** was studied by spectrophotometric titration at 20±1 °C by varying the $Ba(ClO_4)_2$ concentration, the ligand concentration being maintained constant. The complexation of ligands **6a** or **6b** was studied in the presence of ligand *E*-**4** by performing spectrophotometric titration of a mixture of ligand **6** and *E*-**4** with a $Ba(ClO_4)_2$ solution. All experiments were carried out at red light. The complexation constants were calculated using the HYPERQUAD program.[37]

2-[(*E*)-2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)ethen-1-yl]-1,3-benzothiazole (*E*-4) was prepared according to a known procedure.[30] The reagents $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$ (Aldrich and Merck) were dried *in vacuo* at 240 °C. Oxalic, malonic, succinic, glutaric, and adipic acids, MeCN-d_3 (Aldrich and Merck), and MeCN (special purity grade) with a water content <0.005% were used without additional purification.

Synthesis of cyclobutanes 6a,b. A solution of compound **4** (12.8 mg, 0.03 mmol) and $Ba(ClO_4)_2$ (12.6 mg, 0.0375 mmol) in anhydrous MeCN (6 mL) was placed in a quartz cell and irradiated at a wavelength of 365 nm for 1 h until **4** was completely consumed (spectrophotometric control), the solvent was evaporated *in vacuo*, and isomers **6a** and **6b** were isolated from the residue by HPLC in yields of 6.5 and 0.7 mg, respectively.

1-*r*,2-*c*-Di(benzothiazol-2-yl)-3,4-*t*,*t*-di(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)cyclobutane (*rctt*-6a). The yield was 45%. M.p 115—117 °C. ^1H NMR (MeCN-d_3, 45 °C), δ: 3.61—3.86 (m, 28 H, 14 CH_2O); 4.09—4.16 (m, 4 H, α-CH_2O, α″-CH_2O); 4.90 (m, 2 H, H(3*), H(4*), $J_{H(3^*),H(4^*)} = 5.1$ Hz, $J_{H(3^*),H(2^*)} = J_{H(4^*),H(1^*)} = 5.9$ Hz); 5.07 (m, 2 H, H(1*), H(2*), $J_{H(1^*),H(2^*)} = 5.2$ Hz, $J_{H(1^*),H(4^*)} = J_{H(2^*),H(3^*)} = 5.9$ Hz); 6.06 (br.s, 2 H, H(2″), H(2‴)); 6.90 (d, 2 H, H(5″), H(5‴), $J_{H(5''),H(6'')} = J_{H(5'''),H(6''')} = 8.1$ Hz); 7.10 (br.d, 2 H, H(6″), H(6‴), $J_{H(6''),H(5'')} = J_{H(6'''),H(5''')} = 8.1$ Hz); 7.33 (m, 2 H, H(6), H(6′)); 7.43 (m, 2 H, H(5), H(5′)); 7.82 (d, 2 H, H(7), H(7′), $J_{H(7),H(6)} = J_{H(7'),H(6')} = 7.9$ Hz); 7.87 (d, 2 H, H(4), H(4′), $J_{H(4),H(5)} = J_{H(4'),H(5')} = 8.1$ Hz). MS: *m/z* = 894 $[M + K]^+$, 878 $[M + Na]^+$. Found (%): C, 58.14; H, 6.27; N, 3.27. $C_{46}H_{50}N_2O_{10}S_2 \cdot 5H_2O$. Calculated (%): C, 58.46; H, 6.40; N, 2.96.

1-*r*,2-*t*-Di(benzothiazol-2-yl)-3,4-*c*,*c*-di(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)cyclobutane (*rcct*-6b). The yield was 5%. ^1H NMR (MeCN-d_3, 45 °C), δ: 3.54—3.90 (m, 24 H, 12 CH_2O); 3.94—4.02 (m, 2 H, α-CH_2O); 4.09 (m, 2 H, α″-CH_2O); 4.16 (m, 4 H, α′-CH_2O, α‴-CH_2O); 4.60 (m, 1 H, H(4*), $J_{H(4^*),H(1^*)} = 9.7$ Hz, $J_{H(4^*),H(3^*)} = 9.5$ Hz); 4.69 (m, 1 H, H(3*), $J_{H(3^*),H(2^*)} = 9.7$ Hz, $J_{H(3^*),H(4^*)} = 9.5$ Hz); 5.06 (m, 1 H, H(1*), $J_{H(1^*),H(2^*)} = 9.9$ Hz, $J_{H(1^*),H(4^*)} = 9.7$ Hz); 5.50 (m, 1 H, H(2*), $J_{H(2^*),H(1^*)} = 9.9$ Hz, $J_{H(2^*),H(3^*)} = 9.7$ Hz); 5.99 (br.s, 1 H, H(2″)); 6.01 (br.s, 1 H, H(2‴)); 6.63 (d*, 1 H, H(5″), $J_{H(5''),H(6'')} = 8.2$ Hz); 6.75 (br.d, 1 H, H(6″), $J_{H(6''),H(5'')} = 8.2$ Hz); 6.88 (d*, 1 H, H(5‴), $J_{H(5'''),H(6''')} = 8.2$ Hz); 7.06 (br.d, 1 H, H(6‴), $J_{H(6'''),H(5''')} = 8.2$ Hz); 7.38 (m, 1 H, H(6′)); 7.43—7.50 (m, 2 H, H(5′), H(6)); 7.54 (m, 1 H, H(5)); 7.89 (d*, 1 H, H(7′), $J_{H(7'),H(6')} = 7.8$ Hz); 7.97 (d*, 1 H, H(4′), $J_{H(4'),H(5')} = 8.1$ Hz); 8.01 (m, 2 H, H(4), H(7)). MS: *m/z* = 894 $[M + K]^+$, 878 $[M + Na]^+$.

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* Protons of the same type belonging to two conformers have almost the same chemical shifts.

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