Stereospecific [2+2] photocycloaddition in a pseudodimeric complex between *N*-ammoniopropylstyrylpyridine and 18-crown-6-containing styrylpyridine

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A quaternary 4-styrylpyridinium salt having the *N*-ammoniopropyl substituent forms a pseudodimeric head-to-tail complex with neutral 18-crown-6-containing 4-styrylpyridine in MeCN through H-bonding. This complex undergoes stereospecific [2+2] photocycloaddition due to preorganization of the ethylene bonds in the *syn*-arranged chromophoric fragments of the components. The structure of the *rctt*-isomer of the cyclobutane derivative obtained was established by NMR spectroscopy and X-ray diffraction analysis.

Key words: styryl dyes, styrylheterocycles, crown ethers, ammonium ions, complexation, [2+2] photocycloaddition, cyclobutanes, X-ray diffraction study.

The self-assembly of organic and bioorganic molecules into supramolecular assemblies in solutions through relative weak H-bonds is widely known.[1,2] At the same time, the self-assembly of the photosensitive compounds involving hydrogen bonding is poorly studied, while it is of great interest due to possible photochemical reactions within the supramolecular assemblies formed that are not observed under other conditions. Crown-containing unsaturated compounds undergo self-assembly in the presence of different cations.[3] These photosensitive compounds containing the C=C bond are subject to *E*—*Z*-isomerization, electrocyclization, and [2+2] photocycloaddition (PCA). We suggested that a versatile approach to the self-assembly of crown-containing unsaturated compounds can make use of the primary ammonium groups incorporated into the unsaturated compound itself or a photoinsensitive substrate. Such type of self-assembly may be illustrated by the example of the following supramolecular structures. Bis(18-crown-6)stilbene forms extremely stable donor—acceptor complexes with the *N*,*N*´-di(ammonioalkyl) derivatives of viologen analogs that can serve as fluorescent molecular sensors for the alkaline-earth metal cations.[4,5] 18-Crown-6-containing bis-styryl dyes behave as selective optical molecular sensors for diammonioalkane ions;[6] the stereospecific intramolecular PCA reaction can proceed in the pseudosandwich head-to-head complexes of dyes that formed to afford a single isomer of a cyclobutane derivative.[7] Due to the H-bonding between the ammonium groups and the crown-ether fragments, the crown-containing styryl dyes having the *N*-ammonioalkyl substituent in the heterocyclic residue form stable head-to-tail dimeric complexes wherein efficient stereospecific autophotocycloaddition[8] occurs. Alternatively, on exposure to light, the formation of a relatively stable cation-"capped" complex occurs in the *Z*-form of a dye with intramolecular coordination of the ammonium group by the crown-ether fragment.[9] The above-mentioned phototransformations result in considerable hypsochromic shifts in the absorption spectra of the unsaturated compounds, which can be used for the design of the systems for optical recording of information.

Recently, we have shown[10] that two yellow styryl dyes of the 4-pyridyl series, one of which contained the *N*-ammoniopropyl substituent ((*E*)-**1**) and the second one contained the fragment of 18-crown-6 ((*E*)-**2**), formed a sufficiently stable pseudodimeric complex ($\log K = 3.52$) in MeCN. Due to cooperative action of the binding of the NH_3^+ group of dye **1** with the crown-ether fragment of dye **2** and of the stacking interaction between the planar conjugated fragments, the stereospecific PCA reaction proceeds in complex (*E*)-**1** • (*E*)-**2** to form a single isomer of the cyclobutane derivative *rctt*-**3** (Scheme 1). The photoreaction occurs under exposure to visible light due to the effective intramolecular charge transfer in dyes (*E*)-**1** and

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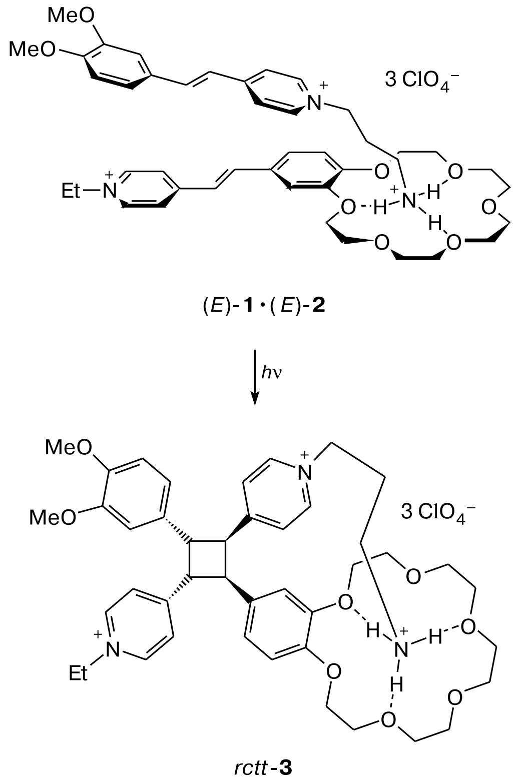
(*E*)-**2** responsible for considerable absorption in the visible region ($\lambda_{max} \approx 400$ nm). Stereospecifity is achieved by the head-to-tail *syn*-assembly of the chromophoric fragments disposed one above the other in the pseudodimeric complex (*E*)-**1** • (*E*)-**2**, which favors the approach and parallel orientation of their ethylene bonds.

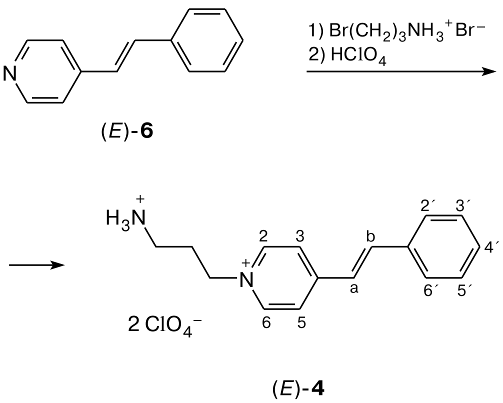
Scheme 1



We assumed that efficient self-assembly in a pseudodimeric complex occurs in the case of the components having different substituents in the fragments that are remote from the binding site built in the host—guest mode. The nature of these substituents strongly influences the spectral characteristics of the compounds. Consequently, the PCA reaction can be induced by light of different wavelength. For example, PCA can be carried out on exposure to UV light in cases where the ammonium and crown-containing unsaturated components are colorless compounds. Such systems are of interest for the design of phototropic systems for information recording at the molecular level. Here we present the investigation into the self-assembly, structural features, and photochemical properties of a pseudodimeric complex of unsubstituted styryl dye (*E*)-**4** with 4-styrylpyridine (*E*)-**5**, the former containing the terminal NH_3^+ group in the *N*-substituent and the latter containing the fragment of 18-crown-6. The stereochemistry of the photocycloadduct in this complex, *viz*., 1,2,3,4-tetrasubstituted cyclobutane, was determined by ^{1}H NMR spectroscopy and additionally confirmed by the X-ray diffraction data.

The synthesis of a styrylpyridinium quaternary salt with *N*-ammoniopropyl substituent (*E*)-**4** was carried out by quaternization of styrylpyridine (*E*)-**6** (see Ref. 11) with 3-bromopropylammonium bromide followed by the anion exchange (bromide by perchlorate) upon treatment with perchloric acid (Scheme 2). The ethylenic bond in compound **4** has the *E*-configuration according to the value of $J_{CH=CH}$ equal to 16.2 Hz. The synthesis of 18-crown-6-containing styrylpyridine (*E*)-**5** have been described earlier.[12]

Scheme 2



In MeCN, styrylpyridines (*E*)-**4** and (*E*)-**5** demonstrate intense absorption in the near-UV region with λ_{max} at 349 and 334 nm, respectively (Fig. 1, curves *1* and *2*). Such absorption shift, as compared with (*E*)-**1** and (*E*)-**2**, is caused undoubtedly by the absence of electron-donating substituents in the benzene ring of (*E*)-**4** in conjugation with chromophore, and by the presence of the uncharged pyridine residue in (*E*)-**5**, which complicates the intramolecular charge transfer from the benzene fragment to the pyridine fragment of styrylpyridine, which is responsible for the emergence of the long-wave absorption band. UV irradiation of solutions of free dyes **4** and **5** only resulted in their reversible *E*—*Z*-isomerization to a photo-steady-state mixture of *trans*- and *cis*-isomers and, on long-term exposure, in the formation of negligible amounts of the photodegradation products (NMR monitoring). The absorption of a solution of a 1 : 1 mixture of compounds (*E*)-**4** and (*E*)-**5** at their concentrations of $5 \cdot 10^{-5}$ mol L^{-1} differs insignificantly from the arithmetical sum of the absorption spectra of the individual components, which suggests their weak interaction under these conditions.

The ^{1}H NMR study of the solution of a 1 : 1 mixture of (*E*)-**4** and (*E*)-**5** in $MeCN-d_3$ at higher concentrations

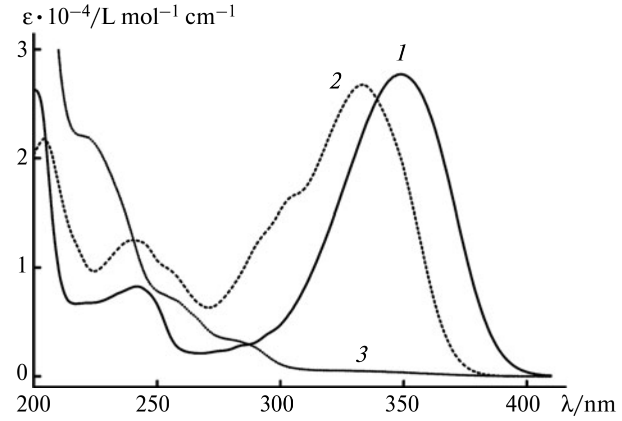


Fig. 1. The absorption spectra of styrylpyridines (*E*)-**4** (*1*), (*E*)-**5** (*2*), and the cyclobutane derivative *rctt*-**7** (*3*) ($C = 5 \cdot 10^{-5}$ mol L^{-1}, MeCN).

($\sim 1 \cdot 10^{-3}$ mol L^{-1}) showed noticeable change in the chemical shifts of the majority of the protons of both components compared to free dyes (*E*)-**4**, (*E*)-**5**, which is analogous to the effects found previously[10] in the system (*E*)-**1**—(*E*)-**2**. For example, the signals for the methylene groups of the crown-ether fragment of compound (*E*)-**5** are downfield shifted (up to $\Delta\delta_H$ 0.09) upon mixing with dye (*E*)-**4**, which provides evidence of the binding of the 18-crown-6 fragment with the NH_3^+ group. This fact is caused by the electron-accepting influence of this group in the complex. Conversely, the signals for the ethylenic protons and most of the aromatic protons of both components are upfield shifted (up to $\Delta\delta_H$ −0.19) (Fig. 2). Such spectral behavior suggests that the chromophoric fragments in complex (*E*)-**4** • (*E*)-**5** that formed are predominantly stacked due to the intermolecular stacking interactions of the conjugated systems (Scheme 3).

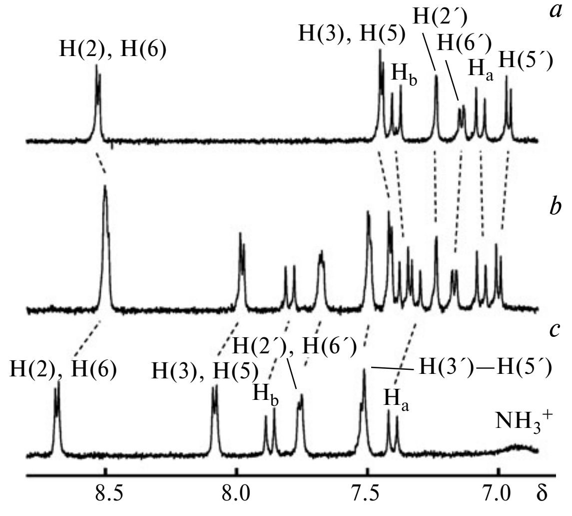
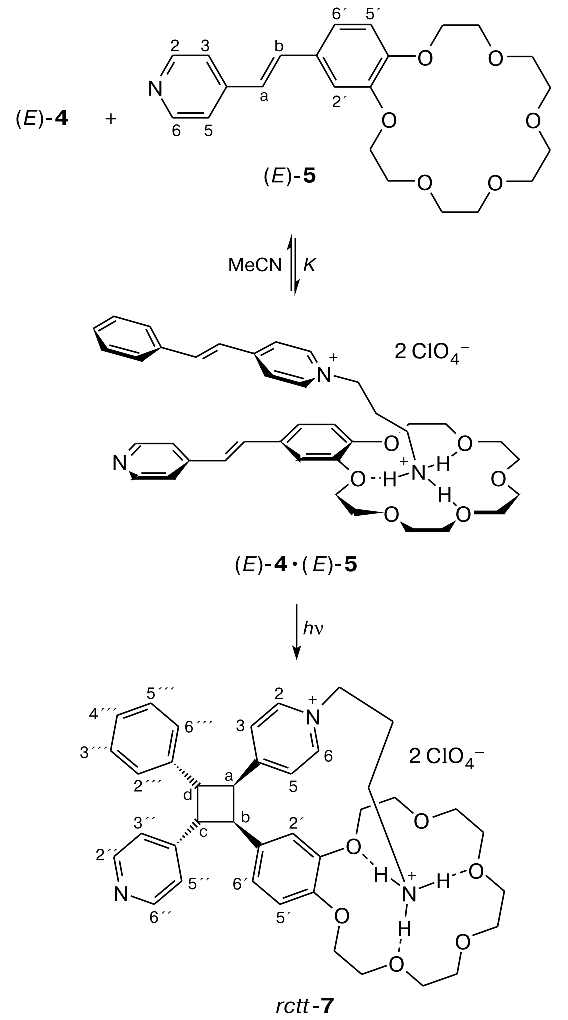


Fig. 2. The ^{1}H NMR spectra (the region of aromatic protons) for compound (*E*)-**5** (*a*), the equimolar mixture of (*E*)-**4** and (*E*)-**5** (*b*), and compound (*E*)-**4** (*c*) ($C = 1 \cdot 10^{-3}$ mol L^{-1}, MeCN-d$_3$, 30 °C).

Scheme 3



By means of ^{1}H NMR titration, we determined the value of the stability constant (log*K*) for pseudodimeric complex (*E*)-**4** • (*E*)-**5**, which is equal to 3.47±0.05. This value differs little from the value of the stability constant for complex (*E*)-**1** • (*E*)-**2** (*vide supra*), which suggests the crucial contribution of the H-bonding between the ammonium group and the crown fragment to the stability of such supramolecular systems and, conversely, suggests weak influence of the stacking interactions of the chromophoric fragments of the components. Complex (*E*)-**4** • (*E*)-**5** was isolated as a solid by slow crystallization of a solution of an equimolar mixture of components; its stoichiometry (1 : 1) was confirmed by the data from ^{1}H NMR spectroscopy and elemental analysis.

The UV irradiation of a solution of a mixture of compounds **4** and **5** led to a significant decrease in the long-wave absorption intensity. The ^{1}H NMR spectrum of photolyzate displays, along with the signals for the minor *E*- and *Z*-isomers of the starting compounds, a set of signals suggesting the formation of a new product. The absorption spectrum of this photoproduct isolated by crystallization is shown in Fig. 1 (curve *3*). The absence of the absorption in the long-wave spectral region evidences violation of conjugation in the photoproduct.

The structure of the photoproduct was established based on the analysis of the COSY and NOESY homo- and heteronuclear spectra. The distinctive feature of these spectra is the disapperance of the ethylenic proton signals in the low-field region and the appearance of four new one-proton signals in the ^{1}H NMR spectrum in the region of δ 4.7—4.9 (Fig. 3). The positions and shapes of these signals (all doublets of doublets) suggest the formation of a nonsymmetric cyclobutane derivative *rctt*-**7** (an ABCD spin system with $^3J_{cis\text{-}H_a,H_b}$ = 10.0 Hz, $^3J_{trans\text{-}H_b,H_c}$ = 7.5 Hz, $^3J_{cis\text{-}H_c,H_d}$ = 10.1 Hz, and $^3J_{trans\text{-}H_d,H_a}$ = 8.0 Hz), which resulted from PCA in the pseudodimeric complex (*E*)-**4** • (*E*)-**5** (see Scheme 3). The ^{13}C NMR spectrum of the photoadduct also contains four new signals in the typical region of δ 42—47, which correspond to the carbon atoms of the nonsymmetric cyclobutane ring (see Experimental). Note that the charachteristics of the signals for the cyclobutane ring in the isomer **7** obtained are very close to analogous signals of *rctt*-**3** (see Ref. 10). As in the system (*E*)-**1**—(*E*)-**2**, the head-to-tail *syn*-arrangement of the conjugated fragments of compounds (*E*)-**4** and (*E*)-**5** pre-conditions the chromophoric fragments of the components for the PCA reaction to form a single isomer of the cyclobutane derivative among 16 theoretically possible. Thus, the cooperative effect of two types of weak intermolecular interactions in the stabilization of the supramolecular complex (*E*)-**4** • (*E*)-**5**, *viz.*, complexation of the NH_3^+ group with the crown-ether fragment and stacking interactions of the planar conjugated fragments, provides superior stereospecifity of the photoprocess.

We succeeded in determining the structure of the cyclobutane derivative *rctt*-**7** that formed by X-ray diffraction analysis. The structure of the principal component of the crystal is shown in Fig. 4. The pyridine residues of two neighboring cyclobutane molecules linked through the symmetry center are joined by the H-bond $C_5N(3)...H(3N)...N(3A)C_5$ to form the protonated pair. The isotropic refinement of the H(3N) atom shows that it is formally localized at the crystal symmetry center, although its true position should obviously be shifted with equal probability towards either the N(3) or N(3A) atom, since the distance N(3)...H(3N), equal to 1.326(4) Å, is too large for the ordinary bond $H—N^+_{Py}$. Thus, the crystal of the cyclobutane derivative studied is a protonated form of *rctt*-**7** • $0.5HClO_4$, which is probably formed as a result of partial dissociation of the ammonium groups in other molecules of *rctt*-**7**. Two perchlorate anions, $Cl(1)O_4^-$ and $Cl(2)O_4^-$, have complete populations of the positions; the third anion, $Cl(3)O_4^-$, is disordered around the crystal symmetry center, which is related to the other system of centers, and has population of the positions 0.50. In addition to the principal component, the solvate molecules of benzene and water were found in the crystalline lattice. The water molecule O(1W) forms the relative weak H-bond with the oxygen atom of the perchlorate anion $O(1W)—H(1W)...O(23)—Cl(2)O_3^-$: the distance H(1W)...O(23) is 2.00(4) Å, the angle at the hydrogen atom is ~166°. The second hydrogen atom of the water molecule O(1W) is not located. Apparently, it can be directed towards the O(11) or O(13) atom of the $Cl(1)O_4^-$ anion by forming weak H-bonds with it: the distances O(1W)...O(11) and O(1W)...O(13) are equal to 3.16 and 2.98 Å, respectively.

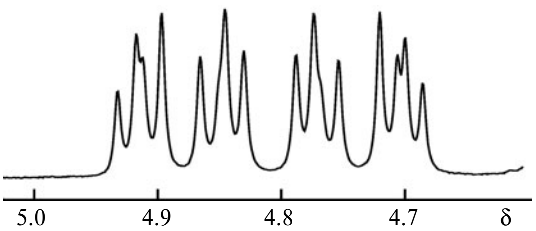


Fig. 3. The ^{1}H NMR spectrum in the region of cyclobutane protons of the derivative *rctt*-**7** (DMSO-d$_6$, 30 °C).

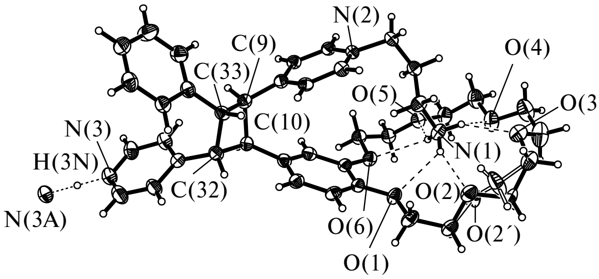


Fig. 4. The structure of the principal crystal component of *rctt*-**7** • $0.5HClO_4$ • C_6H_6 • H_2O. The nonhydrogen atoms are depicted as thermal ellipsoids with 40% probability. The H-bonds are shown as dashed lines. The atom N(3A) was obtained through symmetry operation.

The arrangement of four substituents in the cyclobutane ring of compound **7** directly confirms the conclusions drawn on the basis of the NMR spectral data. The $N(1)H_3^+$ group in the dication forms the intramolecular coordination with the fragment of 18-crown-6 of the neighboring *cis*-subsituent through three bifurcate H-bonds $N^+—H...O$; the corresponding distances H...O being in the range of 2.05(5)—2.34(4) Å, the angles at the H atoms being 123—155°. Due to the "contracting" effect of the ammonium group bound in the complex, the dihedral angle between the planes of the pyridine ring $N(2)C_5$ and the benzene ring of the benzocrown fragment is 35°, whereas the angle between the planes of the pyridine ring $N(3)C_5$ and the phenyl substituent *cis*-oriented toward $N(3)C_5$ is 63°. The carbon-carbon bond lengths in the cyclobutane ring vary in the range of 1.543(5)—1.594(6) Å and the $C_{Ar/Py}$—C(cyclobutane) bond lengths vary in the range of 1.498(5)—1.513(6) Å. The endocyclic bond angles C(9)—C(10)—C(32)—C(33) in the cyclobutane ring are in the range of 88.4(3)—90.2(3)°, the torsion angles in this ring are from −14 to 14°, *i.e.*, the cyclobutane ring has a nonplanar conformation. This fact distinguishes the nonsymmetric isomer of *rctt*-**7** from the centrosymmetric 1,2,3,4-tetrasubstituted *rctt*-isomers of the cyclobutane derivatives obtained by us previously[8,12,13] by the solid-phase autophotocycloaddition reaction in the styryl dyes and neutral styrylheterocycles. In the crystal, the cyclobutane rings of the centrosymmetric isomers have the ideal planar conformation, while in solution their conformational mobility is apparently increased.

Thus, we have established that the styryl dye containing the *N*-ammoniopropyl substituent can form a stable head-to-tail pseudodimeric complex with the neutral 18-crown-6-containing 4-styrylpyridine in solution due to the binding of the ammonium group with the crown fragment through H-bonding. In the complex, the ethylenic bonds of the molecules are pulled together due to the advantageous stacking interactions caused by the secondary orbital p_z-interactions of the conjugated fragments. *syn*-Orientation of the conjugated fragments in the complex results in the stereospecific [2+2] photocycloaddition reaction to form the single *rctt*-isomer of the cyclobutane derivative the structure of which was determined by X-ray diffraction analysis. Such pseudodimeric complexes can be used for creation of the phototropic systems for information recording and storage at the molecular level.

Experimental

Melting points (uncorrected) were measured in a capillary on a Mel-Temp II instrument. Elemental analysis was performed at the laboratory of microanalysis of the A. N. Nesmeyanov Institute of Ogranoelement Compounds of the Russian Academy of Sciences (Moscow). ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 (500.13 and 125.76 MHz, respectively) spectrometer in DMSO-d_6 and MeCN-d_3 at 25—30 °C using the solvent signal as the internal standard (δ_H 2.50 and 1.96, respectively, δ_C 39.43 for DMSO-d_6). Chemical shifts were measured with the accuracy of 0.01 ppm and the spin-spin coupling constants were measured with the accuracy of 0.1 Hz. Two-dimensional ^1H—^1H COSY and NOESY homonuclear spectra and ^1H—^{13}C COSY (HSQC and HMBC) heteronuclear spectra were used for the assignment of the signals for the hydrogen and carbon atoms. 2D Experiments were performed using default parameters included in the software package of the Bruker company. UV spectra were recored on a Shimadzu UV-3101PC spectrophotometer in the region of 200—600 nm with a spacing of 0.5 nm (MeCN, 1 cm quartz cell, room temperature).

3-Bromopropylammonium bromide and 70% perchloric acid (Aldrich) were used without additional purification. 4-[(*E*)-1-Phenyl-2-vinyl]pyridine ((*E*)-**6**)[11] and 4-[(*E*)-1-phenyl-2-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecyn-18-yl)]pyridine ((*E*)-**5**)[12] were prepared according to known procedures.

1-(3-Ammoniopropyl)-4-[(*E*)-styryl]pyridinium diperchlorate ((*E*)-4). A mixture of 4-styrylpyridine (*E*)-**6** (0.23 g, 1.25 mmol) and 3-bromopropylammonium bromide (0.82 g, 3.75 mmol) was heated in the dark for 4 h at 150 °C (oil bath), dissolved with heating in anhydrous EtOH (3 mL) and then cooled to 5 °C. The precipitate was filtered off, washed with chloroform (3 mL) and dried in air. The dibromide salt of the dye (0.23 g, 0.57 mmol) was obtained as a pale-yellow powder. The dibromide salt was dissolved with heating in anhydrous EtOH (4 mL) and 70% perchloric acid (0.20 mL, 2.3 mmol) was added. The mixture was cooled to 5 °C. The precipitate that formed was filtered off, washed with cold anhydrous EtOH (3 mL) and dried *in vacuo* at 80 °C. Compound (*E*)-**4** (0.18 g) was obtained in the total yield of 34% as pale-yellow crystals. M.p. 232—234 °C (decomp.). Found (%): C, 43.80; H, 4.45; N, 6.37. $C_{16}H_{20}Cl_2N_2O_8$. Calculated (%): C, 43.75; H, 4.59; N, 6.38. ^1H NMR (25 °C, DMSO-d_6), δ: 2.20 (m, 2 H, $C\underline{H}_2CH_2N$); 2.86 (m, 2 H, $C\underline{H}_2NH_3$); 4.58 (t, 2 H, CH_2N, *J* = 6.8 Hz); 7.47 (t, 1 H, H(4´), *J* = 7.0 Hz); 7.51 (t, 2 H, H(3´), H(5´), *J* = 7.0 Hz); 7.56 (d, 1 H, $CH{=}C\underline{H}Py$, *J* = 16.2 Hz); 7.77 (d, 2 H, H(2´), H(6´), *J* = 7.0 Hz); 7.78 (br.s, 3 H, NH_3); 8.05 (d, 1 H, $C\underline{H}{=}CHPy$, *J* = 16.2 Hz); 8.30 (d, 2 H, H(3), H(5), *J* = 6.8 Hz); 8.96 (d, 2 H, H(2), H(6), *J* = 6.8 Hz). ^{13}C NMR (30 °C, DMSO-d_6), δ: 28.39 ($\underline{C}H_2CH_2N$); 35.61 (CH_2NH_3); 56.69 (CH_2N); 123.18 ($CH{=}\underline{C}HPy$); 123.98 (C(3), C(5)); 128.05 (C(2´), C(6´)); 129.01 (C(3´), C(5´)); 130.37 (C(4´)); 134.99 (C(1´)); 140.94 ($\underline{C}H{=}CHPy$); 144.22 (C(2), C(6)); 153.02 (C(4)).

Complex (*E*)-4 • (*E*)-5. A solution of dye (*E*)-**4** (10.0 mg, 22.7 mol) and compound (*E*)-**5** (10.0 mg, 24.0 mol) in MeCN (~5 mL) was slowly saturated with vapor of a ~1 : 1 mixture of benzene and dioxane at room temperature in the dark until a precipitate formed, which was separated by decantation and dried *in vacuo* at 80 °C. Complex (*E*)-**4** • (*E*)-**5** (8.0 mg, 41%) was obtained as a pale-yellow powder. M.p. 168—170 °C. Found (%): C, 54.21; H, 5.59; N, 4.48. $C_{39}H_{49}Cl_2N_3O_{14} \cdot 0.5H_2O$. Calculated (%): C, 54.23; H, 5.84; N, 4.87.

1-(3-Ammoniopropyl)-*r*-4-[*c*-2-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecyn-18-yl)-*t*-4-phenyl-*t*-3-(4-pyridyl)cyclobutyl]pyridinium diperchlorate (*rctt*-7). A solution of dye (*E*)-**4** (7.7 mg, 17.5 mol) and compound (*E*)-**5** (8.0 mg, 19.3 mol) in MeCN (15 mL) was irradiated with stirring in a quartz cell (5 cm × 4.5 cm × 1 cm) from the side of its largest face by the light of L8253 Xe lamp (Hamamatsu, peak power, A9616-05 light filter (transmission at 320—420 nm), the light source distance is 10 cm). According to the ^1H NMR spectral data, the photolyzate contained compounds (*E*)-**4**, (*Z*)-**4**, (*E*)-**5**, (*Z*)-**5**, and *rctt*-**7** in molar ratios of 2.2 : 2.9 : 1 : 5.6 : 3.3 and 0.3 : 0.9 : 1 : 1.6 : 8.0 upon irradiation of the solution for 2 and 10 h, respectively. The reaction mixture was concentrated to ~5 mL and slowly saturated with vapor of a ~2 : 1 mixture of benzene and dioxane at room temperature until white crystals formed, which were separated by decantation and dried *in vacuo* at 80 °C. Derivative *rctt*-**7** was obtained in a yield of 12.0 mg (80%). M.p. 224—227 °C. Found (%): C, 53.83; H, 5.98; N, 4.86. $C_{39}H_{49}Cl_2N_3O_{14} \cdot H_2O$. Calculated (%): C, 53.67; H, 5.89; N, 4.82. ^1H NMR (22 °C, DMSO-d_6), δ: 2.10 (m, 2 H, $C\underline{H}_2CH_2N$); 2.26 (m, 1 H, $C\underline{H}H'NH_3$); 2.37 (m, 1 H, $CH\underline{H}'NH_3$); 3.63 (s, 4 H, 2 CH_2O); 3.65, 3.71 (both m, 4 H each, 4 CH_2O);

3.78 (m, 4 H, 2 C$\underline{\mathrm{H}}_2$CH$_2$OAr′); 3.92 (m, 2 H, 3′-C$\underline{\mathrm{H}}_2$OAr′); 4.08 (m, 2 H, 4′-C$\underline{\mathrm{H}}_2$OAr′); 4.53 (t, 2 H, CH$_2$N, J = 5.9 Hz); 4.66 (dd, 1 H, C$\underline{\mathrm{H}}$Py″, J = 10.1 Hz, J = 7.5 Hz); 4.72 (dd, 1 H, C$\underline{\mathrm{H}}$Ar′, J = 10.0 Hz, J = 7.5 Hz); 4.83 (dd, 1 H, C$\underline{\mathrm{H}}$Py, J = 10.0 Hz, J = 8.0 Hz); 4.91 (dd, 1 H, C$\underline{\mathrm{H}}$Ar‴, J = 10.1 Hz, J = 8.0 Hz); 6.50 (d, 1 H, H(2′), J = 1.4 Hz); 6.93 (d, 1 H, H(5′), J = 8.4 Hz); 7.06 (dd, 1 H, H(6′), J = 8.4 Hz, J = 1.4 Hz); 7.10 (br.t, 1 H, H(4‴), J = 7.1 Hz); 7.16 (br.s, 3 H, NH$_3$); 7.20 (br.t, 2 H, H(3‴), H(5‴), J = 7.6 Hz); 7.22 (d, 2 H, H(3″), H(5″), J = 5.0 Hz); 7.23 (br.d, 2 H, H(2‴), H(6‴), J = 7.7 Hz); 7.95 (d, 2 H, H(3), H(5), J = 6.6 Hz); 8.35 (d, 2 H, H(2″), H(6″), J = 5.0 Hz); 8.78 (d, 2 H, H(2), H(6), J = 6.6 Hz). ^{13}C NMR (30 °C, DMSO-d$_6$), δ: 28.11 ($\underline{\mathrm{C}}$H$_2$CH$_2$N); 35.64 (CH$_2$NH$_3$); 42.75 ($\underline{\mathrm{C}}$HPy); 43.60 ($\underline{\mathrm{C}}$HAr′); 46.74 ($\underline{\mathrm{C}}$HPy″); 46.91 ($\underline{\mathrm{C}}$HAr‴); 57.08 (CH$_2$N); 67.06 (4′-$\underline{\mathrm{C}}$H$_2$OAr′); 67.16 (3′-$\underline{\mathrm{C}}$H$_2$OAr′); 68.24 ($\underline{\mathrm{C}}$H$_2$CH$_2$OAr′); 68.41 ($\underline{\mathrm{C}}$H$_2$CH$_2$OAr′); 68.53 (2 CH$_2$O); 69.12 (CH$_2$O); 69.19 (CH$_2$O); 69.56 (CH$_2$O); 69.69 (CH$_2$O); 111.60 (C(5′)); 111.66 (C(2′)); 120.35 (C(6′)); 123.58 (C(3″), C(5″)); 126.36 (C(4‴)); 127.23 (C(3), C(5)); 127.84 (C(2‴), C(6‴)); 127.96 (C(3‴), C(5‴)); 131.03 (C(1′)); 138.60 (C(1‴)); 143.06 (C(2), C(6)); 145.46 (C(4′)); 146.29 (C(3′)); 148.16 (C(2″), C(6″)); 150.01 (C(4″)); 161.06 (C(4)).

^{1}H NMR titration was performed on a Bruker DRX-500 spectrometer in MeCN-d$_3$ at 30 °C. In the course of titration, the concentration of compound (*E*)-**5** was maintained at ~$1 \cdot 10^{-3}$ mol L^{-1} and the concentration of compound (*E*)-**4** ranged from 0 to $3 \cdot 10^{-3}$ mol L^{-1}. The stability constant for the complex was measured by the change in the signal positions for the protons of the molecule of (*E*)-**5** depending on the ratio C_5/C_4. The $\Delta\delta_{\mathrm{H}}$ values were measured with the accuracy of 0.001 ppm. The HYPNMR program was used for calculation of the constant.[14]

X-ray diffraction study. The colorless single crystals of the cyclobutane derivative *rctt*-**7** • 0.5HClO$_4$ were obtained by slow saturation of an acetonitrile solution of *rctt*-**7** with vapor of a mixture of benzene and dioxane at room temperature. The single crystal of the complex was placed on a Bruker SMART-CCD diffractometer under the stream of cold nitrogen (T = 120.0(2) K), where the measurements of the unit cell parameters and experimental intensities of reflections at the Mo-Kα radiation (λ = 0.71073 Å, graphite monochromator, ω-scanning technique) were performed. The data interpretation was performed using the SAINT program.[15] The structure was solved by direct methods and refined by the least-squares method based on F^2 in the anisotropic approximation for all nonhydrogen atoms, except for the oxygen atoms of the anion Cl(3)O$_4^-$. The position of this anion is strongly disordered, therefore we succeeded in determining only two its rotamers with the 0.56 : 0.44 ratio of the populations of the positions (rotation around the center of mass). Note that numerous weak peaks of the residual electron density were observed around the Cl(3) atom in the differential Fourier syntheses, which evidence the presence of its other positions with minimum populations. However, attempts to determine these peaks of electron density as the oxygen atoms with partial populations of the positions failed. The fragment of the macrocycle O(2)—C(19) is disordered over two conformations of the polyether chain with the 0.64 : 0.36 ratio of populations of the positions. The above described irregularities of the anion and the macrocycle strongly decrease the accuracy of the X-ray diffraction experiment. The most of the hydrogen atoms at the carbon atoms were revealed as a result of the differential Fourier synteses, but afterwards their positions were calculated geometrically and then refined using the riding model. The hydrogen atoms of the NH$_3^+$ group were calculated geometrically and refined isotropically using the soft geometric constraints (SADI command). The position of the H(1W) atom of the water molecule O(1W) was found from the Fourier syntheses and refined isotropically. The second hydrogen atom of this molecule was not localized. The X-ray diffraction data, crystallographic parameters, and the results of structure refinement by the least-squares method are given in Table 1. All calculations were performed according to the SHELXTL-Plus program.[16] The coordinates of the atoms and other experimental data have been deposited at the Cambridge Crystallographic Data Center* (No. 696184).

Table 1. Crystal parameters and X-ray diffraction data for *rctt*-**7** • 0.5HClO$_4$ • C$_6$H$_6$ • H$_2$O

Parameter	*rctt*-**7** • 0.5HClO$_4$ • C$_6$H$_6$ • H$_2$O
Molecular formula	C$_{45}$H$_{57.5}$Cl$_{2.5}$N$_3$O$_{17}$
Molecular weight/g mol^{-1}	1001.07
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	9.8403(7)
b/Å	13.8984(10)
c/Å	17.5560(12)
α/deg	83.250(2)
β/deg	85.424(2)
γ/deg	78.151(2)
V/Å^3	2329.8(3)
Z	2
d_{calc}/g cm^{-3}	1.427
F(000)	1021
μ(Mo-Kα)/mm^{-1}	0.245
Crystal size/mm	0.22×0.12×0.08
Scan mode/region in θ/deg	ω/1.51—29.00
Intervals of reflection indexes	$-13 \le h \le 13$, $-18 \le k \le 17$, $-23 \le l \le 23$
Number of measured reflections	22393
Number of independent reflections with R_{int} = 0.0743	12237
Number of reflections with $I > 2\sigma(I)$	4525
Number of refinement parameters	665
R-Factors over $I > 2\sigma(I)$	R_1 = 0.0849, wR_2 = 0.2036
over all reflections	R_1 = 0.2163, wR_2 = 0.2520
GOOF	0.888
Residual electron density (min/max)/e Å^{-3}	–0.553/0.664

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References

1. R. Vilar, *Structure and Bonding*, 2004, **111**, 85.
2. G. A. Hembury, V. V. Borovkov, Y. Inoue, *Chem. Rev.*, 2008, **108**, 1.
3. S. P. Gromov, *Ros. nanotekhnologii* [*Nanotechnologies in Russia*], 2006, **1**, No. 1—2, 29 (in Russian).
4. S. P. Gromov, E. N. Ushakov, A. I. Vedernikov, N. A. Lobova, M. V. Alfimov, Yu. A. Strelenko, J. K. Whitesell, M. A. Fox, *Org. Lett.*, 1999, **1**, 1697.
5. S. P. Gromov, A. I. Vedernikov, E. N. Ushakov, N. A. Lobova, A. A. Botsmanova, S. S. Basok, L. G. Kuz´mina, A. V. Churakov, Yu. A. Strelenko, M. V. Alfimov, E. I. Ivanov, J. A. K. Howard, D. Johnels, U. G. Edlund, *New J. Chem.*, 2005, **29**, 881.
6. A. I. Vedernikov, E. N. Ushakov, N. A. Lobova, A. A. Kiselev, M. V. Alfimov, S. P. Gromov, *Izv. Akad. Nauk. Ser. Khim.*, 2005, 656 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 666].
7. A. I. Vedernikov, N. A. Lobova, E. N. Ushakov, M. V. Alfimov, S. P. Gromov, *Mendeleev Commun.*, 2005, **15**, 173.
8. S. P. Gromov, A. I. Vedernikov, N. A. Lobova, L. G. Kuz´mina, S. N. Dmitrieva, O. V. Tikhonova, M. V. Alfimov, Pat. RF 2278134; *Byul. izobret.* [*Bull. Invent.*], 2006, No. 17 (in Russian).
9. A. I. Vedernikov, D. V. Kondratuk, N. A. Lobova, T. M. Valova, V. A. Barachevskii, M. V. Alfimov, S. P. Gromov, *Mendeleev Commun.*, 2007, **17**, 264.
10. A. I. Vedernikov, S. K. Sazonov, P. S. Loginov, N. A. Lobova, M. V. Alfimov, S. P. Gromov, *Mendeleev Commun.*, 2007, **17**, 29.
11. J. L. R. Williams, R. E. Adel, J. M. Carlson, G. A. Reynolds, D. G. Borden, J. A. Ford, *J. Org. Chem.*, 1963, **28**, 387.
12. A. I. Vedernikov, S. P. Gromov, N. A. Lobova, L. G. Kuz´mina, Yu. A. Strelenko, J. A. K. Howard, M. V. Alfimov, *Izv. Akad. Nauk. Ser. Khim.*, 2005, 1896 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 1954].
13. L. G. Kuz´mina, A. I. Vedernikov, N. A. Lobova, A. V. Churakov, J. A. K. Howard, M. V. Alfimov, S. P. Gromov, *New J. Chem.*, 2007, **31**, 980.
14. C. Frassineti, S. Ghelli, P. Gans, A. Sabatini, M. S. Moruzzi, A. Vacca, *Anal. Biochem.*, 1995, **231**, 374.
15. *SAINT, Version 6.02A*, Bruker AXS Inc., Madison, Wisconsin (USA), 2001.
16. *SHELXTL-Plus, Version 5.10*, Bruker AXS Inc., Madison, Wisconsin (USA), 1997.

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