Supramolecular assemblies of crown-containing 2-styrylbenzothiazole with amino acids

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Assemblies of 2-styrylbenzothiazole containing an 18-crown-6 ether fragment with perchlorates of amino acids $ClO_4^-NH_3^+(CH_2)_nCOOH$ ($n = 2$, 10) were studied by UV, NMR spectroscopy, time-resolved fluorescence spectroscopy and quantum-chemical calculations. The obtained data showed that complex formation of the crown-containing 2-styrylbenzothiazole with amino acids occurs through mono- or ditopic coordination. The formation of a ditopic complex influences the *E–Z* photoisomerization reaction of 2-styrylbenzothiazole.

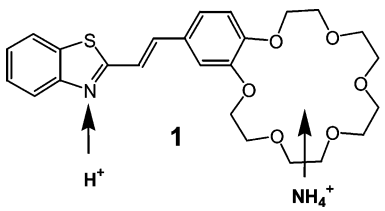
Introduction

The design of synthetic receptors for neutral molecules is an area of intense current interest.[1,2] The area has grown from early work on cyclodextrin or single crown ether complexation to a wide array of receptor shapes and structures. Furthermore, the range of substrates has increased from simple aromatic or metal ion substrates to peptides and carbohydrates. The construction of synthetic molecules capable of recognizing and binding small organic molecular substrates (ammonium salts, carboxylic acids)[3–7] is important in the perspective that bioactive molecules such as amino acids, peptides and proteins containing amino and carbonyl groups can also associate with the same type of receptors.[8–11] However, compared to the large number of chromo/fluororeceptors for cations or anions, the development of artificial receptors for amino acids is quite limited and still a challenge due to their highly hydrophilic character. In order to recognise the amino acid effectively, simultaneous binding of the ammonium and carboxylate groups is required. In the reported examples, crown ethers were chosen as ammonium binding sites,[12–15] and quaternary ammonium,[16] guanidinium[17,18] or metals[19] were used as carboxylate binding centers.

In this work, we selected benzo-18-crown-6 ether as the ammonium binding site and a benzothiazole residue as the carboxylate binding site. The two binding centers are connected with each other through an ethylenic double bond. The irradiation of the receptor with light results in the reversible reaction of *E–Z* isomerization around the C=C double bond which substantially changes the structure of the receptor. The occurrence of the phototransformation will change the ability of the receptor to bind with amino acids. The photoswitchable ability of the photochromic crown ethers to bind the metal cations is a well known phenomenon in the literature.[20–25] The creation of photocontrolled receptors for organic molecules is a less developed topic. The receptors may be interesting for the development of photocontrolled membrane transport systems and photocontrolled artificial catalytic systems.

Results and discussion

In the present investigation, the assemblies of crown-containing 2-styrylbenzothiazole (*E*)-**1** with perchlorates of amino acids $ClO_4^-NH_3^+(CH_2)_nCOOH$ ($n = 2$ (**A2**) and $n = 10$ (**A10**)) were studied by optical and NMR spectroscopy. In the design of the appropriate receptor, we used molecule (*E*)-**1** possessing two binding centres of different nature (Scheme 1).[26] The ligand was prepared as described in refs. 27 and 28. According to the NMR data, the ligand is formed as the *E*-isomer.



Bathochromic shift in UV spectrum — Hypsochromic shift in UV spectrum

Scheme 1

The addition of perchloric acid to a solution of (*E*)-**1** in MeCN leads to the coordination of a proton with the heterocyclic N atom accompanied by a large bathochromic shift of the long wavelength band up to 60 nm (see Fig. 1). The complex formation of (*E*)-**1** with ammonium cations occurs through the crown ether moiety what causes the hypsochromic shift in UV spectrum (see Fig. 1). The spectrophotometric method was used for the determination of the stability constants. The magnitudes of the constants are listed in Table 1.

We supposed that perchlorates of amino acids **A2** and **A10** can form complexes with receptor (*E*)-**1** due to hydrogen bond formation between the carboxylic proton and the heterocyclic

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Table 1 Stability constants, time-resolved fluorescence data and reorientation time for (*E*)-**1** and its complexes with amino acids **A2**, **A10** in MeCN, $C_1 = 5 \times 10^{-5}$ mol l^{-1}, $C_{complex} = 5 \times 10^{-5}$mol l^{-1}, 25 °C

	(*E*)-**1**	[(*E*)-**1**]·**A2**	[(*E*)-**1**]·**A10**	[(*E*)-**1**]·NH_4^+	[(*E*)-**1**]·H^+
Log K_{11}		4.11 ± 0.006	4.18 ± 0.01	4.52 ± 0.02	6.4 ± 0.5
τ_{fl} (reorientation time)	20 ps (100 ps)	20 ps (150 ps)	20 ps (>350 ps)	17 ps (47 ps)	26 ps (100 ps)

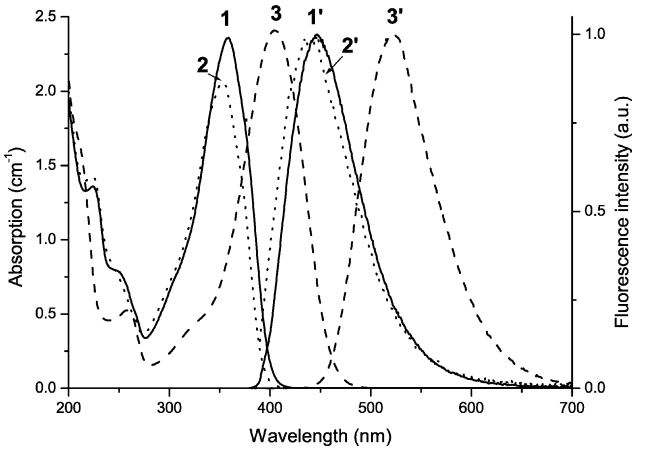


Fig. 1 Absorption and fluorescence spectra: 1, 1′ = free ligand **1**; 2, 2′ = complex **1**·H^+, and 3, 3′ = complex **1**·NH_4^+ in MeCN, $C_1 = 1 \times 10^{-4}$ mol l^{-1}, $C_{complex} = 1 \times 10^{-4}$ mol l^{-1}, 25 °C.

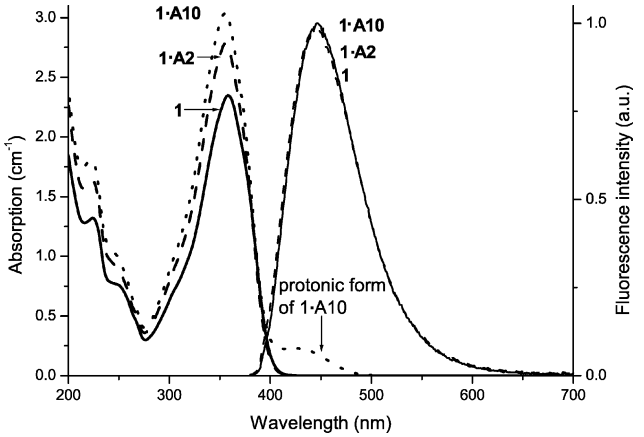


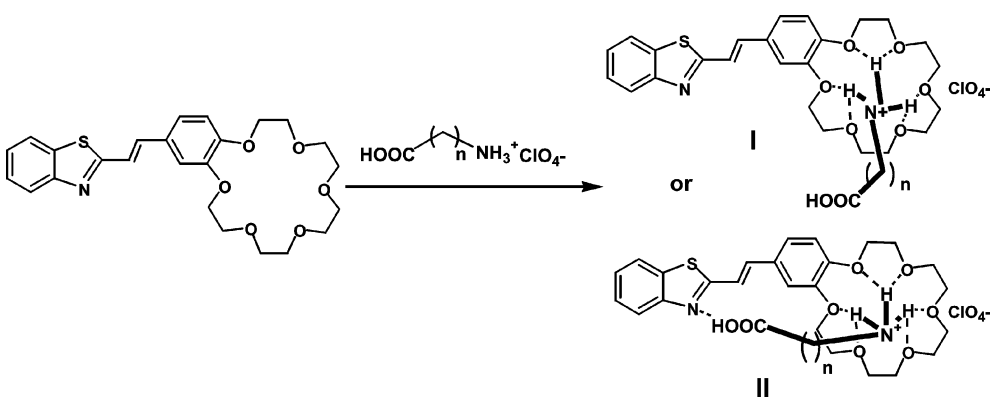
Fig. 2 UV spectra of initial ligand **1** and complexes of **1** with amino acids **A2** and **A10** in MeCN, $C_1 = 1 \times 10^{-4}$ mol l^{-1}, $C_{complex} = 1 \times 10^{-4}$ mol l^{-1}, 25 °C.

residue and between the ammonium protons and the oxygen heteroatoms of the crown ether moiety. The appropriate linker length between the ammonium and carboxylic group, and the relative orientations of the two recognition moieties also play important roles in the formation of supramolecular complexes.

When amino acids **A2**, **A10** were added to an MeCN solution of (*E*)-**1**, a hypsochromic shift of the long wavelength band and an increase of absorption intensity were found (Fig. 2). The observed spectral changes were used for the calculation of the stability constants and the obtained data are presented in Table 1. The value of the stability constant of complex [(*E*)-**1**]·**A10** is higher than that obtained for [(*E*)-**1**]·**A2**. The possible structures of complexes are presented in Scheme 2. In monotopic complex **I**, the interaction between ligand (*E*)-**1** and the amino acid occurs through the coordination of the ammonium group with the crown ether moiety.

In the ditopic complex **II**, as well as the coordination of the crown ether complex with the ammonium group, the coordination of the carboxylic group with the heterocyclic residue is assumed. It is obvious, that the ditopic coordination of amino acid **A2** with two binding centers of (*E*)-**1** is hardly possible. Thus, for [(*E*)-**1**]·**A2** the formation of a complex with structure **I** can be suggested. The amino acid **A10** contains a long enough alkyl chain in order to form the complex with structure **II** in which ditopic coordination is realised. The ditopic complex demonstrates greater stability in comparison with the monotopic one.

In the case of [(*E*)-**1**]·**A10**, a novel band in the long wavelength region (420 nm) appeared. The position of the band in the UV spectrum coincidences with that obtained when perchloric acid was added to an acetonitrile solution of ligand (*E*)-**1**. This fact indicates the presence of a small amount of a protonic form of complexed ligand (*E*)-**1** (Scheme 3). The interaction of the



Scheme 2

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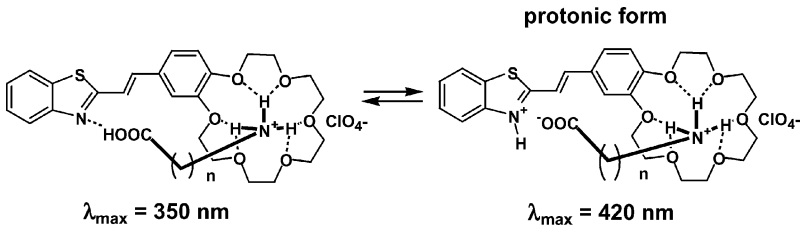

Scheme 3

carboxylic group with the N atom of the benzothiazole residue can promote the dissociation of the proton from the carboxylic group. The heterocyclic residue coordinates the removed proton while the carboxylate anion becomes a counterion.

The lifetimes of the exited states of initial ligand (*E*)-**1** and its complexes were determined (Table 1). The complex formation of ligand (*E*)-**1** with ammonium perchlorate decreases the lifetime of the exited state to 17ps in comparison with 20 ps for the free ligand (*E*)-**1** (Table 1). The lifetime of the exited state of complex [(*E*)-**1**]·$HClO_4$ is 26 ps, thus, the protonation of the N heterocyclic atom leads to an increase of the lifetime of the exited state. For complexes [(*E*)-**1**]·**A2** and [(*E*)-**1**]·**A10** the values of the exited state lifetime are between those for complexes [(*E*)-**1**]·H^+ and [(*E*)-**1**]·NH_4^+. These excited state lifetimes are in good correlation with the understanding of the charge transfer variations of the excited species when the electron donor and acceptor strengths are altered by the complexation.[29] Indeed, the complexation in the crown ether redistributes the electron density of the negative charge donor (dimethoxyphenyl) on the positive charged cation (NH_4^+). Such redistribution reduces the dipole and the polarizability of the ground state and reduces the ability of charge transfer in the excited state which leads to a lower excited state dipole moment. If we take into account the high dielectric permittivity of the surrounding solvent (acetonitrile), the excited state is fixed weaker by the solvation and its potential energy could become higher which could increase the rate of relaxation through the isomerization channel if we suppose that the potential energy barrier changes by a smaller amount than the lowest excited singlet state (S1) potential energy. Inversely, the positive charge (H^+) coordinated on the acceptor part of the compound can reduce the rate of the isomerization through lowering of the S1 potential energy. The double coordination could result in some intermediate cases which could be very similar to free ligand relaxation. The measured lifetimes of the excited states are in good agreement with such a model.

The measured reorientation times (fluorescence anisotropy decay time constants) represent the rotational inertia of excited species (including the solvated shell of the excited ligand or complex). Here, discrimination between different molecular configurations characterized by similar excited state lifetimes could be done and the coordination could be confirmed. In fact, the increase in mass (and similarly the inertia) of the complexed ligand in comparison with the non-complexed one is the explanation for the increase in measured reorientation times. When the ligand is coordinating the ammonium cation, the decrease of the dipole moment will result in a decrease of the volume (and mass) of the solvated shell in both the ground and excited states which results in faster reorientation of the complex.

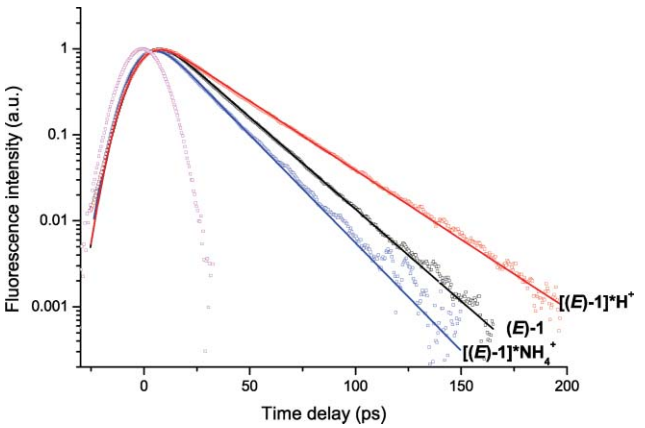

Fig. 3 Fluorescence decay kinetics for (*E*)-**1** and its complexes with NH_4^+ and H^+ in MeCN, $C_1 = 5\times 10^{-5}$ mol l^{-1}.

In the ^1H NMR spectra the addition of amino acids to a solution of ligand (*E*)-**1** in CD_3CN causes changes in the chemical shifts of all protons (Table 2). The downfield shifts of the methylene resonances of the crown ether moiety indicate the formation of a hydrogen bond between oxygen macrocyclic atoms and protons of the ammonium group. The analysis of the coordination of the ammonium group in the crown ether moiety in complexes [(*E*)-**1**]·**A2** and [(*E*)-**1**]·**A10** by use of COSY and NOESY spectroscopy as well as geometry optimization calculations with the Chem 3D program using the MM2 force field showed the same disposition of the ammonium group in the macrocycles of both complexes (Scheme 4). In NOESY spectra of both complexes, an interaction between H^γ and the protons of the $CH_2NH_3^+$ group was found (Scheme 4).

The changes of the proton signals of the heterocyclic part are small for complex [(*E*)-**1**]·**A2** ($\Delta\delta = 0.01$). In the case of complex [(*E*)-**1**]·**A10**, the heterocyclic proton signal changes are more pronounced ($\Delta\delta = 0.06$–0.09). This fact is accounted for by complex [(*E*)-**1**]·**A10** possessing structure **II** (Scheme 4), in which the interaction of the heterocyclic N atom with the carboxylic group results in the substantial changes of the heterocyclic proton chemical shifts in the NMR spectrum (Table 2). In complex [(*E*)-**1**]·**A10**, the amino acid chain displays along the chromophore system. The methylene protons are affected by the chromophore system (the anisotropic effect) which should cause a shift of the amino acid proton signals to the upfield region in the NMR spectra. In our experiments, we found that the positions of the **A10** alkyl chain proton signals are shifted to the upfield region in the NMR spectra (Table 2). This is the additional argument that complex [(*E*)-**1**]·**A10** can be represented as having structure **II**.

Table 2 Changes of the proton chemical shifts ($\Delta\delta = \delta$(complex) $- \delta$(ligand **1**), ppm) in complexes (*E*)-**1** with amino acids **A2** and **A10** in CD_3CN, $C_1 = 2 \times 10^{-2}$ mol l^{-1}, $C_{complex} = 2 \times 10^{-2}$ mol l^{-1}, 25 °C

	H-4	H-7	H-6	H-5	H-a	H-b	H-2′	H-6′	H-5′	H-α′	H-α	H-β,β′	H-γ,γ′	H-δ,δ′	H-ω,ω′	$^+NH_3$	CH_2–COOH	NH_3–CH_2	$(CH_2)_2$	$(CH_2)_{n-4}$
(*E*)-**1**	7.99	7.96	7.52	7.43	7.58	7.42	7.31	7.23	6.99	4.26	4.21	3.79	3.63	3.59	3.57	—	—	—	—	—
(*Z*)-**1**	7.96	7.91	7.50	7.40	7.03	6.81	7.66	7.09	6.96	4.19	4.12	3.78, 3.69	3.63	3.59	3.57	—	—	—	—	—
A2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	6.33	2.71	3.21	—	—
[(*E*)-**1**]·**A2**	8.00	7.97	7.53	7.44	7.59	7.46	7.37	7.29	7.06	4.32	4.27	3.89	3.73	3.71	3.67	7.25	2.54	3.07	—	—
$\Delta\delta_M$	0.01	0.01	0.01	0.01	0.01	0.04	0.06	0.06	0.07	0.06	0.06	0.10	0.10	0.12	0.10	0.92	–0.17	–0.14		
[(*Z*)-**1**]·**A2**	7.98	7.92	7.51	7.42	7.04	6.83	7.83	7.17	7.01	4.26	4.20	3.87, 3.81	3.73	3.69	3.66	—	2.52	3.06	—	
$\Delta\delta_M$	0.02	0.01	0.01	0.02	0.01	0.02	0.17	0.08	0.05	0.07	0.08	0.09, 0.12	0.10	0.10	0.09	—	–0.19	–0.15		
A10	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	6.19	2.29	2.95	1.59	1,11
[(*E*)-**1**]·**A10**	8.03	7.98	7.58	7.49	7.66	7.49	7.40	7.34	7.09	4.33	4.28	3.91	3.75	3.71	3.68	7.11	2.21	2.80	1.50, 1.40	1.18
$\Delta\delta_M$	0.04	0.02	0.06	0.06	0.08	0.07	0.09	0.11	0.10	0.07	0.07	0.12	0.12	0.12	0.11	0.92	–0.08	–0.15	–0.09, –0.19	–0.07
[(*Z*)-**1**]·**A10**	7.98	7.92	7.55	7.45	7.07	6.86	7.83	7.20	7.05	4.28	4.22	3.89, 3.83	3.74	3.70	3.67	7.05	2.17	2.82	1.46	1.26
$\Delta\delta_M$	0.02	0.01	0.05	0.05	0.04	0.05	0.17	0.11	0.09	0.09	0.10	0.11, 0.14	0.11	0.11	0.10	0.86	–0.12	–0.13	0.13	0.15

As was found earlier, the free ligand **1** in acetonitrile solution exists as a mixture of *syn*- and *anti*-isomers (Scheme 5).[26] The analysis of the NOESY and COSY spectra of complexes [(*E*)-**1**]·**A2** and [(*E*)-**1**]·**A10** showed that in complex [(*E*)-**1**]·**A2** the ligand (*E*)-**1** exists as the same mixture of *syn*- and *anti*-isomers. Thus, in the NOESY spectra, the interactions between $H^a \leftrightarrow H^{6'}$, $H^b \leftrightarrow H^{6'}$, $H^a \leftrightarrow H^{2'}$ and $H^b \leftrightarrow H^{2'}$ belonging to both isomers were found. In the NOESY spectra of complex [(*E*)-**1**]·**A10**, only $H^a \leftrightarrow H^{6'}$, $H^b \leftrightarrow H^{2'}$ were observed which means that in complex [(*E*)-**1**]·**A10** the ligand (*E*)-**1** exists as the *anti*-isomer. Probably, this result can be explained by the fact that the relative orientation of the two binding moieties in the *anti*-isomer of (*E*)-**1** is more appropriate for ditopic coordination with **A10** in comparison with the situation in the *syn*-isomer.

The irradiation of an acetonitrile solution of (*E*)-**1** with light at 365 nm causes the reversible *E*–*Z* isomerization reaction.[30] According to the NMR data after 45 min irradiation of (*E*)-**1**, a photostationary mixture contains isomers *E* : *Z* in a 2 : 1 ratio. Under the same conditions, complex [(*E*)-**1**]·**A2** forms the photostationary mixture with an *E* : *Z* isomer ratio of 1.8 : 1. The monotopic complexation in [(*E*)-**1**]·**A2** with participation of the crown ether does not substantially influence the photoisomerization reaction. After irradiation of [(*E*)-**1**]·**A10**, an *E* : *Z* isomer ratio equal to 0.7 : 1 was found. The ditopic complex [(*E*)-**1**]·**A10** possesses the more rigid structure which prevents the occurrence of the *E*–*Z* isomerization reaction.

The chemical shifts of the proton signals in the NMR spectra of complexes [(*Z*)-**1**]·**A2** and [(*Z*)-**1**]·**A10** are presented in Table 2. We found similar magnitudes of all proton signal shifts for both complexes. The situation is different in comparison with that found for complexes [(*E*)-**1**]·**A2** and [(*E*)-**1**]·**A10**. The phenomenon could be connected with the fact that *E*–*Z* isomerization leads to the destruction of coordination between the carboxy group and the heterocyclic residue in complex [(*E*)-**1**]·**A10**. The structure of the formed complex [(*Z*)-**1**]·**A10** becomes similar to the structure of complex [(*Z*)-**1**]·**A2** (Scheme 6).

Conclusion

The data obtained from UV, NMR spectroscopy, time-resolved data and quantum-chemical calculations showed that complex formation of the crown-containing 2-styrylbenzothiazole with amino acids containing 2 or 10 methylene groups between the ammonium and carboxylic fragments occurs through mono- and ditopic coordination. The coordination of the ammonium group with the crown ether moiety is stronger in comparison with binding of the proton of the carboxylic group with the N atom of the heterocyclic residue. The ditopic complex formation prevents the photoinduced reaction of *E*–*Z* isomerization. The isomerization leads to the destruction of the hydrogen bond between the carboxylic proton and the heterocyclic residue.

Knowledge concerning the interactions between synthetic molecules with amino acids, polypeptides and nucleic acids is important for the construction of optical sensors, markers and especially in the design and development of nucleic acid binding and cleaving agents, which may be used as structural probes or therapeutic agents.

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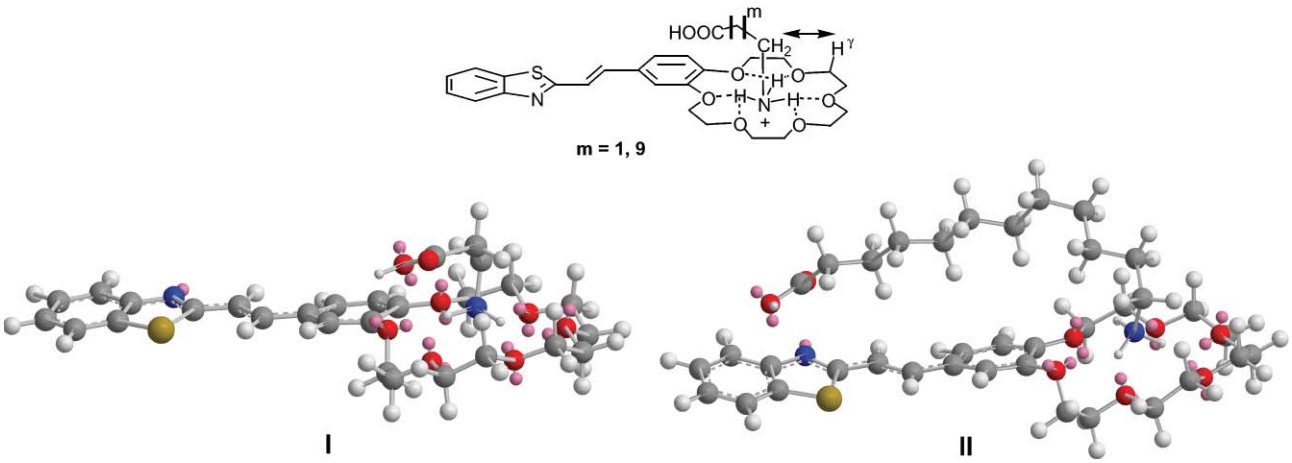
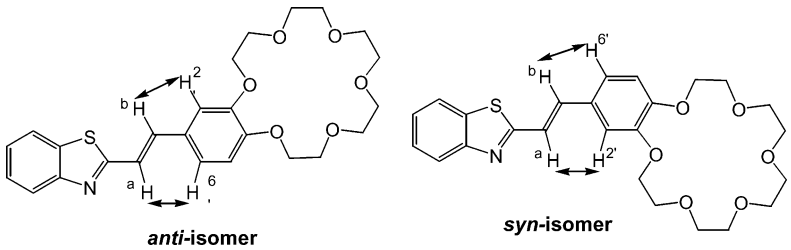
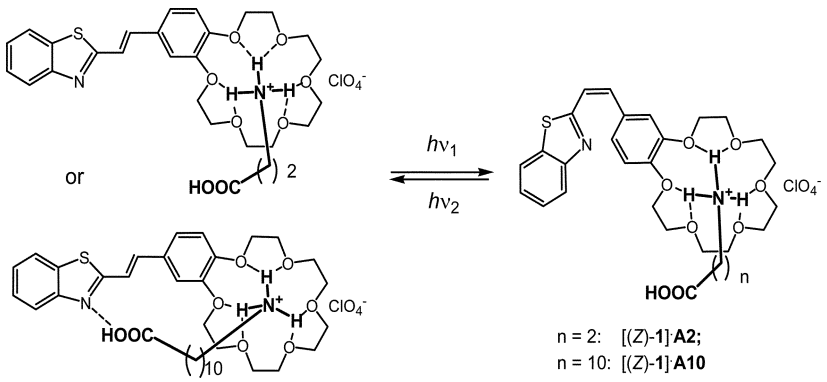


Scheme 4



Scheme 5



Scheme 6

Experimental

Materials

2-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-benzohexaoxa-cyclooctadecan-18-yl)ethenyl]-1,3-benzothiazole (**1**) was synthesized according to a known procedure.[27,28]

β-Alanine and 11-aminoundecanoic acid are commercially available. For synthesis of amino acid perchlorates $HClO_4$ was added to the suspension of β-alanine or 11-aminoundecanoic acid in CH_3CN in the ratio $HClO_4$: amino acid = 0.5 : 1. Insoluble excess of amino acid was filtered off, the remaining solvent containing amino acid perchlorates was evaporated to dryness.

Synthesis and characterization

NMR study. ^1H NMR spectra were recorded on a Bruker DRX500 instrument (500.13 MHz) and a Bruker DPX400 instrument (400.16 MHz) by means of a 5 mm direct QNP 1H/X probe with gradient capabilities. The NMR samples were prepared in CD_3CN, this solvent being used as the internal reference at 1.96 ppm for ^1H; 2D homonuclear NOESY (mixing time 500 ms) spectra were used to assign the proton signals.

Synthesis of the complex of (*E*)-1 with perchlorates of amino acids A2, A10. (*E*)-**1** (2.4 mg, 0.005 mmol) and perchlorate of β-alanine (**A2**) (0.9 mg, 0.005 mmol) or 11-aminoundecanoic acid (**A10**) (1.5 mg, 0.005 mmol) were dissolved in 0.6 ml CD_3CN under

red light. The resulting [(*E*)-**1**]·**A2** and [(*E*)-**1**]·**A10** were used for NMR investigation (see Table 2).

The irradiation of (*E*)-1 and its complexes with amino acids. The solution of (*E*)-**1** (2.4 mg, 0.005 mmol) or [(*E*)-**1**]·**A2**, [(*E*)-**1**]·**A10** in 0.6 ml CD_3CN was irradiated with 365 nm light during 45 min. The resulting mixture was used for NMR investigation (see Table 2).

Spectroscopic measurements

UV-Vis spectra. Preparation of solutions and all experiments were carried out under red light. The absorption spectrum measurements were provided using Varian-Cary (Fig. 1, 2) or Specord-M40 (titration experiments) spectrophotometers.

Equilibrium constant determination. Complex formation of (*E*)-**1** with **A2**, **A10**, $HClO_4$ or NH_4ClO_4 in acetonitrile at 20 ± 1 °C was studied by spectrophotometric titration. The ratio of **1** to **A2**, **A10**, $HClO_4$ or NH_4ClO_4 was varied by adding aliquots of a solution containing known (0.00004 M) concentrations of **1** and of the corresponding salt or acid to a solution of **1** alone of the same concentration. The absorption spectrum of each solution was recorded with a Specord-M40 spectrophotometer and the stability constants of the complexes were determined using the "Hyperquad" program,[31] designed for use in connection with studies of chemical equilibrium in solution from data obtained on potentiometric and/or spectrophotometric titrations. The program uses a least-squares approach. The following equilibrium was studied:

$$L + M = LM \{K_1 = [LM]/([L][M])\}$$

where M = **A2**, **A10**, H^+ or NH_4^+.

Time resolved fluorescence studies. The fluorescence excitation light pulses were obtained by frequency doubling and tripling of a Ti : sapphire femtosecond laser system (Femtopower Compact Pro) output. All excited state lifetimes were obtained using depolarized excitation light. The highest pulse energies used to excite fluorescence did not exceed 100 nJ and the average power of excitation beam was 0.1 mW at a pulse repetition rate of 1 kHz focussed into a spot with a diameter of 0.1 mm in the 10 mm long fused silica cell. The fluorescence emitted in the forward direction was collected by reflective optics and focussed with a spherical mirror onto the input slit of a spectrograph (Chromex 250) coupled to a streak camera (Hamamatsu 5680 equipped with a fast single sweep unit M5676, temporal resolution 2 ps). The convolution of a rectangular streak camera slit in the sweep range of 250 ps with an electronic jitter of the streak camera trigger pulse provided a Gaussian (over 4 decades) temporal apparatus function with a FWHM of ~20 ps. The fluorescence kinetics were later fitted by using the Levenberg–Marquardt least-squares curve-fitting method using a solution of the differential equation describing the evolution in time of a single excited state and neglecting depopulation of the ground state:

$$\frac{dI(t)}{dt} = \text{Gauss}\,(t0,\ \Delta t,\ A) - \frac{I(t)}{\tau}$$

where $I(t)$ is the fluorescence intensity, Gauss is the Gaussian profile of the excitation pulse, where $t0$ stands for the excitation pulse arrival delay, Δt is the excitation pulse width, and A is the amplitude. The parameter τ represents the lifetime of the excited state. The initial condition for the equation is $I(-\infty) = 0$. Typically, the fit shows a χ^2 value better than 10^{-4} and a correlation coefficient $R > 0.999$. The uncertainty of the lifetime was better than 0.1 ps. Routinely, the fluorescence accumulation time in our measurements did not exceed 90 s.

The fluorescence anisotropy was measured using a linearly polarized excitation pulse. The fluorescence polarization, before sending to the spectrograph, was analysed using a thin film polarizer. The fluorescence anisotropy decay was obtained using the following formula:

$$r(t) = \frac{I_{par}(t) - I_{perp}(t)}{I_{par}(t) + 2I_{perp}(t)}$$

where $I_{par}(t)$ is the fluorescence decay in parallel polarization with respect to the excitation and $I_{perp}(t)$ is the fluorescence decay in perpendicular polarization. The high dynamic range of fluorescence intensity measurements made possible the determination of molecular reorientation times up to 350 ps for the studied molecular systems. The uncertainty of these measurements was better than 3 ps for the fastest reorientation time of 47 ps and 10 ps for the slower ones.

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