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Synthesis, Structure, and Properties of Supramolecular Photoswitches Based on Ammonioalkyl Derivatives of Crown Ether Styryl Dyes

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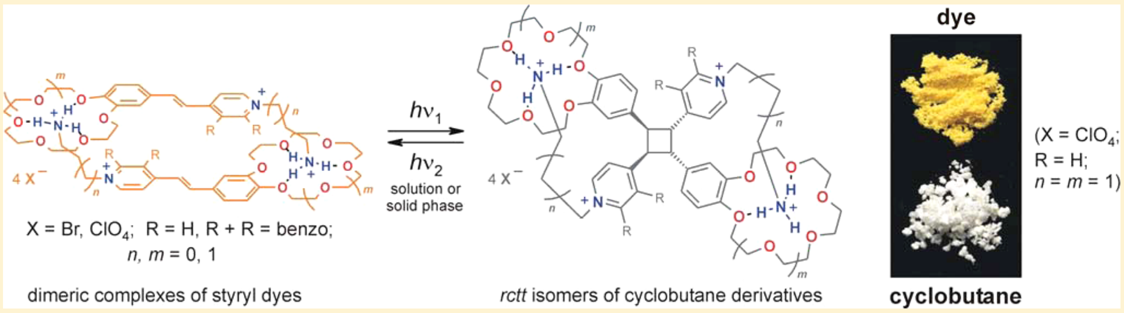
Ⓢ *Supporting Information*



ABSTRACT: The synthesis of new styryl dyes derived from 4-pyridine and 4-quinoline and having an ammonioalkyl *N*-substituent and benzocrown ether moieties of different sizes and with different sets of heteroatoms was developed. Spontaneous "head-to-tail" dimerization of these dyes via the formation of numerous hydrogen bonds between the terminal NH_3^+ groups and crown ether moieties was detected in MeCN solutions. The stability constants of the dimeric complexes having pseudocyclic structure were studied by ^{1}H NMR titration. The most stable complexes (log K_d up to 8.2) were found in the case of dyes with the 18-crown-6 ether moiety, which is most complementary for binding a primary ammonium group. Stacking interaction of the conjugated systems in the dimeric complexes contributes to their stability to a much lesser extent. In dimeric complexes, the ethylene bonds of the dyes are preorganized for stereospecific [2 + 2] photocycloaddition (PCA) induced by visible light. PCA yields only *rctt* isomers of bis-crown-containing cyclobutane derivatives. The dyes were studied by X-ray diffraction; it was found that the dimeric arrangement is also retained in the crystalline state. The possibility of topochemical PCA of the dyes in single crystals without their destruction was demonstrated. The possibility of retro-PCA of the obtained cyclobutane derivatives to give the starting dyes was shown. The elucidated regularities of PCA can be used to fabricate optical data recording systems based on ammonioalkyl derivatives of crown ether styryl dyes.

■ INTRODUCTION

The vigorous development of supramolecular chemistry in the past two decades was related to studies of promising ways of self-assembly of organic molecules in solution and in the solid phase by means of weak (noncovalent) interactions.[1] In supramolecular assemblies, it becomes possible to stabilize intermediates and states that possess practically useful properties but are normally unstable.[2] A prominent place among most promising molecules—building blocks—is occupied by crown-containing unsaturated compounds[3] that can form host−guest complexes between the macrocyclic fragment and metal or ammonium ions and, at the same time, exhibit photosensitive properties due to the presence of an ethylene fragment in the chromophore.

A highly effective but still insufficiently comprehensively studied method for self-assembly of crown-containing unsaturated compounds is hydrogen bonding between a primary ammonium group and a complementary 18-crown-6 ether part. Earlier we demonstrated[4] that bis(18-crown-6)-containing bis-styryl dyes exhibit chemosensing properties with respect to alkanediammonium ions $H_3N^+(CH_2)_nNH_3^+$ (*n* = 2−6) and that the pseudocyclic 1:1 complex thus formed (Chart 1a) may

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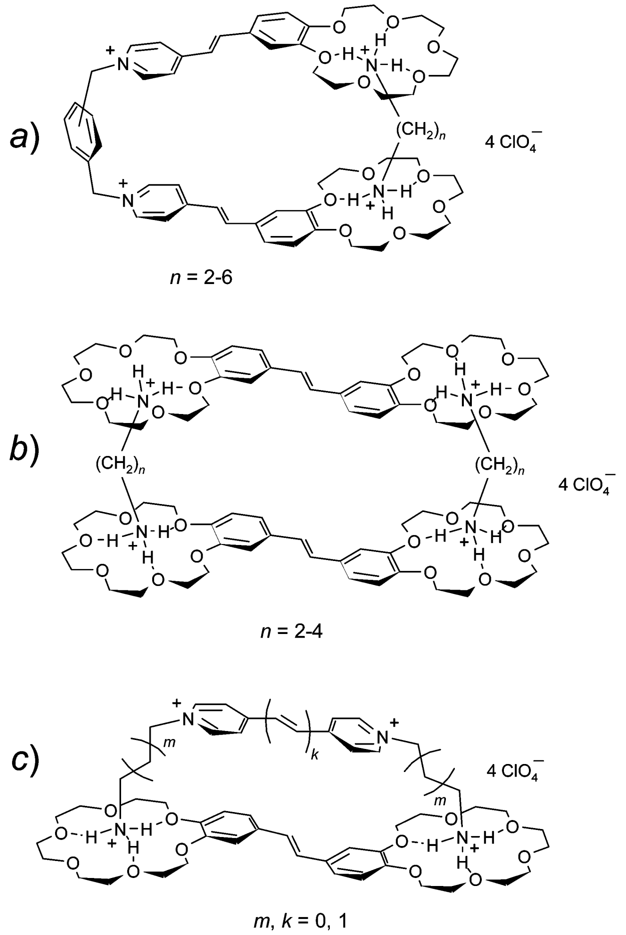
Chart 1



undergo stereospecific intramolecular [2 + 2] photocycloaddition (PCA) reaction to give a cyclobutane derivative. In the presence of relatively short $H_3N^+(CH_2)_nNH_3^+$ ions ($n = 2–4$) in a MeCN solution, bis(18-crown-6)stilbene forms bis-pseudosandwich 2:2 complexes (Chart 1b) in which stereoselective PCA reaction takes place effectively to give mainly the *rctt* isomer of tetrakis(benzo-18-crown-6)cyclobutane.[5] The formation of exceptionally stable (log *K* up to 9.42) donor–acceptor (D–A) charge transfer complexes was found[6] between bis(18-crown-6)stilbene and *N*,*N*′-bis(ammonioalkyl) derivatives of viologen and its analogues owing to homoditopic complexation of the NH_3^+ groups with the crown ether fragments (Chart 1c). Despite the close positions of the C═C double bonds in the D–A complexes, no PCA reaction takes place in them due to the competing photoinduced fast electron transfer, which suppresses all other photoprocesses.

The interchange of the D–A parts of the complex results in the dimeric complex of styryl dye **1c** owing to the presence of both an ammonioalkyl group and an 18-crown-6 ether moiety in the molecule of this dye (Chart 2). In this complex, (**1c**)$_2$, organic cations are arranged in a *syn*-"head-to-tail" fashion to form a pseudocycle. Our preliminary studies demonstrated[7] that the positions of the C═C double bonds in complex (**1c**)$_2$ are favorable for effective stereospecific auto-PCA reaction to give a cyclobutane derivative.

The objective of the present study was to develop methods for the synthesis of a series of styryl dyes, **1a–i**, having a crown ether moiety with different sizes and sets of heteroatoms (O

Chart 2

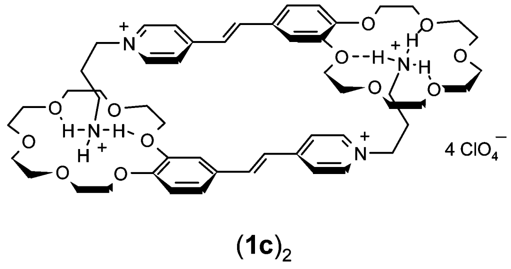
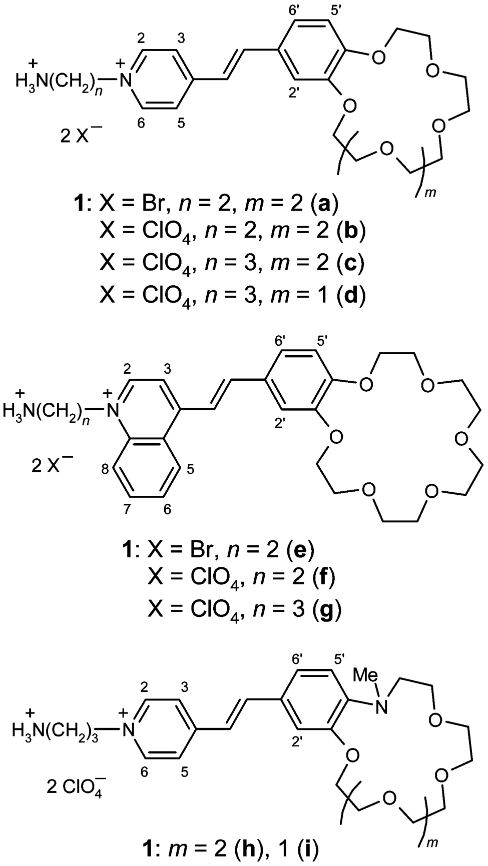


Chart 3



1: X = Br, $n = 2$, $m = 2$ (**a**)
X = ClO$_4$, $n = 2$, $m = 2$ (**b**)
X = ClO$_4$, $n = 3$, $m = 2$ (**c**)
X = ClO$_4$, $n = 3$, $m = 1$ (**d**)

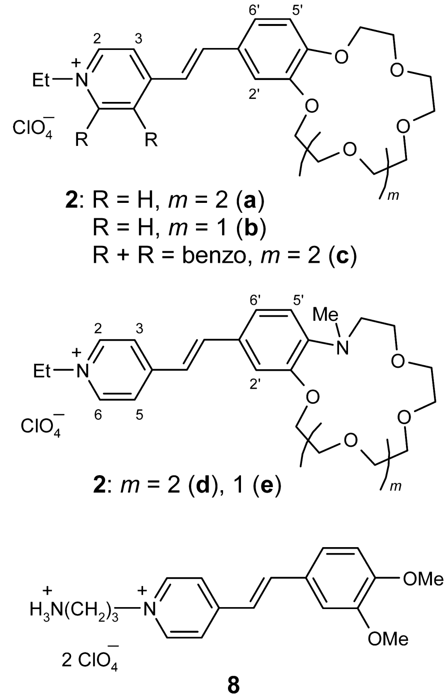
1: X = Br, $n = 2$ (**e**)
X = ClO$_4$, $n = 2$ (**f**)
X = ClO$_4$, $n = 3$ (**g**)

1: $m = 2$ (**h**), 1 (**i**)

and N) and a heterocyclic residue with *N*-*ω*-ammonioalkyl substituents of different lengths in this residue (Chart 3). The influence of the above structural factors on the structure and stability of dimeric complexes of these dyes and on the efficiency and stereoselectivity of PCA in these complexes was studied. The effects of the physical state (solution or solid) on the dimerization and the outcome of PCA reactions in dyes **1** were studied by X-ray crystallography and electronic and NMR spectroscopy (including ^{1}H NMR titration). The reverse [2 + 2] photocycloaddition reaction (retro-PCA), resulting in the formation of the starting styryl dyes, was implemented using two examples.

Model dyes **2a–e** having no ammonium group in the *N*-substituent (Chart 4) were used as reference compounds to study the complexing properties of dyes **1a–i**. Compounds **1** and **2** have identical chromoionophores; however, the latter do not undergo spontaneous dimerization in solution.

Chart 4



RESULTS AND DISCUSSION

Synthesis of Dyes. The crown ether styryl dyes **1** and **2** were synthesized using heterocyclic salts **3**−**7** having an ammonioalkyl or ethyl *N*-substituent (Scheme 1). The syntheses of compounds **5b**[6] and **7**[8] and dyes **1c**,[7] **2a**,[9] **2b**,[10] and **2c**[11] were reported previously.

Heterocyclic salts **3**−**6** were condensed with the formyl derivatives of benzocrown ethers in ethanol in the presence of pyridine to give *N*-ammonioalkyl crown styryl dyes **1a**−**i** (Scheme 2).

Model dyes **2d,e** were prepared by condensation of salt **7** with formyl derivatives of azacrown ethers[12] in ethanol in the presence of pyrrolidine (Scheme 3).

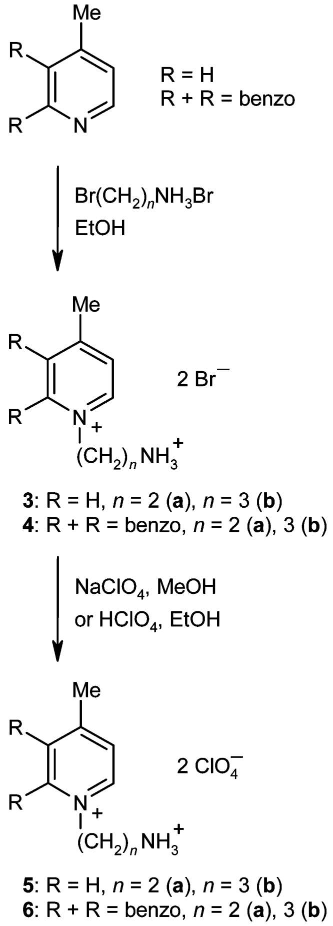
We also studied model dye **8**,[13] which has two methoxy groups instead of the crown ether moiety in the benzene ring (see Chart 4).

All of the obtained compounds were characterized by UV−vis and ^{1}H and ^{13}C NMR spectroscopy methods, and their structures were confirmed by elemental analysis data (^{1}H and ^{13}C NMR, 2D COSY, NOESY, HSQC, and HMBC, and UV−vis spectra of compounds **1**−**6** are shown in Figures S1−S19, S26−S45, S52−S81, S99, and S100 in the Supporting Information). According to the spin−spin coupling constant $^3J_{HC=CH}$ = 15.7−16.5 Hz, all compounds **1** and **2** have the *trans* configuration of the C=C double bond.

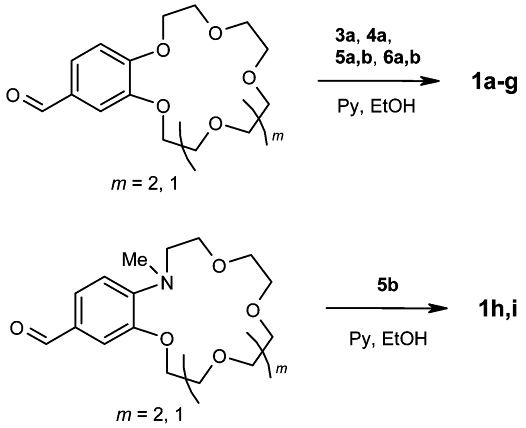
Dimerization of Dyes. Studies in acetonitrile solutions demonstrated that all styryl dyes **1a**−**i** having ammonioalkyl substituents can form pseudocyclic dimeric complexes (Scheme 4).

The long-wavelength absorption band (LWAB) in the spectra of styryl dyes **1** refers to an electronic transition with intramolecular charge transfer from the electron-donating benzocrown ether moiety to the electron-withdrawing heterocyclic residue. The formation of a complex is accompanied by an increase in the energy of this electronic transition, as the hydrogen bonding between the ammonium cation and the

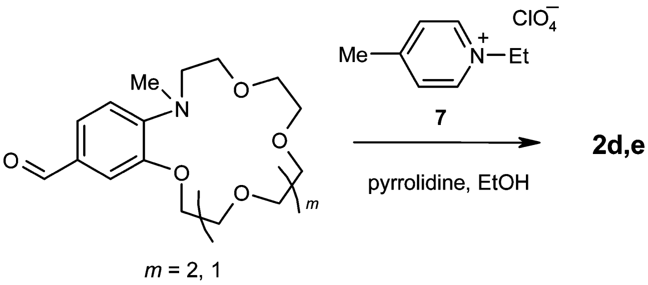
Scheme 1. Synthesis of Compounds 3−6



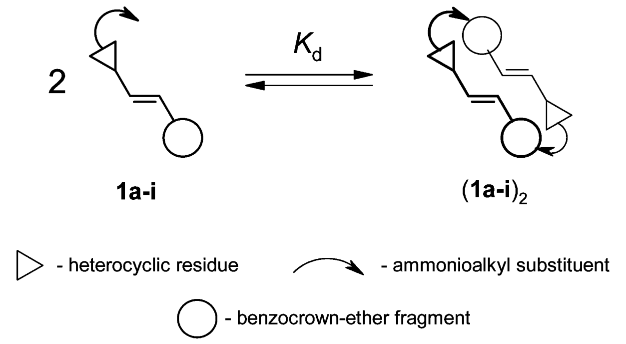
Scheme 2. Synthesis of Dyes 1a−i



Scheme 3. Synthesis of Dyes 2d,e



Scheme 4. Dimerization of Dyes 1a−i



crown ether moiety markedly decreases the electron-donating ability of the benzocrown ether moiety. This results in hypsochromic shifts in the absorption spectra of **1** by up to 71 nm with respect to the LWAB of related dyes **2** having an identical chromoionophore (see the Experimental Section and Figures S99 and S100 in the Supporting Information). A detailed study of dimerization of dyes **1a−i** and the efficiency and photoreversibility of PCA by electronic spectroscopy techniques will be published elsewhere.

Dimerization of ammonioalkyl dyes is clearly manifested in the ^{1}H NMR spectra. Indeed, in a MeCN-d_3 solution, the signals of the ethylene protons and most aromatic protons of dye **1h** are shifted upfield by up to $\Delta\delta_H = -0.35$ with respect to those of model dye **2d** (Figure 1a,c; the proton numbering is shown in Charts 3 and 4). This cannot be purely a complexation effect (without a contribution of dimerization), as the formation of the host−guest complex **2d** with the $EtNH_3^+$ ions results in a slight downfield shift of proton signals for all types of protons (Figure 1a,b), which is typical of crown ether complexes with metal and ammonium cations. Similar changes were observed for the complexation of other dyes **1** (see Figures S101−S105 in the Supporting Information). Thus, the upfield shift observed for dyes **1** can only be interpreted as being due to substantial anisotropic effects of the conjugated moieties of the dye in the dimer $(\mathbf{1})_2$.

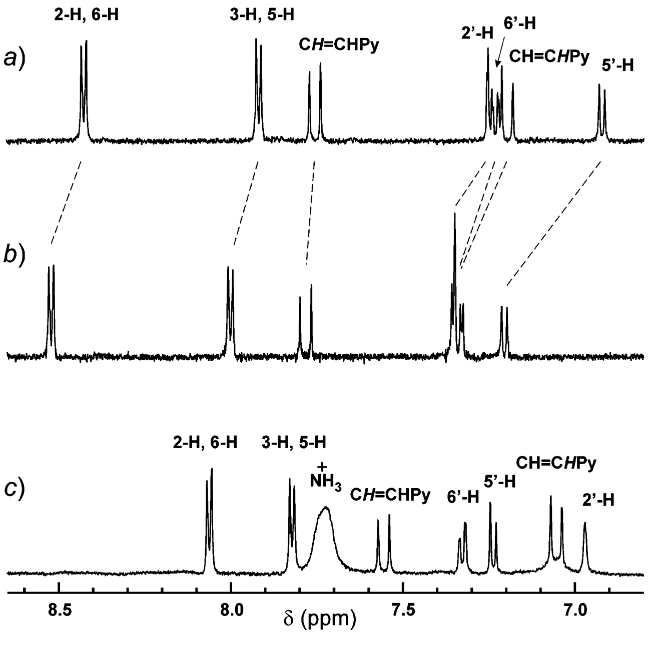


Figure 1. ^{1}H NMR spectra (aromatic proton region) of (a) dye **2d**, (b) a 1:5 mixture of dye **2d** and $EtNH_3ClO_4$, and (c) dye **1h** ($C_{dye} = 1 \times 10^{-3}$ M) (500.13 MHz, MeCN-d_3, 25 °C).

For quantitative determination of the stability of the dimeric complexes of ammonioalkyl dye derivatives by ^{1}H NMR titration, it was first necessary to measure the stability constants for the complexes of model styryl dyes **2** with ethylammonium perchlorate. The results were used to distinguish the contribution to the stability made by hydrogen bonding between the dye crown ether moiety and the $EtNH_3^+$ ion and then estimate the dimerization constants of dyes **1** by competitive ^{1}H NMR titration.

The complexation of dyes **1** and **2** with ethylammonium perchlorate in MeCN-d_3 is described by the following equilibrium:

$$\mathbf{1},\ \mathbf{2} + EtNH_3^+ \overset{K}{\rightleftarrows} (\mathbf{1},\ \mathbf{2})\cdot EtNH_3^+ \qquad (1)$$

where K (M^{-1}) is the stability constant of the complex dye·$EtNH_3^+$ (1:1).

The stability constants of the complexes **2**·$EtNH_3^+$ were determined using the HYPNMR program[14] by analyzing the changes in the positions of the dye proton signals depending on the concentration of the salt $EtNH_3ClO_4$ added. The results are presented in Table 1.

Table 1. Effective Stability Constants of Dimeric Complexes of Dyes 1b−d,g,h and Complexes of Dyes 2a−e with $EtNH_3ClO_4$[a]

dye	log K_d	dye	log K
1h	8.2	**2d**	3.9
1g	8.0	**2a**	3.6[b]
1b	7.9	**2c**	3.5
1c	7.1[b]	**2e**	1.9
1i	3.6	**2b**	1.8
1d	2.4		
1f	c		

[a]Competitive (for **1**) or direct (for **2**) ^{1}H NMR titration with $EtNH_3ClO_4$, $C_{dye} = (1{-}5) \times 10^{-3}$ M, MeCN-d_3, 25 ± 1 °C. The determination errors for constants K and K_d are ±20% and ±30%, respectively. [b]From ref 7. [c]Insoluble in MeCN-d_3.

It can be seen that model dyes **2a,c,d** containing a benzo-18-crown-6 ether moiety form much stronger complexes with the $EtNH_3^+$ ion than compounds **2b,e** containing a benzo-15-crown-5 ether moiety. This is well correlated with known published data indicating that the geometric parameters of 18-crown-6 ether are best fitted for binding the primary ammonium ion.[15] The nature of the heterocyclic residue in dyes **2a** and **2c** with the same crown ether part has almost no influence on the stability of the complexes.

The dimerization constants of dyes **1** containing ammonioalkyl substituents were estimated by competitive titration using $EtNH_3ClO_4$ as the competing guest. Equilibria 1 and 2 were simultaneously taken into account:

$$2(\mathbf{1}) \overset{K_d}{\rightleftarrows} (\mathbf{1})_2 \qquad (2)$$

K (M^{-1}) is the stability constant of the complex of dye **1** with $EtNH_3ClO_4$, and K_d (M^{-1}) is the stability constant of the dimeric complex of dye **1**.

The stability constants of the dimeric complexes $(\mathbf{1})_2$ were determined using the HYPNMR program by analyzing changes in the positions of the dye proton signals as functions of the concentration of the salt $EtNH_3ClO_4$ added. Direct measurement of the stability constants for the complexes of ammonioalkyl dye derivatives **1** with $EtNH_3ClO_4$ by ^1H NMR titration was impossible. Therefore, our calculations were made with the assumption that the stability constants of the complexes **1**·$EtNH_3^+$ do not depend on the *N*-substituent in the heterocyclic dye residue. Thus, the constant for the first equilibrium (K) was set to be invariable and the same as found for model compound **2** with the same chromogen and crown ether moiety. The resulting K_d values are given in Table 1.

On comparison of the K_d values of dyes **1c** and **1d** and dyes **1h** and **1i**, one can conclude that the size of the crown ether moiety is crucial for dimerization. The K_d values decrease by ~4.5 orders of magnitude on going from 18-crown-6 to 15-crown-5 ethers. This is in line with the results of stability determination for the complexes of dyes **2** with $EtNH_3^+$; this decrease is caused by the fact that 15-crown-5 ethers bind the ammonium cation much more weakly. That is, the stability of dimeric complexes is mainly determined by the number and strength of the hydrogen bonds, being much less dependent on the contribution of stacking interactions (secondary interactions of the p_z-orbitals of the conjugated moieties).

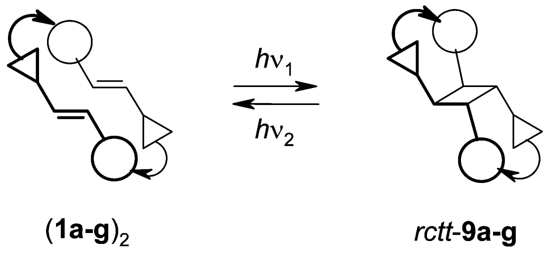
In the series of dyes **1b**,**c**,**g** containing identical crown ether moieties, more stable dimeric complexes were found for **1b**,**g** with a more extended system of conjugation or a shorter ammonioalkyl substituent, which obviously brings about closer positions of the conjugated groups and facilitates more effective stacking interactions of these groups.

Comparison of the results for **1c** and **1h** indicates that the benzoazacrown ether moiety present in the dye promotes dimerization. This is probably caused by the high basicity of the macrocyclic nitrogen atom, which ensures stronger hydrogen bonding with the ammonium cation. Furthermore, *N*-methylbenzoazacrown ethers have a conformation favorable for complexation; in other words, they are preorganized for complexation. This conclusion was made in our previous study of related dyes containing an *N*-methylbenzoazacrown ether moiety but devoid of ammonioalkyl groups.[12]

[2 + 2] Photocycloaddition of Dyes in Solution. On exposure of MeCN solutions of dyes **1** to visible light, in most cases, a pronounced and rather fast color change is observed (decoloration; the hypsochromic shift of the LWAB reached 130 nm). These changes were related to effective and stereospecific PCA reaction resulting in quantitative formation of cyclobutane derivatives **9** involving the C═C double bonds of two dye molecules that are closely located in space due to spontaneous dimerization (Scheme 5).

This is exemplified in Figure 2 by data on the photolysis of a solution of dye **1g** ($C = 5 \times 10^{-5}$ M) at $\lambda > 410$ nm (see also the photolysis data on dye **1c** in Figure S106 in the Supporting Information). According to the results of K_d measurements in MeCN, this dye at this concentration exists almost entirely as dimeric complexes. Short-term irradiation results in almost complete disappearance of the visible absorption due to disruption of the conjugation chain between the quinoline and benzene residues upon the formation of cyclobutane derivative **9g**.

Scheme 5. Photochemical Formation of Cyclobutane Derivatives 9 and Dyes 1



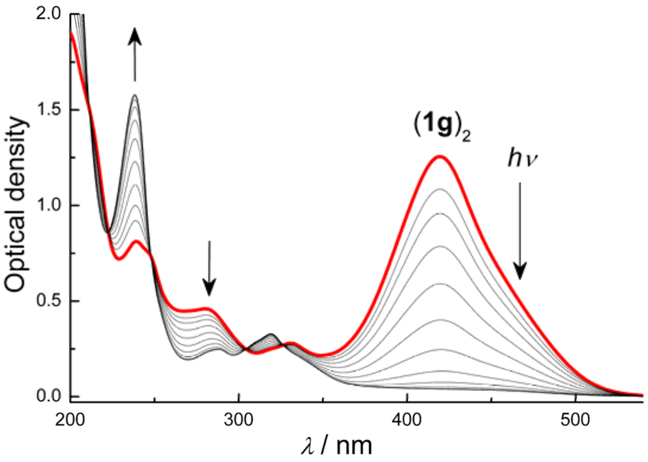


Figure 2. Photolysis of a solution of dye **1g** over 0, 0.3, 0.5, 0.8, 1.2, 1.7, 2.3, 3.1, 4.1, 5.6, 8.6, and 14 s (MeCN, $C_{1g} = 5 \times 10^{-5}$ M, $V = 3$ mL, 1 cm quartz cell, light with $\lambda > 410$ nm).

In all cases, only *rctt* isomers of cyclobutanes **9** are formed. This is accompanied by the disappearance of signals for the ethylene bond from the ^1H NMR spectra and the appearance of a new set of signals at 5 ppm. The typical form[9−11,13] of these new signals—two doublets of doublets with $^3J_{cis\text{-H,H}} = 9.0$–$9.5$ Hz and $^3J_{trans\text{-H,H}} = 7.4$–$8.6$ Hz—confirms the assumed stereochemistry of the PCA product (for example, see Figure 3 for compound *rctt*-**9d** and Figures S20−S25 in the Supporting Information). The structure of compound *rctt*-**9c** was established by X-ray diffraction analysis.[7]

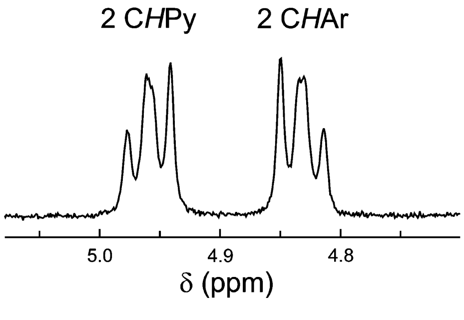


Figure 3. ^1H NMR spectrum (cyclobutane proton region) of compound *rctt*-**9d** (500.13 MHz, DMSO-d_6, 30 °C).

Ammonioalkyl dyes **1a**−**d**,**g**−**i** and model dyes **2a** and **8** were studied under comparable conditions for the ability to undergo the PCA reaction in MeCN; the results are summarized in Table 2. The dyes containing the 18-crown-6 ether moiety and a sufficiently long ammoniopropyl substituent were found to be most susceptible to PCA; in the case of **1c**,**g**, a quantitative yield was obtained over a period of 4 h. This corresponds to high stability constants of their dimers. The phototransformation was noticeably slower for dye **1b** than for **1c**,**g**, despite the high stability of the dimeric complex and close positions of the

Table 2. Study of the Formation Rate of Cyclobutane Derivatives from Dyes **1b**−**d**,**g**−**i**, **2a**, and **8**[a]

dye	irradiation time, h	cyclobutane	χ,[b] %
1c	4	*rctt*-**9c**	100
1g	4	*rctt*-**9g**	100
1d	4	*rctt*-**9d**	40
	20		100
1b	4	*rctt*-**9b**	33
	200		100
8	30		<1
1h	40		0
1i	40		0
2a[c]	30		0

[a] MeCN, $C_{\text{dye}} = 1 \times 10^{-3}$ M, $V = 15$ mL, a 60 W incandescent lamp as the radiation source, 15 cm distance to the source. [b] Degree of conversion into the cyclobutane derivative (from ^{1}H NMR data). [c] From ref 9.

conjugated moieties in the case of **1b**. Apparently, the short ammonioethyl spacer holds the dye molecules in the dimeric complex $(\mathbf{1b})_2$ too rigidly and thus hampers the displacement of the carbon atoms of the ethylene bridges toward each other, which is needed for PCA.

In the case of 15-crown-5-containing dye **1d** having a relatively low dimerization constant (see Table 1), PCA was also much slower than for **1c**,**g**. Obviously, in this case, the efficiency of photoreaction is reduced due to the low concentration of the dimeric complexes in solution. The importance of this factor was demonstrated even more clearly by the study of model dye **8** in which the crown ether moiety is replaced by two methoxy groups. Long-term photolysis of a solution of **8** afforded only traces of the *rctt* isomer of the expected cyclobutane derivative. Apparently, the methoxy groups of the dye can be only weakly coordinated to the NH_3^+ groups, and this accounts for the vanishingly small content of the dimeric complex $(\mathbf{8})_2$. Dyes **1h**,**i** containing a stronger electron-donating moiety (benzoazacrown ether) and model dye **2a** having no ammonium group in the *N*-substituent were unreactive under these conditions. The absence of PCA for dyes **1h**,**i** is probably related to the formation of a twisted internal charge-transfer (TICT) exited state, as has been noted previously for related dyes of type **2d**,**e** devoid of the ammonium group in the *N*-substituent.[12] In the case of **2a**, only the photostationary state between the *E* and *Z* isomers of the dye was established rather quickly.[9]

Note that dyes **1e**,**f** having a quinoline residue and ammonioethyl *N*-substituent proved to be poorly soluble in MeCN. Nevertheless, irradiation of these dyes as dispersions in water−acetonitrile mixtures or as thin polycrystalline films on a glass substrate also produced the corresponding cyclobutane derivatives (see the Experimental Section).

Cyclobutane derivatives *rctt*-**9b**−**g** were synthesized on a reasonable scale. Their structures were determined by ^{1}H and ^{13}C NMR and UV−vis spectroscopy and confirmed by elemental analysis data (^{1}H and ^{13}C NMR, 2D COSY, NOESY, HSQC, and HMBC, and UV−vis spectra of compounds *rctt*-**9b**−**g** are shown in Figures S20−S25, S46−S51, S82−S98, and S107 in the Supporting Information).

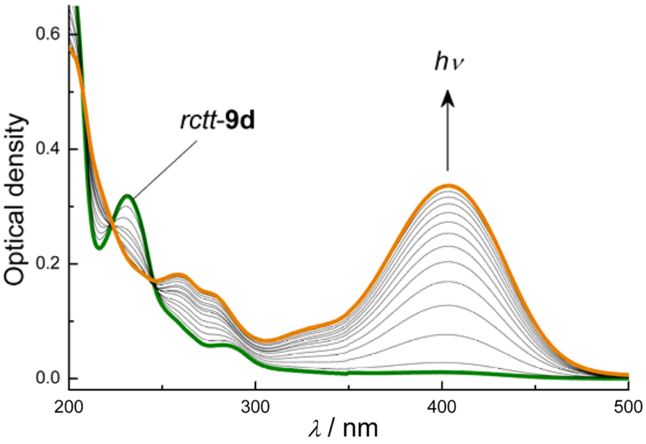


Figure 4. Photolysis of a solution of cyclobutane *rctt*-**9d** for 0, 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60 min (MeCN, $C_{\mathbf{9d}} = 1 \times 10^{-5}$ M, $V = 3$ mL, 1 cm quartz cell, light with $\lambda = 280−320$ nm). The orange curve is a photostationary mixture consisting of *rctt*-**9d**, (*E*)-**1d**, and (*Z*)-**1d**.

The irradiation of dilute MeCN solutions of cyclobutane derivatives **9d** and **9g** at a shorter wavelength results in restoration of the visible color due to the retro-PCA reaction giving the initial styryl dyes (see Scheme 5). Figure 4 shows data on the photolysis of a solution of cyclobutane *rctt*-**9d** ($C = 1 \times 10^{-5}$ M) at $\lambda = 280−320$ nm. The intensity of the new LWAB with a maximum at 404 nm reaches 58% of the value expected for a 2×10^{-5} M solution of dye **1d**. Evidently, we are dealing with a mixture of *rctt*-**9d** and *E* and *Z* isomers of dye **1d**, which occur in photostationary equilibrium with one another. The resulting photostationary mixture is enriched in dye **1d** due to the low stability constant of its dimer (see Table 1). The occurrence of reversible *E*−*Z* photoisomerization was proven by irradiation at $\lambda = 280−320$ nm of a solution of model dye **2b** ($C = 2 \times 10^{-5}$ M), which is unable to form dimers and, therefore, does not undergo PCA in solution. As photostationary equilibrium is attained, the intensity of the LWAB with a maximum at 397 nm decreases to 82% of the initial value (see Figure S108 in the Supporting Information), obviously due to the appearance of the *Z* isomer, which has an LWAB maximum at shorter wavelength than the *E* isomer. Previously, we obtained similar spectral characteristics for the *E* and *Z* isomers of dye **2a**.[9]

In the case of irradiation of a solution of cyclobutane *rctt*-**9g**, the content of dye **1g** in the photostationary mixture is relatively low (see Figure S109 in the Supporting Information), because this dye mainly exists as the dimer even in dilute solutions and has a considerable absorption at 280−320 nm.

Thus, we demonstrated the reversibility of the PCA reaction with transformation of styryl dyes into cyclobutane derivatives and back. Probably, the efficiencies of both forward and reverse PCA reactions can be controlled by using solvents in which the stability of the dimeric complexes $(\mathbf{1})_2$ differs from the stability in MeCN or by adding metal cations able to displace the ammonium groups from the complexes with crown ether moieties and, hence, to decrease the degree of dimerization of dyes **1**. These options will be considered elsewhere.

X-ray Diffraction Study of Dyes and Cyclobutanes. The X-ray diffraction study of dye **2a** was performed previously.[9] It was found that the organic cations of **2a** are stacked in the crystal according to the *syn*-head-to-tail pattern with extensive stacking interaction of the conjugated systems. The stacks are split into dimeric pairs of cations in which the ethylene bonds have approached each other at a distance of 3.55 Å and are antiparallel. According to Schmidt's rule (parallel arrangement of ethylene compounds spaced by up to

4.2 Å),[16] the conditions found in the crystal of **2a** were favorable for solid-state PCA according to the "single-crystal-to-single-crystal" (SCSC) type, i.e., with retention of crystallinity.[9] It should be noted, however, that the presence of a crown ether moiety is not a sufficient condition for the PCA reaction in the crystals, as shown by our studies of styryl dyes.[9,10]

We succeeded in growing a single crystal of the model dye **2c** for X-ray diffraction analysis; the determined structure is shown in Figure 5.

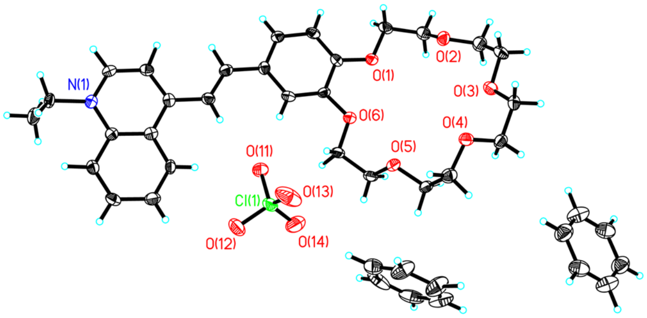


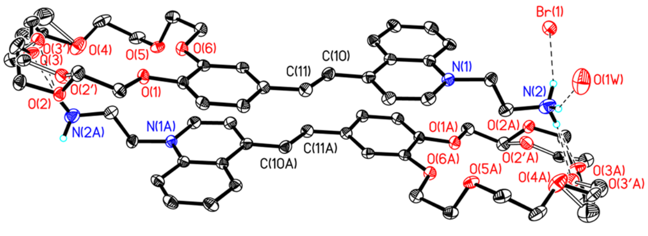
Figure 5. Structure of $2c\cdot1.5C_6H_6$. Thermal ellipsoids are drawn at the 50% probability level.

Similarly to dye **2a**, the cations of dye **2c** in the crystal also form *syn*-head-to-tail dimeric pairs with a proximate (3.57 Å) and strictly antiparallel arrangement of the ethylene moieties, which implies the possibility of solid-state [2 + 2] PCA reaction. The neighboring dimeric pairs are separated by interlayers of benzene solvent molecules (see Figure S110 in the Supporting Information). Previously,[11] we demonstrated that dye **2c** is indeed rapidly converted to the corresponding centrosymmetric *rctt*-cyclobutane upon irradiation of its polycrystalline film. Visible light irradiation of the single crystals of dye **2c** induces the PCA reaction with transition of the crystals to the amorphous state.

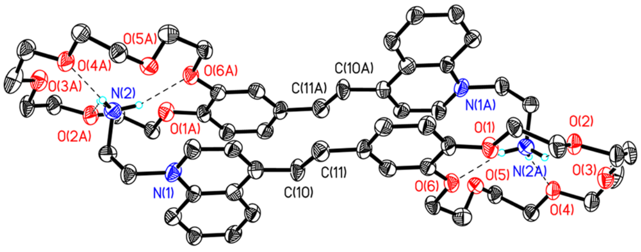
Ammonioalkyl dyes **1a,b,e,f** were also prepared as single crystals and studied by X-ray crystallography.

In the crystals of $\mathbf{1e}\cdot0.5C_4H_8O_2\cdot2H_2O$ and **1f**, the organic cations form relatively isolated centrosymmetric *syn*-head-to-tail dimeric pairs (see Figure 6 and Figures S111 and S112 in the Supporting Information). The extended flat conjugated moieties present in these dimers are projected onto one another, being located in parallel planes spaced by ~3.4 Å, which implies strong stacking interactions between them. The ethylene bonds in the dimers of **1e** and **1f** are strictly antiparallel, and the distances between the carbon atoms of these bonds [C(10)···C(11A) and C(10A)···C(11)] are 3.40 and 3.49 Å, respectively. Thus, dyes **1e** and **1f** are preorganized for stereospecific PCA in the solid phase. On visible light irradiation, the crystals were destroyed, apparently as a result of photoreaction. As shown above, dyes **1e** and **1f** are actually quantitatively converted to cyclobutane derivatives *rctt*-**9e,f** upon irradiation of their dispersions or polycrystalline films. Apparently, the organic cations in the solid phase of these dyes are arranged in dimers similarly to the cations in $\mathbf{1e}\cdot0.5C_4H_8O_2\cdot2H_2O$ and **1f**.

The key difference between $\mathbf{1e}\cdot0.5C_4H_8O_2\cdot2H_2O$ and **1f** is in the mode of interaction between the ammonium groups and 18-crown-6 ether moieties. In **1f**, the ammonioethyl *N*-substituent occurs in the *gauche* conformation, which allows the NH_3^+ group to reside approximately in the middle of the round cavity of an 18-membered macroheterocycle and to form three hydrogen bonds with its oxygen atoms. The N(2)−H···O(2A,4A,6A) distances vary in the range of 1.94−2.08 Å, and the corresponding angles at the H atoms are 139−163°. These parameters characterize a relatively weak hydrogen bond, probably due to insufficient conformational flexibility of the short ammonioethyl spacer, which does not allow dimer $(\mathbf{1f})_2$ to have the optimal geometry. In $\mathbf{1e}\cdot0.5C_4H_8O_2\cdot2H_2O$, the hydrogen bond NH_3^+···18-crown-6 is even more weakened, as the ammonioethyl spacer adopts the *trans* conformation, which allows for the formation of only one hydrogen bond, N(2)−H···O(3A) or N(2)−H···O(3′A), with the oxygen atoms of the disordered macrocycle: the corresponding distances and angles are 1.93 and 2.22 Å and 165° and 156°. Additionally, the ammonium group of **1e** forms weak hydrogen bonds with the Br(1) anion [N(2)−H···Br(1), 2.43 Å and 162°] and one of the solvate water molecules [N(2)−H···O(1W), 1.98 Å and 146°] (see Figure 6).



$\mathbf{1e}\cdot0.5C_4H_8O_2\cdot2H_2O$

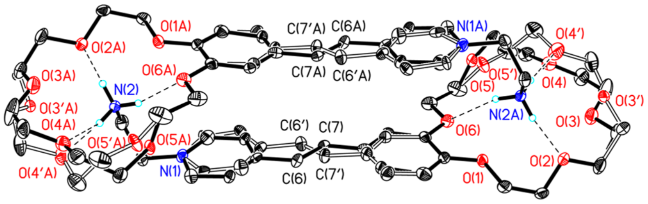


1f

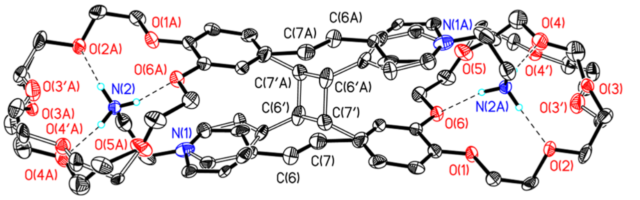
Figure 6. Cations forming dimeric complexes in structures $\mathbf{1e}\cdot0.5C_4H_8O_2\cdot2H_2O$ and **1f**. Thermal ellipsoids are drawn at the 40% probability level. Most of the hydrogen atoms are omitted for clarity. Hydrogen bonds are drawn with dashed lines. The additional letters "A" indicate that the atoms are in symmetrically related positions.

In relation to **1e,f**, we demonstrated that crown-containing styryl dyes having ammonioalkyl groups are dimerized not only in solutions but, owing to hydrogen bonds, also in single crystals. The single crystals of the dimeric complexes of **1e,f** maintain the arrangement of C═C bonds favorable for PCA reaction; therefore, irradiation results in stereospecific formation of cyclobutane derivatives similarly to the reactions in the polycrystalline phase and in solution. Unfortunately, photoreaction is accompanied by degradation of the single crystals of **1e,f** to the amorphous state. We were hoping that the single crystals of the dimeric complexes of the other dyes would prove to be stable during irradiation and expected to elucidate the reasons.

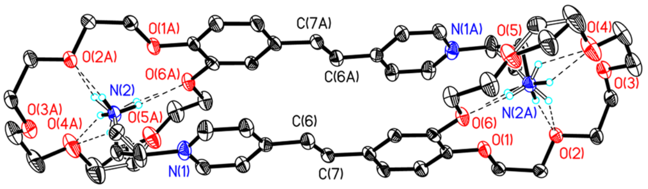
For this purpose, the single crystals of dyes **1a** and **1b** were studied by X-ray diffraction analysis; the structures of their principal components are shown in Figure 7 (see their crystal packings in Figures S113 and S114 in the Supporting Information). Similarly to quinoline dyes **1e** and **1f**, in the



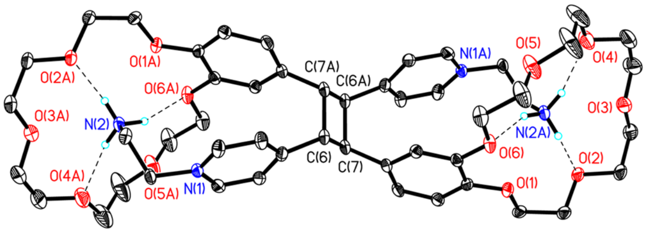
1a·$3H_2O$



(**1a**/**9a**)·$3H_2O$



1b



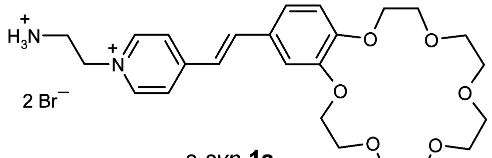
9b

Figure 7. Cations forming dimeric complexes in structures **1a**·$3H_2O$ and **1b** and cyclobutane dications in structures (**1a**/**9a**)·$3H_2O$ and **9b** formed through SCSC transformation. Thermal ellipsoids are drawn at the 40% probability level. Most of the hydrogen atoms are omitted for clarity. Hydrogen bonds are drawn with dashed lines. The additional letters "A" indicate that the atoms are in symmetrically related positions.

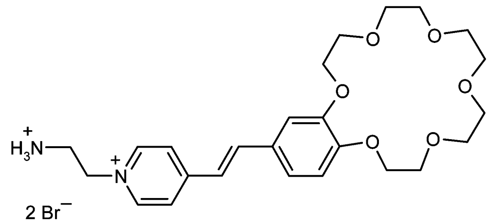
crystal, pyridine dyes **1a** and **1b** form pseudocyclic centrosymmetric head-to-tail dimers via binding of the ammonium groups to the crown ether moieties with extended overlap of the p_z-orbitals of the conjugated groups within a dimeric complex. The N(2)−H···O(2A,4A,4′A,6A) distances vary in the range of 1.88−2.11 Å, and the corresponding angles at H atoms are 132−177°.

The structures of **1a** and **1b** contain numerous disordered groups—peripheral regions of the crown ether moieties, ammonioethyl *N*-substituents, and perchlorate anions. In addition, in **1a**, the chromophore moiety is disordered; i.e., there are simultaneously two *s*-conformational isomers of the dye (*s-anti* and *s-syn*; see Chart 5) which differ by the orientation of the benzocrown ether residue with respect to the ethylene bond and occupy the same crystal sites with occupancies of 0.58:0.42.

Chart 5



s-syn-**1a**



s-anti-**1a**

Although dyes **1a** and **1b** crystallize in different space groups (*C*2/*c* and *P*2$_1$/*c*), they have similar packing motifs (see Figures S113 and S114 in the Supporting Information), according to which the dye dimeric complexes form loose stacks and are surrounded by conformationally flexible crown ether moieties of the neighboring dimeric complexes and mobile anions, which do not hamper substantial deflections of the atoms of dimeric complex components toward one another to provide the topochemical PCA reactions.

The centrosymmetric structure of dimeric complexes (**1a**)$_2$ and (**1b**)$_2$ implicates that the ethylene bonds of the cations occur in parallel planes, being antiparallel and close to each other [the C(6)···C(7A), C(7)···C(6A), C(6′)···C(7′A), and C(7′)···C(6′A) distances are 3.50−3.77 Å]. Thus, in both cases, spatial conditions are favorable for the PCA reaction.

Topochemical PCA occurring as an SCSC reaction was indeed detected by X-ray diffraction analysis for dyes **1a** and **1b**. The sets of experimental reflections were collected from the same single crystals of dyes **1a** and **1b** before and after irradiation with a 60 W incandescent lamp. The structures of reaction products **1a**/**9a** and **9b** are shown in Figure 7.

Dye **1b** is completely converted to cyclobutane derivative **9b** over a period of 20 h. PCA results in considerable changes in the length of the unit cell edges (by up to 6.1% of the initial value) and in a 0.5% decrease in the unit cell volume. This crystal "contraction" reduces the degree of disorder of its components, and thus, the X-ray diffraction experiment and, hence, structure determination become more accurate for **9b** than for the initial **1b**. The hydrogen bond parameters differ slightly from those of the starting dimeric complex: the N(2)−H···O(2A,4A,6A) distances are 1.95−2.00 Å, and the angles are 145−160°.

When a crystal of **1a** is irradiated for 10 days, out of the two *s*-conformers present in the crystal, only the minor *s-syn* conformer participates in PCA to give the mixed crystal *s-anti*-**1a**/*rctt*-**9a**. The ratio of the dimeric complex to cyclobutane derivative in this crystal is 0.36:0.64. Apparently, the PCA is accompanied by so-called "pedal" isomerization of the ethylene bond,[17] resulting in accumulation of the *s-syn* conformer, which then enters into PCA. The changes in the unit cell parameters (up to 0.6%) and volume (decreased by 0.04%) were minor; without the contraction effect, the crystal quality and degree of disorder of the components changed only slightly. The low rate of PCA is probably due to the presence in the crystal of **1a**·$3H_2O$ of an extended hydrogen bond network involving bromide anions and solvate water molecules, which increases the rigidity of the environment of the dimers.

It is noteworthy that although topochemical PCA reactions that are not accompanied by destruction of the single crystal arouse enormous interest and are vigorously investigated,[9−11,13,18] reported cases of such reactions are rare. In many works, authors attempt to model dimeric pairs with proximate parallel ethylene groups while noting that the single-crystal reaction without crystal destruction requires an appropriate crystal packing, which is most often unpredictable. In the case of crown-containing styryl dyes with *N*-ammonioalkyl substituents, we can employ hydrogen bonds to deliberately form strong dimeric complexes with double bond arrangement favorable for PCA which are not destroyed in the crystal. The presence of conformationally flexible moieties in the dimeric complex and the "soft" environment comprising rotationally mobile compact counterions that are not prone to hydrogen bonding facilitate the PCA reaction without destruction of the single crystal. Hence, the targeted design of the structure of dimeric complexes of crown ether styryl dyes and the crystalline matrix based on them may provide in the future new promising optical data recording systems operating on organic single crystals with high efficiency in the specified spectral range.

■ CONCLUSIONS

We developed the synthesis of a series of new styryl dyes having a crown ether moiety and an ammonioalkyl group on the opposite ends of the chromophore. These dyes were found to spontaneously form highly stable pseudocyclic dimeric complexes in solution and in the solid phase, in particular in single crystals, owing to hydrogen bonding of the terminal NH_3^+ group to the macrocycle heteroatoms. The dimeric complexes have a *syn*-head-to-tail structure in which the C═C double bonds are antiparallel and rather closely spaced. This preorganizes the dyes in question for stereospecific [2 + 2] photocycloaddition reaction both in solution and in the crystal to give the only centrosymmetric *rctt* isomers of cyclobutane derivatives. Owing to the dimeric arrangement of the dyes in single crystals, it is possible to find conditions for photocycloaddition with retention of the crystalline sample. Short-wavelength irradiation of the cyclobutane derivatives gives rise to the starting dyes; this confirms the photoreversibility of the supramolecular systems. The type of styryl dyes comprising ammonioalkyl substituents and crown ether moieties can be used to fabricate optical data recording systems, in particular based on single crystals.

■ EXPERIMENTAL SECTION

General Methods. The ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 using the solvent as the internal reference (δ_H 2.50 and δ_C 39.43). 2D ^{1}H−^{1}H COSY and NOESY and ^{1}H−^{13}C correlation (HSQC and HMBC) spectra were used to assign the proton and carbon signals (see Charts 3 and 4 for atom numbering in dyes **1** and **2**); the mixing time in the NOESY experiment was 300 μs. Absorption spectra were recorded in the range of 200−650 nm with an increment of 1 nm in MeCN (spectroscopic grade) or a MeCN−water (10:1, v/v) mixture at ambient temperature using 1 cm quartz cells. IR spectra were recorded in KBr pellets. The samples for elemental analysis were dried in vacuo at 80 °C. All of the obtained compounds containing perchlorate anions are nonexplosive substances.

Synthesis. *N*-Methyl-5′-formylbenzoaza-15(18)-crown-5(6) ethers,[12] salt **7**,[8] styryl dyes **1c**,[7] **2a**,[9] **2c**,[11] and **8**,[13] and cyclobutane *rctt*-**9c**[7] were synthesized according to published procedures.

*1-(2-Ammonioethyl)-4-methylpyridinium Dibromide (**3a**).* A solution of a mixture of 4-picoline (1.12 mL, 11.48 mmol) and (2-bromoethyl)ammonium bromide (2.14 g, 10.43 mmol) in absolute EtOH (20 mL) was heated at 80 °C (oil bath) for 52 h. After the solution was cooled to room temperature, the precipitate was filtered off, washed with absolute EtOH (4 × 10 mL), and dried in air to yield compound **3a** (1.89 g, 61%) as a light-beige solid: mp 234−237 °C; ^{1}H NMR (500.13 MHz, 25 °C) δ 2.63 (s, 3H, Me), 3.49 (m, 2H, CH_2NH$_3$), 4.78 (t, ^3J = 6.0 Hz, 2H, CH$_2$N), 8.04 (br s, 3H, NH$_3$), 8.05 (d, ^3J = 6.5 Hz, 2H, 3-H, 5-H), 8.88 (d, ^3J = 6.5 Hz, 2H, 2-H, 6-H) ppm; ^{13}C NMR (125.76 MHz, 30 °C) δ 21.3 (Me), 38.8 (CH$_2$NH$_3$), 56.7 (CH$_2$N), 128.4 (3-C, 5-C), 144.2 (2-C, 6-C), 159.4 (4-C) ppm. Anal. Calcd for $C_8H_{14}Br_2N_2$ (298.02): C, 32.24; H, 4.74; N, 9.40. Found: C, 31.99; H, 4.76; N, 9.21.

*1-(3-Ammoniopropyl)-4-methylpyridinium Dibromide (**3b**).* Compound **3b** (white solid; 1.27 g, 57% yield) was obtained similarly to compound **3a** by heating a mixture of 4-picoline (0.76 mL, 7.85 mmol) and (3-bromopropyl)ammonium bromide (1.56 g, 7.13 mmol) in absolute EtOH (20 mL) for 34 h: mp 216−219 °C; ^{1}H NMR (500.13 MHz, 24 °C) δ 2.19 (m, 2H, CH_2CH$_2$NH$_3$), 2.62 (s, 3H, Me), 2.84 (m, 2H, CH_2NH$_3$), 4.63 (t, ^3J = 7.1 Hz, 2H, CH$_2$N), 7.84 (br s, 3H, NH$_3$), 8.03 (d, ^3J = 6.5 Hz, 2H, 3-H, 5-H), 8.95 (d, ^3J = 6.5 Hz, 2H, 2-H, 6-H) ppm; ^{13}C NMR (125.76 MHz, 30 °C) δ 21.3 (Me), 28.4 (CH$_2$CH$_2$NH$_3$), 35.4 (CH$_2$NH$_3$), 56.7 (CH$_2$N), 128.4 (3-C, 5-C), 143.7 (2-C, 6-C), 159.0 (4-C) ppm. Anal. Calcd for $C_9H_{16}Br_2N_2$ (312.04): C, 34.64; H, 5.17; N, 8.98. Found: C, 34.37; H, 5.21; N, 8.78.

*1-(2-Ammonioethyl)-4-methylquinolinium Dibromide (**4a**).* A solution of a mixture of lepidine (1.44 mL, 10.86 mmol) and (2-bromoethyl)ammonium bromide (2.02 g, 9.87 mmol) in absolute EtOH (20 mL) was heated at 80 °C (oil bath) for 82 h. After the solution was cooled to room temperature, the precipitate was filtered off, washed with *i*-PrOH (3 × 10 mL), and dried in air to yield compound **4a** (0.83 g, 22%) as a beige solid: mp 260−262 °C dec; ^{1}H NMR (500.13 MHz, 26 °C) δ 3.04 (s, 3H, Me), 3.51 (m, 2H, CH_2NH$_3$), 5.25 (t, ^3J = 6.2 Hz, 2H, CH$_2$N), 8.07 (br s, 3H, NH$_3$), 8.09 (m, 1H, 6-H), 8.13 (d, ^3J = 6.1 Hz, 1H, 3-H), 8.29 (m, 2H, 7-H), 8.59 (d, ^3J = 9.0 Hz, 1H, 5-H), 8.62 (d, ^3J = 6.4 Hz, 1H, 8-H), 9.33 (d, ^3J = 6.1 Hz, 1H, 2-H) ppm; ^{13}C NMR (125.76 MHz, 30 °C) δ 19.7 (Me), 37.9 (CH$_2$NH$_3$), 53.7 (CH$_2$N), 119.1 (8-C), 122.8 (3-C), 127.2 (5-C), 129.1 (4a-C), 129.5 (6-C), 135.2 (7-C), 137.0 (8a-C), 149.5 (2-C), 159.4 (4-C) ppm. Anal. Calcd for $C_{12}H_{16}Br_2N_2\cdot 1.5H_2O$ (375.10): C, 38.42; H, 5.11; N, 7.47. Found: C, 38.61; H, 4.81; N, 7.74.

*1-(3-Ammoniopropyl)-4-methylquinolinium Dibromide (**4b**).* A mixture of lepidine (1.37 mL, 10.34 mmol) and (3-bromopropyl)-ammonium bromide (1.51 g, 6.90 mmol) was heated at 150 °C (oil bath) for 2 h. After the mixture was cooled, the resulting mass was treated with absolute EtOH (2 × 10 mL) and the insoluble substance was filtered off, washed with absolute EtOH (3 × 5 mL), and dried in air to yield compound **4b** (1.58 g, 63%) as a light-gray solid: mp 281−282 °C dec; ^{1}H NMR (500.13 MHz, 20 °C) δ 2.24 (m, 2H, CH_2CH$_2$NH$_3$), 2.98 (m, 2H, CH_2NH$_3$), 3.02 (s, 3H, Me), 5.09 (t, ^3J = 7.4 Hz, 2H, CH$_2$N), 7.84 (br s, 3H, NH$_3$), 8.08 (m, 1H, 6-H), 8.11 (d, ^3J = 6.0 Hz, 1H, 3-H), 8.29 (m, 1H, 7-H), 8.57 (d, ^3J = 8.4 Hz, 1H, 5-H), 8.63 (d, ^3J = 8.9 Hz, 1H, 8-H), 9.43 (d, ^3J = 6.0 Hz, 1H, 2-H) ppm; ^{13}C NMR (125.76 MHz, 30 °C) δ 19.6 (Me), 27.2 (CH$_2$CH$_2$NH$_3$), 35.8 (CH$_2$NH$_3$), 54.0 (CH$_2$N), 119.2 (8-C), 122.7 (3-C), 127.1 (5-C), 128.9 (4a-C), 129.5 (6-C), 135.0 (7-C), 136.7 (8a-C), 148.4 (2-C), 158.8 (4-C) ppm. Anal. Calcd for $C_{13}H_{18}Br_2N_2$ (362.10): C, 43.12; H, 5.01; N, 7.74. Found: C, 43.25; H, 5.11; N, 7.84.

*1-(2-Ammonioethyl)-4-methylpyridinium Diperchlorate (**5a**).* A solution of NaClO$_4$ (439 mg, 3.57 mmol) in MeOH (1 mL) was added to a hot solution of compound **3a** (442 mg, 1.48 mmol) in MeOH (12 mL), and the resulting mixture was cooled to −10 °C. The precipitate thus formed was filtered off, washed with cold absolute EtOH (2 × 5 mL), and dried in air to yield compound **5a** (320 mg, 64%) as a light-beige solid: mp 155−157 °C; ^{1}H NMR (500.13 MHz, 26 °C) δ 2.63 (s, 3H, Me), 3.48 (m, 2H, CH_2NH$_3$), 4.75 (t, ^3J = 5.7 Hz, 2H, CH$_2$N), 7.96 (br s, 3H, NH$_3$), 8.05 (d, ^3J = 6.4 Hz, 2H, 3-H, 5-H), 8.85 (d, ^3J = 6.4 Hz, 2H, 2-H, 6-H) ppm; ^{13}C NMR (125.76 MHz, 24 °C) δ 21.3 (Me), 38.8 (CH_2NH_3), 57.0 (CH_2N), 128.4 (3-C, 5-C), 144.3 (2-C, 6-C), 159.5 (4-C) ppm; IR (KBr) ν = 3400 cm^{-1} (br, NH_3). Anal. Calcd for $C_8H_{14}Cl_2N_2O_8$ (337.11): C, 28.50; H, 4.19; N, 8.31. Found: C, 28.41; H, 4.21; N, 8.37.

*1-(3-Ammoniopropyl)-4-methylpyridinium Diperchlorate (**5b**).* Compound **5b** was obtained according to a published procedure:[6] ^{13}C NMR (125.76 MHz, 24 °C) δ 21.3 (Me), 28.5 ($CH_2CH_2NH_3$), 35.7 (CH_2NH_3), 57.0 (CH_2N), 128.5 (3-C, 5-C), 143.7 (2-C, 6-C), 159.1 (4-C) ppm.

*1-(2-Ammonioethyl)-4-methylquinolinium Diperchlorate (**6a**).* A solution of $NaClO_4$ (355 mg, 2.89 mmol) in MeOH (1 mL) was added to a hot solution of compound **4a** (419 mg, 1.12 mmol) in MeOH (6 mL), and the resulting mixture was cooled to −10 °C. The precipitate thus formed was filtered off, washed with cold absolute EtOH (3 × 5 mL), and dried in air to yield compound **6a** (345 mg, 80%) as a beige solid: mp 254−256 °C dec; ^{1}H NMR (500.13 MHz, 26 °C) δ 3.04 (s, 3H, Me), 3.49 (m, 2H, CH_2NH_3), 5.20 (t, ^3J = 6.2 Hz, 2H, CH_2N), 7.95 (br s, 3H, NH_3), 8.09 (m, 1H, 6-H), 8.13 (d, ^3J = 6.4 Hz, 1H, 3-H), 8.30 (m, 2H, 7-H), 8.56 (d, ^3J = 9.1, 1H, 8-H), 8.59 (d, ^3J = 8.6, 1H, 5-H), 9.25 (d, ^3J = 6.4 Hz, 1H, 2-H) ppm; ^{13}C NMR (125.76 MHz, 25 °C) δ 19.7 (Me), 37.9 (CH_2NH_3), 54.1 (CH_2N), 118.9 (8-C), 122.7 (3-C), 127.2 (5-C), 129.1 (4a-C), 129.6 (6-C), 135.3 (7-C), 137.0 (8a-C), 149.5 (2-C), 159.6 (4-C) ppm. Anal. Calcd for $C_{12}H_{16}Cl_2N_2O_8$ (387.17): C, 37.23; H, 4.17; N, 7.24. Found: C, 36.89; H, 4.13; N, 7.23.

*1-(3-Ammoniopropyl)-4-methylquinolinium Diperchlorate (**6b**).* Perchloric acid (70%, aq) (0.25 mL, 2.90 mmol) was added to a solution of compound **4b** (260 mg, 0.72 mmol) in absolute EtOH (5 mL) ,and the resulting mixture was cooled to −10 °C. The precipitate thus formed was filtered off, washed with cold absolute EtOH (2 × 3 mL), and dried in air to yield compound **6b** (220 mg, 76%) as a light-beige solid: mp 228−230 °C dec; ^{1}H NMR (500.13 MHz, 30 °C) δ 2.23 (m, 2H, $CH_2CH_2NH_3$), 2.96 (m, 2H, CH_2NH_3), 3.03 (s, 3H, Me), 5.05 (t, ^3J = 7.3 Hz, 2H, CH_2N), 7.72 (br s, 3H, NH_3), 8.08 (m, 1H, 6-H), 8.10 (d, ^3J = 6.4 Hz, 1H, 3-H), 8.29 (m, 1H, 7-H), 8.58 (d, ^3J = 7.3 Hz, 1H, 5-H), 8.59 (d, ^3J = 7.9 Hz, 1H, 8-H), 9.35 (d, ^3J = 6.4 Hz, 1H, 2-H) ppm; ^{13}C NMR (125.76 MHz, 30 °C) δ 19.6 (Me), 27.2 ($CH_2CH_2NH_3$), 36.0 (CH_2NH_3), 54.0 (CH_2N), 119.0 (8-C), 122.8 (3-C), 127.2 (5-C), 129.0 (4a-C), 129.6 (6-C), 135.1 (7-C), 136.7 (8a-C), 148.5 (2-C), 158.9 (4-C) ppm; IR (KBr) ν = 3427 cm^{-1} (br, NH_3). Anal. Calcd for $C_{13}H_{18}Cl_2N_2O_8$ (401.20): C, 38.91; H, 4.52; N, 6.98. Found: C, 38.94; H, 4.61; N, 6.99.

*1-(2-Ammonioethyl)-4-[(E)-2-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)vinyl]pyridinium Dibromide (**1a**).* A solution of a mixture of **3a** (200 mg, 0.67 mmol), 4′-formylbenzo-18-crown-6 ether (251 mg, 0.74 mmol), and pyridine (1 mL) in absolute EtOH (10 mL) was heated at 80 °C (oil bath) for 25 h in the dark and then cooled to −10 °C, and the glassy precipitate thus formed was decanted. The precipitate was extracted with boiling benzene (6 × 15 mL), and the insoluble residue was dissolved in hot absolute EtOH (15 mL) and then cooled to −10 °C. The precipitate thus formed was filtered off and recrystallized under the same conditions to yield dye **1a** (133 mg, 31%) as a yellow solid: mp 248−252 °C dec; ^{1}H NMR (500.13 MHz, 30 °C) δ 3.49 (m, 2H, CH_2NH_3), 3.54 (s, 4H, 2 CH_2O), 3.57 (m, 4H, 2 CH_2O), 3.63 (m, 4H, 2 CH_2O), 3.78 (m, 2H, CH_2CH_2OAr), 3.81 (m, 2H, CH_2CH_2OAr), 4.17 (m, 4H, 2 CH_2OAr), 4.70 (m, 2H, CH_2N), 7.09 (d, ^3J = 8.4 Hz, 1H, 5′-H), 7.30 (dd, ^3J = 8.4 Hz, ^4J = 1.8 Hz, 1H, 6′-H), 7.41 (d, ^4J = 1.8 Hz, 1H, 2′-H), 7.44 (d, ^3J = 16.2 Hz, 1H, CH═CHPy), 7.97 (br s, 3H, NH_3), 7.99 (d, ^3J = 16.2 Hz, 1H, CH═CHPy), 8.20 (d, ^3J = 6.8 Hz, 2H, 3-H, 5-H), 8.81 (d, ^3J = 6.8 Hz, 2H, 2-H, 6-H) ppm; ^{13}C NMR (125.76 MHz, 25 °C) δ 38.8 (CH_2NH_3), 56.4 (CH_2N), 68.1 (4′-CH_2OAr), 68.2 (3′-CH_2OAr), 68.5 (CH_2CH_2OAr), 68.5 (CH_2CH_2OAr), 69.6 (CH_2O), 69.6 (CH_2O), 69.7 (2 CH_2O), 69.8 (CH_2O), 69.8 (CH_2O), 111.2 (2′-C), 112.7 (5′-C), 120.8 (CH═CHPy), 123.2 (3-C, 5-C), 123.4 (6′-C), 128.0 (1′-C), 141.6 (CH═CHPy), 144.4 (2-C, 6-C), 148.2 (3′-C), 150.5 (4′-C), 153.9 (4-C) ppm; UV−vis (MeCN−water, 10:1, v/v) λ_{max} (ε) = 262 (9300), 403 nm (29900 M^{-1}·cm^{-1}); IR (KBr) ν = 3400 cm^{-1} (br, NH_3, H_2O). Anal. Calcd for $C_{25}H_{36}Br_2N_2O_6 \cdot H_2O$ (638.39): C, 47.04; H, 6.00; N, 4.39. Found: C, 47.23; H, 6.02; N, 4.07.

*1-(2-Ammonioethyl)-4-[(E)-2-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)vinyl]pyridinium Diperchlorate (**1b**).* A solution of a mixture of **5a** (126 mg, 0.37 mmol), 4′-formylbenzo-18-crown-6 ether (140 mg, 0.41 mmol), and pyridine (1 mL) in absolute EtOH (5 mL) was heated at 80 °C (oil bath) for 20 h in the dark and then cooled to −10 °C. The precipitate thus formed was filtered off, washed with absolute EtOH (2 × 3 mL) and CH_2Cl_2 (2 × 3 mL), and redissolved in a mixture of absolute EtOH (30 mL) and MeCN (3 mL) on heating. After the resulting solution was cooled to −10 °C, the precipitate thus formed was filtered off, washed with absolute EtOH (2 × 3 mL), and dried in air in the dark to yield dye **1b** (84 mg, 35%) as a yellow solid: mp 288−290 °C dec; ^{1}H NMR (500.13 MHz, 30 °C) δ 3.48 (m, 2H, CH_2NH_3), 3.54 (s, 4H, 2 CH_2O), 3.57 (m, 4H, 2 CH_2O), 3.63 (m, 4H, 2 CH_2O), 3.78 (m, 2H, CH_2CH_2OAr), 3.81 (m, 2H, CH_2CH_2OAr), 4.18 (m, 4H, 2 CH_2OAr), 4.68 (m, 2H, CH_2N), 7.09 (d, ^3J = 8.5 Hz, 1H, 5′-H), 7.30 (br d, ^3J = 8.5 Hz, 1H, 6′-H), 7.40 (br s, 1H, 2′-H), 7.43 (d, ^3J = 15.9 Hz, 1H, CH═CHPy), 7.91 (br s, 3H, NH_3), 7.99 (d, ^3J = 15.9 Hz, 1H, CH═CHPy), 8.20 (d, ^3J = 6.7 Hz, 2H, 3-H, 5-H), 8.79 (d, ^3J = 6.7 Hz, 2H, 2-H, 6-H) ppm; ^{13}C NMR (125.76 MHz, 30 °C) δ 38.8 (CH_2NH_3), 56.8 (CH_2N), 68.1 (2 CH_2OAr), 68.5 (CH_2CH_2OAr), 68.5 (CH_2CH_2OAr), 69.6 (CH_2O), 69.6 (CH_2O), 69.7 (2 CH_2O), 69.8 (CH_2O), 69.8 (CH_2O), 111.3 (2′-C), 112.8 (5′-C), 120.7 (CH═CHPy), 123.2 (3-C, 5-C), 123.3 (6′-C), 127.9 (1′-C), 141.6 (CH═CHPy), 144.4 (2-C, 6-C), 148.3 (3′-C), 150.6 (4′-C), 153.9 (4-C) ppm; UV−vis (MeCN) λ_{max} (ε) = 262 (10000), 383 nm (33600 M^{-1}·cm^{-1}). Anal. Calcd for $C_{25}H_{36}Cl_2N_2O_{14}$ (659.46): C, 45.53; H, 5.50; N, 4.25. Found: C, 45.44; H, 5.54; N, 4.21.

*1-(3-Ammoniopropyl)-4-[(E)-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)vinyl]pyridinium Diperchlorate (**1d**).* A solution of a mixture of compound **5b** (100 mg, 0.29 mmol), 4′-formylbenzo-15-crown-5 ether (93 mg, 0.31 mmol), and pyridine (1 mL) in absolute EtOH (5 mL) was heated at 80 °C (oil bath) for 25 h in the dark and then cooled to 20 °C. The precipitate thus formed was filtered off, washed with absolute EtOH (2 × 3 mL) and CH_2Cl_2 (5 mL), and dried in air in the dark to yield dye **1d** (144 mg, 79%) as a yellow solid: mp 170−172 °C dec; ^{1}H NMR (500.13 MHz, 30 °C) δ 2.17 (m, 2H, $CH_2CH_2NH_3$), 2.85 (m, 2H, CH_2NH_3), 3.63 (m, 8H, 4 CH_2O), 3.79 (m, 2H, CH_2CH_2OAr), 3.82 (m, 2H, CH_2CH_2OAr), 4.14 (m, 4H, 2 CH_2OAr), 4.53 (m, 2H, CH_2N), 7.07 (d, ^3J = 8.6 Hz, 1H, 5′-H), 7.30 (br d, ^3J = 8.6 Hz, 1H, 6′-H), 7.39 (br s, 1H, 2′-H), 7.40 (d, ^3J = 16.5 Hz, 1H, CH═CHPy), 7.70 (br s, 3H, NH_3), 7.95 (d, ^3J = 16.5 Hz, 1H, CH═CHPy), 8.18 (d, ^3J = 6.5 Hz, 2H, 3-H, 5-H), 8.85 (d, ^3J = 6.5 Hz, 2H, 2-H, 6-H) ppm; ^{13}C NMR (125.76 MHz, 30 °C) δ 28.4 ($CH_2CH_2NH_3$), 35.7 (CH_2NH_3), 56.6 (CH_2N), 68.2 (CH_2OAr), 68.5 (CH_2CH_2OAr), 68.6 (CH_2OAr), 68.7 (CH_2CH_2OAr), 69.5 (CH_2O), 69.6 (CH_2O), 70.4 (CH_2O), 70.4 (CH_2O), 112.0 (2′-C), 113.2 (5′-C), 120.8 (CH═CHPy), 123.3 (3-C, 5-C), 123.5 (6′-C), 128.0 (1′-C), 141.4 (CH═CHPy), 143.9 (2-C, 6-C), 148.7 (3′-C), 151.0 (4′-C), 153.5 (4-C) ppm; UV−vis (MeCN) λ_{max} (ε) = 262 (9700), 404 nm (29200 M^{-1}·cm^{-1}); IR (KBr) ν = 3421 cm^{-1} (br, NH_3). Anal. Calcd for $C_{24}H_{34}Cl_2N_2O_{13}$ (629.44): C, 45.80; H, 5.44; N, 4.45. Found: C, 45.68; H, 5.59; N, 4.47.

*1-(2-Ammonioethyl)-4-[(E)-2-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)vinyl]quinolinium Dibromide (**1e**).* A solution of a mixture of **4a** (72 mg, 0.19 mmol), 4′-formylbenzo-18-crown-6 ether (84 mg, 0.25 mmol), and pyridine (0.5 mL) in absolute EtOH (10 mL) was heated at 80 °C (oil bath) for 24 h in the dark, and then the solvent was thoroughly evaporated in vacuo. The residue was heated with absolute EtOH (7 mL) at 70 °C, and then the mixture was cooled to 5 °C. The precipitate thus formed was filtered off, washed with cold absolute EtOH (2 × 1.5 mL) and benzene (2 × 5 mL), and dried in air in the dark to yield dye **1e** (88 mg, 67%) as a red solid: mp 254−255 °C dec; ^{1}H NMR (500.13 MHz, 26 °C) δ 3.51 (m, 2H, CH_2NH_3), 3.54 (s, 4H, 2 CH_2O), 3.58 (m, 4H, 2 CH_2O), 3.64 (m, 4H, 2 CH_2O), 3.79 (m, 2H, 4′-CH_2CH_2OAr), 3.84 (m, 2H, 3′-CH_2CH_2OAr), 4.20 (m, 2H, 4′-CH_2OAr), 4.27 (m, 2H, 3′-CH_2OAr), 5.17 (t, ^3J = 6.0 Hz, 2H, CH_2N), 7.12 (d, ^3J = 8.5 Hz, 1H, 5′-H), 7.50 (dd, ^3J = 8.5 Hz, ^4J = 1.7 Hz, 1H, 6′-H), 7.71 (d, ^4J = 1.7 Hz, 1H, 2′-H), 8.02 (br s, 3H, NH_3), 8.07 (m, 1H, 6-H), 8.20 (d, ^3J = 15.8 Hz, 1H, CH=CHHet), 8.25 (d, ^3J = 15.8 Hz, 1H, CH=CHHet), 8.28 (m, 1H, 7-H), 8.51 (d, ^3J = 6.7 Hz, 1H, 3-H), 8.53 (d, ^3J = 8.4 Hz, 1H, 8-H), 9.13 (d, ^3J = 8.6 Hz, 1H, 5-H), 9.20 (d, ^3J = 6.7 Hz, 1H, 2-H) ppm; ^{13}C NMR (125.76 MHz, 30 °C) δ 37.8 (CH_2NH_3), 53.2 (CH_2N), 68.2 (4′-CH_2OAr), 68.2 (3′-CH_2OAr, 4′-CH_2CH_2OAr), 68.6 (3′-CH_2CH_2OAr), 69.5 (CH_2O), 69.6 (CH_2O), 69.7 (2 CH_2O), 69.8 (2 CH_2O), 111.7 (2′-C), 112.5 (5′-C), 115.6 (3-C), 117.0 (CH=CHHet), 118.7 (8-C), 124.8 (6′-C), 126.6 (4a-C), 127.0 (5-C), 128.3 (1′-C), 128.8 (6-C), 135.1 (7-C), 138.1 (8a-C), 144.2 (CH=CHHet), 147.8 (2-C), 148.3 (3′-C), 151.0 (4′-C), 153.9 (4-C) ppm; UV–vis (MeCN–water, 10:1, v/v) λ_{max} (ε) = 247 (17600), 284 (10600), 449 nm (28200 M^{-1}·cm^{-1}). Anal. Calcd for $C_{29}H_{38}Br_2N_2O_6 \cdot 1.5H_2O$ (697.45): C, 49.94; H, 5.93; N, 4.02. Found: C, 49.82; H, 6.04; N, 3.98.

*1-(2-Ammonioethyl)-4-[(E)-2-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)vinyl]quinolinium Diperchlorate (**1f**).* A solution of a mixture of **6a** (78 mg, 0.20 mmol), 4′-formylbenzo-18-crown-6 ether (82 mg, 0.24 mmol), and pyridine (0.5 mL) in absolute EtOH (10 mL) was heated at 80 °C (oil bath) for 27 h in the dark, and then the mixture was cooled to room temperature. The precipitate thus formed was filtered off and washed with absolute EtOH (2 × 5 mL) and benzene (10 mL) to give crude **1f** (99 mg). This substance was extracted with boiling MeCN (3 × 30 mL), and the hot mother solutions were filtered and then evaporated in vacuo. The residue was washed with water (30 mL) at 5 °C for 8 days, and then the insoluble substance was filtered off and dried in air in the dark to yield dye **1f** (47 mg, 33%) as a yellow-orange solid: mp > 290 °C dec; ^{1}H NMR (500.13 MHz, 23 °C) δ 3.49 (m, 2H, CH_2NH_3), 3.54 (s, 4H, 2 CH_2O), 3.57 (m, 4H, 2 CH_2O), 3.64 (m, 4H, 2 CH_2O), 3.79 (m, 2H, 4′-CH_2CH_2OAr), 3.84 (m, 2H, 3′-CH_2CH_2OAr), 4.20 (m, 2H, 4′-CH_2OAr), 4.27 (m, 2H, 3′-CH_2OAr), 5.13 (t, ^3J = 5.9 Hz, 2H, CH_2N), 7.13 (d, ^3J = 8.5 Hz, 1H, 5′-H), 7.49 (dd, ^3J = 8.5 Hz, ^4J = 1.8 Hz, 1H, 6′-H), 7.70 (d, ^4J = 1.8 Hz, 1H, 2′-H), 7.95 (br s, 3H, NH_3), 8.08 (m, 1H, 6-H), 8.19 (d, ^3J = 15.7 Hz, 1H, CH=CHHet), 8.25 (d, ^3J = 15.7 Hz, 1H, CH=CHHet), 8.29 (m, 1H, 7-H), 8.50 (d, ^3J = 9.1 Hz, 1H, 8-H), 8.51 (d, ^3J = 6.5 Hz, 1H, 3-H), 9.13 (d, ^3J = 8.6 Hz, 1H, 5-H), 9.14 (d, ^3J = 6.5 Hz, 1H, 2-H) ppm; ^{13}C NMR (125.76 MHz, 30 °C) δ 37.8 (CH_2NH_3), 53.6 (CH_2N), 68.1 (4′-CH_2OAr), 68.3 (3′-CH_2OAr), 68.4 (4′-CH_2CH_2OAr), 68.6 (3′-CH_2CH_2OAr), 69.5 (CH_2O), 69.6 (CH_2O), 69.7 (2 CH_2O), 69.8 (CH_2O), 69.8 (CH_2O), 111.6 (2′-C), 112.5 (5′-C), 115.5 (3-C), 117.0 (CH=CHHet), 118.5 (8-C), 124.8 (6′-C), 126.6 (4a-C), 126.9 (5-C), 128.2 (1′-C), 128.9 (6-C), 135.2 (7-C), 138.1 (8a-C), 144.2 (CH=CHHet), 147.8 (2-C), 148.3 (3′-C), 151.0 (4′-C), 154.0 (4-C) ppm; UV–vis (MeCN–water, 10:1, v/v) λ_{max} (ε) = 240 (19000), 284 (10400), 448 nm (25400 M^{-1}·cm^{-1}). Anal. Calcd for $C_{29}H_{38}Cl_2N_2O_{14}$ (709.52): C, 49.09; H, 5.40; N, 3.95. Found: C, 48.98; H, 5.35; N, 4.06.

*1-(3-Ammoniopropyl)-4-[(E)-2-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)vinyl]quinolinium Diperchlorate (**1g**).* Dye **1g** (orange solid; 102 mg, 78% yield) was obtained similarly to dye **1d** using compound **6b** (70 mg, 0.18 mmol) and 4′-formylbenzo-18-crown-6 ether (65 mg, 0.19 mmol): mp 302–304 °C dec; ^{1}H NMR (500.13 MHz, 30 °C) δ 2.25 (m, 2H, $CH_2CH_2NH_3$), 2.99 (m, 2H, CH_2NH_3), 3.56 (s, 4H, 2 CH_2O), 3.59 (m, 4H, 2 CH_2O), 3.65 (m, 4H, 2 CH_2O), 3.79 (m, 2H, 4′-CH_2CH_2OAr), 3.84 (m, 2H, 3′-CH_2CH_2OAr), 4.16 (m, 2H, 4′-CH_2OAr), 4.23 (m, 2H, 3′-CH_2OAr), 5.01 (t, ^3J = 7.0 Hz, 2H, CH_2N), 7.02 (d, ^3J = 8.4 Hz, 1H, 5′-H), 7.42 (br d, ^3J = 8.4 Hz, 1H, 6′-H), 7.60 (br s, 1H, 2′-H), 7.69 (br s, 3H, NH_3), 8.04 (m, 1H, 6-H), 8.10 (d, ^3J = 15.8 Hz, 1H, CH=CHHet), 8.14 (d, ^3J = 15.8 Hz, 1H, CH=CHHet), 8.27 (m, 1H, 7-H), 8.43 (d, ^3J = 6.6 Hz, 1H, 3-H), 8.52 (d, ^3J = 8.9 Hz, 1H, 8-H), 9.05 (d, ^3J = 8.5 Hz, 1H, 5-H), 9.24 (d, ^3J = 6.6 Hz, 1H, 2-H) ppm; ^{13}C NMR (125.76 MHz, 30 °C) δ 27.1 ($CH_2CH_2NH_3$), 36.1 (CH_2NH_3), 53.5 (CH_2N), 68.1 (4′-CH_2OAr), 68.3 (3′-CH_2OAr), 68.4 (4′-CH_2CH_2OAr), 68.6 (3′-CH_2CH_2OAr), 69.5 (CH_2O), 69.6 (CH_2O), 69.7 (2 CH_2O), 69.8 (CH_2O), 69.8 (CH_2O), 111.6 (2′-C), 112.5 (5′-C), 115.7 (3-C), 117.1 (CH=CHHet), 118.7 (8-C), 124.6 (6′-C), 126.6 (4a-C), 126.9 (5-C), 128.3 (1′-C), 128.9 (6-C), 135.1 (7-C), 137.8 (8a-C), 143.8 (CH=CHHet), 147.0 (2-C), 148.2 (3′-C), 150.8 (4′-C), 153.4 (4-C) ppm; UV–vis (MeCN) λ_{max} (ε) = 240 (17900), 280 (10400), 330 (6200), 420 nm (28600 M^{-1}·cm^{-1}); IR (KBr) ν = 3412 cm^{-1} (br, NH_3). Anal. Calcd for $C_{30}H_{40}Cl_2N_2O_{14}$ (723.55): C, 49.80; H, 5.57; N, 3.87. Found: C, 49.69; H, 5.47; N, 3.78.

*1-(3-Ammoniopropyl)-4-[(E)-2-(13-methyl-2,3,5,6,8,9,12,13-octahydro-11H-1,4,7,10,13-benzotetraoxazacyclopentadecin-16-yl)vinyl]pyridinium Diperchlorate (**1i**).* A solution of a mixture of compound **5b** (30 mg, 86 μmol), N-methyl-5′-formylbenzoaza-15-crown-5 ether (32 mg, 104 μmol), and pyridine (1 mL) in absolute EtOH (5 mL) was heated at 80 °C (oil bath) for 40 h in the dark, and then the solvent was evaporated in vacuo. The residue was washed with hot benzene (2 × 5 mL) and then dissolved in a mixture of absolute EtOH (5 mL) and MeCN (1 mL) on heating. After the resulting solution was cooled to −10 °C, the precipitate thus formed was filtered off, washed with cold absolute EtOH (2 × 3 mL), and dried in air to yield dye **1i** (26 mg, 47%) as a dark-red solid: mp 178 °C; ^{1}H NMR (500.13 MHz, 19 °C) δ 2.15 (m, 2H, $CH_2CH_2NH_3$), 2.83 (m, 5H, MeN, CH_2NH_3), 3.23 (t, ^3J = 7.3 Hz, 2H, CH_2NMe), 3.58 (s, 4H, 2 CH_2O), 3.62 (m, 4H, 2 CH_2O), 3.85 (m, 2H, CH_2CH_2OAr), 3.86 (t, ^3J = 7.3 Hz, 2H, CH_2CH_2NMe), 4.17 (m, 2H, CH_2OAr), 4.49 (t, ^3J = 7.0 Hz, 2H, CH_2N), 6.89 (d, ^3J = 8.5 Hz, 1H, 5′-H), 7.22 (dd, ^3J = 8.5 Hz, ^4J = 1.6 Hz, 1H, 6′-H), 7.29 (d, ^4J = 1.6 Hz, 1H, 2′-H), 7.34 (d, ^3J = 16.2 Hz, 1H, CH=CHPy), 7.71 (br s, 3H, NH_3), 7.94 (d, ^3J = 16.2 Hz, 1H, CH=CHPy), 8.14 (d, ^3J = 6.8 Hz, 2H, 3-H, 5-H), 8.80 (d, ^3J = 6.8 Hz, 2H, 2-H, 6-H) ppm; ^{13}C NMR (125.76 MHz, 30 °C) δ 28.4 ($CH_2CH_2NH_3$), 35.7 (CH_2NH_3), 39.6 (Me), 54.6 (CH_2NMe), 56.4 (CH_2N), 67.8 (CH_2OAr), 68.2 (CH_2O), 68.6 (CH_2O), 68.8 (CH_2O), 69.0 (2 CH_2O), 70.0 (CH_2O), 110.4 (2′-C), 116.3 (5′-C), 119.3 (CH=CHPy), 122.9 (3-C, 5-C), 123.4 (6′-C), 126.8 (1′-C), 141.9 (CH=CHPy), 143.7 (2-C, 6-C), 144.5 (4′-C), 150.0 (3′-C), 153.7 (4-C) ppm; UV–vis (MeCN) λ_{max} (ε) = 273 (8700), 297 (9200), 469 nm (21900 M^{-1}·cm^{-1}). Anal. Calcd for $C_{25}H_{37}Cl_2N_3O_{12}$ (642.48): C, 46.74; H, 5.81; N, 6.54. Found: C, 46.89; H, 5.76; N, 6.47.

*1-(3-Ammoniopropyl)-4-[(E)-2-(16-methyl-2,3,5,6,8,9,11,12,15,16-decahydro-14H-1,4,7,10,13,16-benzopentaoxazacyclooctadecin-19-yl)vinyl]pyridinium Diperchlorate (**1h**).* Dye **1h** (red-orange solid; 58 mg, 65% yield) was obtained similarly to dye **1i** using compound **5b** (44 mg, 0.13 mmol) and N-methyl-5′-formylbenzoaza-18-crown-6 ether (53 mg, 0.15 mmol): mp 195–196 °C dec; ^{1}H NMR (500.13 MHz, 30 °C) δ 2.15 (m, 2H, $CH_2CH_2NH_3$), 2.83 (m, 2H, CH_2NH_3), 2.90 (s, 3H, MeN), 3.41 (t, ^3J = 5.9 Hz, 2H, CH_2NMe), 3.53 (m, 4H, 2 CH_2O), 3.55 (s, 4H, 2 CH_2O), 3.61 (m, 4H, 2 CH_2O), 3.71 (t, ^3J = 5.9 Hz, 2H, CH_2CH_2NMe), 3.84 (m, 2H, CH_2CH_2OAr), 4.17 (m, 2H, CH_2OAr), 4.49 (t, ^3J = 6.9 Hz, 2H, CH_2N), 6.86 (d, ^3J = 8.7 Hz, 1H, 5′-H), 7.23 (br d, ^3J = 8.7 Hz, 1H, 6′-H), 7.30 (br s, 1H, 2′-H), 7.33 (d, ^3J = 16.1 Hz, 1H, CH=CHPy), 7.70 (br s, 3H, NH_3), 7.94 (d, ^3J = 16.1 Hz, 1H, CH=CHPy), 8.13 (d, ^3J = 6.6 Hz, 2H, 3-H, 5-H), 8.79 (d, ^3J = 6.6 Hz, 2H, 2-H, 6-H) ppm; ^{13}C NMR (125.76 MHz, 30 °C) δ 28.4 ($CH_2CH_2NH_3$), 35.8 (CH_2NH_3), 40.2 (Me), 53.9 (CH_2NMe), 56.4 (CH_2N), 67.4 (CH_2OAr), 68.8 (CH_2CH_2OAr), 69.3 (CH_2O), 69.4 (CH_2O), 69.7 (CH_2O), 69.9 (2 CH_2O), 70.1 (CH_2O), 70.4 (CH_2O), 110.8 (2′-C), 116.5 (5′-C), 119.2 (CH=CHPy), 122.9 (3-C, 5-C), 123.6 (6′-C), 126.6 (1′-C), 141.9 (CH=CHPy), 143.7 (2-C, 6-C), 144.1 (4′-C), 149.6 (3′-C), 153.7 (4-C) ppm; UV–vis (MeCN) λ_{max} (ε) = 391 (21300 M^{-1}·cm^{-1}). Anal. Calcd for $C_{27}H_{41}Cl_2N_3O_{13}$ (686.53): C, 47.24; H, 6.02; N, 6.12. Found: C, 47.18; H, 5.89; N, 6.07.

*1-Ethyl-4-[(E)-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)vinyl]pyridinium Perchlorate (**2b**).* Dye **2b** was obtained according to a published procedure:[10] ^{13}C NMR (125.76 MHz, 30 °C) δ 16.0 (Me), 55.0 (CH_2N), 68.2 (4′-CH_2OAr), 68.5 (3′-CH_2OAr, 4′-CH_2CH_2OAr), 68.6 (3′-CH_2CH_2OAr), 69.5 (CH_2O), 69.6 (CH_2O), 70.4 (CH_2O), 70.4 (CH_2O), 111.8 (2′-C), 113.1 (5′-C), 120.8 (CH=CHPy), 123.2 (3-C, 5-C), 123.3 (6′-C), 128.0 (1′-C), 141.0 (CH═CHPy), 143.7 (2-C, 6-C), 148.6 (3′-C), 150.9 (4′-C), 153.1 (4-C) ppm; UV−vis (MeCN) λ_{max} (ε) = 260 (9600), 273 (8400), 397 nm (30400 $M^{-1}\cdot cm^{-1}$).

*1-Ethyl-4-[(E)-2-(16-methyl-2,3,5,6,8,9,11,12,15,16-decahydro-14H-1,4,7,10,13,16-benzopentaoxazacyclooctadecin-19-yl)vinyl]pyridinium Perchlorate (**2d**).* A solution of a mixture of compound **7** (14 mg, 63 μmol), *N*-methyl-5′-formylbenzoaza-18-crown-6 ether (28 mg, 79 μmol), and pyrrolidine (20 μL) in absolute EtOH (3 mL) was heated at 80 °C (oil bath) for 22 h in the dark and then evaporated in vacuo. The residue was washed with hot benzene (4 × 5 mL) and dissolved in absolute EtOH (1 mL) on heating. The resulting solution was cooled to −10 °C, and the oily precipitate thus formed was decanted, washed with cold absolute EtOH (1 mL), and dried in vacuo at 60 °C to yield dye **2d** (32 mg, 88%) as a dark-red solid: mp 66−68 °C; ^1H NMR (500.13 MHz, 28 °C) δ 1.51 (t, ^3J = 7.2 Hz, 3H, $MeCH_2$), 2.89 (s, 3H, MeN), 3.40 (t, ^3J = 6.0 Hz, 2H, CH_2NMe), 3.53 (m, 4H, 2 CH_2O), 3.55 (s, 4H, 2 CH_2O), 3.61 (m, 4H, 2 CH_2O), 3.71 (t, ^3J = 6.0 Hz, 2H, CH_2CH_2NMe), 3.84 (m, 2H, CH_2CH_2OAr), 4.17 (m, 2H, CH_2OAr), 4.47 (q, ^3J = 7.2 Hz, 2H, CH_2Me), 6.86 (d, ^3J = 8.3 Hz, 1H, 5′-H), 7.22 (dd, ^3J = 8.3 Hz, ^4J = 1.8 Hz, 1H, 6′-H), 7.30 (d, ^4J = 1.8 Hz, 1H, 2′-H), 7.32 (d, ^3J = 16.3 Hz, 1H, CH═CHPy), 7.92 (d, ^3J = 16.3 Hz, 1H, CH═CHPy), 8.10 (d, ^3J = 6.7 Hz, 2H, 3-H, 5-H), 8.84 (d, ^3J = 6.7 Hz, 2H, 2-H, 6-H) ppm; ^{13}C NMR (125.76 MHz, 25 °C) δ 16.0 ($MeCH_2$), 40.2 (MeN), 53.9 (CH_2NMe), 54.8 (CH_2Me), 67.3 (CH_2OAr), 68.9 (CH_2CH_2OAr), 69.3 (CH_2O), 69.5 (CH_2O), 69.7 (CH_2O), 69.9 (2 CH_2O), 70.2 (CH_2O), 70.4 (CH_2O), 110.6 (2′-C), 116.4 (5′-C), 119.2 (CH═CHPy), 122.8 (3-C, 5-C), 123.5 (6′-C), 126.6 (1′-C), 141.5 (CH═CHPy), 143.5 (2-C, 6-C), 144.0 (4′-C), 149.6 (3′-C), 153.3 (4-C) ppm; UV−vis (MeCN) λ_{max} (ε) = 271 (14200), 292 (14200), 462 nm (33100 $M^{-1}\cdot cm^{-1}$). Anal. Calcd for $C_{26}H_{37}ClN_2O_9\cdot H_2O$ (575.05): C, 54.30; H, 6.84; N, 4.87. Found: C, 54.21; H, 6.66; N, 4.95.

*1-Ethyl-4-[(E)-2-(13-methyl-2,3,5,6,8,9,12,13-octahydro-11H-1,4,7,10,13-benzotetraoxazacyclopentadecin-16-yl)vinyl]pyridinium Perchlorate (**2e**).* A solution of a mixture of compound **7** (31 mg, 0.14 mmol), *N*-methyl-5′-formylbenzoaza-15-crown-5 ether (57 mg, 0.19 mmol), and pyrrolidine (40 μL) in absolute EtOH (7 mL) was heated at 80 °C (oil bath) for 50 h in the dark and then evaporated in vacuo. The residue was washed with a mixture of benzene−MeCN (20:1, v/v) (4 × 5 mL) and dried in air to yield dye **2e** (38 mg, 50%) as a dark-red solid: mp 157−159 °C; ^1H NMR (500.13 MHz, 30 °C) δ 1.52 (t, ^3J = 7.2 Hz, 3H, $MeCH_2$), 2.83 (s, 3H, MeN), 3.24 (t, ^3J = 7.2 Hz, 2H, CH_2NMe), 3.58 (s, 4H, 2 CH_2O), 3.62 (m, 4H, 2 CH_2O), 3.85 (m, 4H, CH_2CH_2OAr, CH_2CH_2NMe), 4.18 (m, 2H, CH_2OAr), 4.48 (t, ^3J = 7.2 Hz, 2H, CH_2N), 6.88 (d, ^3J = 8.3 Hz, 1H, 5′-H), 7.22 (dd, ^3J = 8.3 Hz, ^4J = 1.8 Hz, 1H, 6′-H), 7.29 (d, ^4J = 1.8 Hz, 1H, 2′-H), 7.31 (d, ^3J = 16.3 Hz, 1H, CH═CHPy), 7.91 (d, ^3J = 16.3 Hz, 1H, CH═CHPy), 8.09 (d, ^3J = 6.5 Hz, 2H, 3-H, 5-H), 8.83 (d, ^3J = 6.5 Hz, 2H, 2-H, 6-H) ppm; ^{13}C NMR (125.76 MHz, 30 °C) δ 16.0 ($MeCH_2$), 39.3 (MeN), 54.6 (CH_2NMe), 54.8 (CH_2Me), 67.7 (CH_2OAr), 68.2 (CH_2O), 68.6 (CH_2O), 68.7 (CH_2O), 69.0 (CH_2O), 69.0 (CH_2O), 70.0 (CH_2O), 110.3 (2′-C), 116.2 (5′-C), 119.3 (CH═CHPy), 122.8 (3-C, 5-C), 123.2 (6′-C), 126.8 (1′-C), 141.5 (CH═CHPy), 143.4 (2-C, 6-C), 144.4 (4′-C), 149.9 (3′-C), 153.3 (4-C) ppm; UV−vis (MeCN) λ_{max} (ε) = 271 (11600), 290 (11400), 458 nm (24000 $M^{-1}\cdot cm^{-1}$). Anal. Calcd for $C_{24}H_{33}ClN_2O_8\cdot 0.25MeCN\cdot H_2O$ (541.26): C, 54.37; H, 6.66; N, 5.82. Found: C, 54.37; H, 6.59; N, 5.81.

*4,4′-(c-2,t-4-Di-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-ylcyclobutane-r-1,t-3-diyl)bis[1-(3-ammoniopropyl)pyridinium] Tetraperchlorate (rctt-**9d**).* A solution of dye **1d** (14.1 mg, 22.4 μmol) in MeCN (15 mL, $C = 1.5 \times 10^{-3}$ M) in a glass flask was irradiated with unfiltered light from a 60 W incandescent lamp from a distance of 15 cm for 20 h. The resulting solution was evaporated in vacuo to give cyclobutane *rctt*-**9d** (in quantitative yield) as a yellow solid: mp 243−246 °C dec; ^1H NMR (500.13 MHz, 30 °C) δ 2.09 (m, 4H, 2 $CH_2CH_2NH_3$), 2.49 (m, 4H, 2 CH_2NH_3), 3.57−3.68 (m, 16H, 8 CH_2O), 3.74 (m, 4H, 2 4′-CH_2CH_2OAr), 3.77 (m, 4H, 2 3′-CH_2CH_2OAr), 3.92 (m, 4H, 2 3′-CH_2OAr), 3.96 (m, 4H, 2 4′-CH_2OAr), 4.55 (t, ^3J = 6.6 Hz, 4H, 2 CH_2N), 4.83 (dd, ^3J = 9.5 Hz, ^3J = 8.2 Hz, 2H, 2 CHAr), 4.96 (dd, ^3J = 9.5 Hz, ^3J = 8.2 Hz, 2H, 2 CHPy), 6.70 (d, ^4J = 1.9 Hz, 2H, 2 2′-H), 6.82 (d, ^3J = 8.1 Hz, 2H, 2 5′-H), 6.88 (dd, ^3J = 8.1 Hz, ^4J = 1.9 Hz, 2H, 2 6′-H), 7.50 (br s, 6H, 2 NH_3), 7.97 (d, ^3J = 6.8 Hz, 4H, 2 3-H, 2 5-H), 8.82 (d, ^3J = 6.8 Hz, 4H, 2 2-H, 2 6-H) ppm; ^{13}C NMR (125.76 MHz, 30 °C) δ 28.1 (2 $CH_2CH_2NH_3$), 35.5 (2 CH_2NH_3), 44.6 (2 CHAr), 45.7 (2 CHPy), 57.1 (2 CH_2N), 67.6 (2 4′-CH_2OAr), 67.6 (2 3′-CH_2OAr), 67.9 (4 CH_2CH_2OAr), 68.5 (2 CH_2O), 68.5 (2 CH_2O), 69.5 (4 CH_2O), 112.9 (2 5′-C), 113.0 (2 2′-C), 120.5 (2 6′-C), 127.2 (2 3-C, 2 5-C), 130.4 (2 1′-C), 143.4 (2 2-C, 2 6-C), 146.9 (2 4′-C), 147.6 (2 3′-C), 160.6 (2 4-C) ppm; UV−vis (MeCN) λ_{max} (ε) = 231 (31700), 283 nm (5800 $M^{-1}\cdot cm^{-1}$); IR (KBr) ν = 3417 cm^{-1} (br, NH_3). Anal. Calcd for $C_{48}H_{68}Cl_4N_4O_{26}\cdot 2H_2O$ (1294.91): C, 44.52; H, 5.60; N, 4.33. Found: C, 44.65; H, 5.72; N, 3.98.

*4,4′-(c-2,t-4-Di-2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-ylcyclobutane-r-1,t-3-diyl)bis[1-(2-ammonioethyl)pyridinium] Tetraperchlorate (rctt-**9b**).* Cyclobutane *rctt*-**9b** (yellow solid, quantitative yield) was obtained similarly to cyclobutane *rctt*-**9d** using dye **1b** (10.0 mg, 15.2 μmol) and irradiation for 20 h: mp 229−233 °C dec; ^1H NMR (500.13 MHz, 30 °C) δ 3.38 (m, 4H, 2 CH_2NH_3), 3.52 (m, 12H, 6 CH_2O), 3.56 (m, 8H, 4 CH_2O), 3.61 (m, 4H, 2 CH_2O), 3.70 (m, 4H, 2 CH_2CH_2OAr), 3.74 (m, 4H, 2 CH_2CH_2OAr), 3.95 (m, 4H, 2 CH_2OAr), 4.01 (m, 4H, 2 CH_2OAr), 4.69 (m, 4H, 2 CH_2N), 4.80 (dd, ^3J = 9.5 Hz, ^3J = 8.6 Hz, 2H, 2 CHAr), 4.93 (dd, ^3J = 9.5 Hz, ^3J = 8.6 Hz, 2H, 2 CHPy), 6.78 (m, 4H, 2 5′-H, 2 6′-H), 6.88 (br s, 2H, 2 2′-H), 7.85 (br s, 6H, 2 NH_3), 8.02 (d, ^3J = 6.8 Hz, 4H, 2 3-H, 2 5-H), 8.79 (d, ^3J = 6.8 Hz, 4H, 2 2-H, 2 6-H) ppm; ^{13}C NMR (125.76 MHz, 30 °C) δ 38.7 (2 CH_2NH_3), 45.2 (2 CHAr), 46.1 (2 CHPy), 57.2 (2 CH_2N), 67.7 (2 CH_2OAr), 68.0 (2 CH_2OAr), 68.6 (4 CH_2CH_2OAr), 69.6 (2 CH_2O), 69.6 (6 CH_2O), 69.7 (4 CH_2O), 112.3 (2 5′-C), 112.9 (2 2′-C), 119.9 (2 6′-C), 127.1 (2 3-C, 2 5-C), 129.8 (2 1′-C), 144.2 (2 2-C, 2 6-C), 147.1 (2 4′-C), 147.8 (2 3′-C), 160.9 (2 4-C) ppm; UV−vis (MeCN) λ_{max} (ε) = 231 (33700), ∼284 nm (shoulder, 6600 $M^{-1}\cdot cm^{-1}$); IR (KBr) ν = 3484 cm^{-1} (br, NH_3). Anal. Calcd for $C_{50}H_{72}Cl_4N_4O_{28}$ (1318.93): C, 45.53; H, 5.50; N, 4.25. Found: C, 45.48; H, 5.60; N, 4.35.

*4,4′-(c-2,t-4-Di-2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-ylcyclobutane-r-1,t-3-diyl)bis[1-(2-ammonioethyl)quinolinium] Tetrabromide (rctt-**9e**).* A dispersion of dye **1e** (11.7 mg, 16.8 μmol) in a mixture of MeCN (16 mL) and water (0.5 mL) in a glass flask was irradiated with unfiltered light from a 60 W incandescent lamp from a distance of 15 cm for 115 h. The insoluble substance was filtered off and dried in air to yield cyclobutane *rctt*-**9e** (8.1 mg, 72%) as a yellow solid: mp 257−258 °C dec; ^1H NMR (500.13 MHz, 23 °C) δ 3.30−3.45 (m, 4H, 2 CH_2NH_3), 3.45−3.63 (m, 32H, 16 CH_2O), 3.76−3.87 (m, 8H, 4 CH_2OAr), 5.05 (m, 2H, 2 CHH′N), 5.44 (m, 2H, 2 CHH′N), 5.51 (dd, ^3J = 9.0 Hz, ^3J = 7.4 Hz, 2H, 2 CHAr), 5.55 (dd, ^3J = 9.0 Hz, ^3J = 7.4 Hz, 2H, 2 CHHet), 6.58 (d, ^3J = 8.4 Hz, 2H, 2 5′-H), 6.94 (br s, 2H, 2 2′-H), 6.99 (br d, ^3J = 8.4 Hz, 2H, 2 6′-H), 7.99 (br s, 6H, 2 NH_3), 8.05 (m, 2H, 2 6-H), 8.23 (m, 2H, 2 7-H), 8.48 (d, ^3J = 9.1 Hz, 2H, 2 8-H), 8.57 (d, ^3J = 6.3 Hz, 2H, 2 3-H), 8.98 (d, ^3J = 8.7 Hz, 2H, 2 5-H), 9.40 (d, ^3J = 6.3 Hz, 2H, 2 2-H) ppm; ^{13}C NMR (125.76 MHz, 25 °C) δ 37.8 (2 CH_2NH_3), 45.5 and 45.6 (2 CHAr, 2 CHHet), 53.8 (2 CH_2N), 67.6 (2 CH_2OAr), 67.8 (2 CH_2OAr), 68.5 (4 CH_2CH_2OAr), 69.5 (2 CH_2O), 69.6 (4 CH_2O), 69.7 (6 CH_2O), 112.0 (2 5′-C), 113.6 (2 2′-C), 118.8 (2 8-C), 120.5 (2 6′-C), 120.9 (2 3-C), 128.3 (2 5-C), 128.6 (2 4a-C), 129.2 (2 6-C), 130.3 (2 1′-C), 135.0 (2 7-C), 136.6 (2 8a-C), 146.9 (2 4′-C), 147.1 (2 3′-C), 149.2 (2 2-C), 160.3 (2 4-C) ppm; UV−vis (MeCN−water, 10:1, v/v) λ_{max} (ε) = 238 (60600), 286 (10200), 319 nm (13200 $M^{-1}\cdot cm^{-1}$). Anal. Calcd for $C_{58}H_{76}Br_4N_4O_{12}$ (1340.86): C, 51.95; H, 5.71; N, 4.18. Found: C, 51.70; H, 5.78; N, 4.14.

*4,4′-(c-2,t-4-Di-2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-ylcyclobutane-r-1,t-3-diyl)bis[1-(2-ammonioethyl)quinolinium] Tetraperchlorate (rctt-**9f**).* A dispersion of dye **1f** (15.7 mg, 22.1 μmol) in a mixture of MeCN (0.5 mL) and water (0.1 mL) was concentrated in a 10 cm Petri dish until a thin polycrystalline film of the dye formed. The sample thus prepared was irradiated with unfiltered light from a 60 W incandescent lamp from a distance of 15 cm for 36 h. The substance was collected mechanically to yield cyclobutane *rctt*-**9f** (15.1 mg, 96%) as a yellow solid: mp >300 °C dec; ^{1}H NMR (500.13 MHz, 30 °C) δ 3.30−3.45 (m, 4H, 2 C*H*$_2$NH$_3$), 3.45−3.65 (m, 32H, 16 CH$_2$O), 3.73−3.85 (m, 8H, 4 C*H*$_2$OAr), 4.99 (m, 2H, 2 C*H*H′N), 5.41 (m, 2H, 2 CH*H′*N), 5.45 (dd, ^3J = 9.4 Hz, ^3J = 7.5 Hz, 2H, 2 C*H*Ar), 5.52 (dd, ^3J = 9.4 Hz, ^3J = 7.5 Hz, 2H, 2 C*H*Het), 6.59 (d, ^3J = 8.4 Hz, 2H, 2 5′-H), 6.89 (br s, 2H, 2 2′-H), 6.96 (br d, ^3J = 8.4 Hz, 2H, 2 6′-H), 7.89 (br s, 6H, 2 NH$_3$), 8.07 (m, 2H, 2 6-H), 8.24 (m, 2H, 2 7-H), 8.46 (d, ^3J = 9.5 Hz, 2H, 2 8-H), 8.47 (d, ^3J = 6.2 Hz, 2H, 2 3-H), 8.90 (d, ^3J = 8.4 Hz, 2H, 2 5-H), 9.29 (d, ^3J = 6.2 Hz, 2H, 2 2-H) ppm; ^{13}C NMR (125.76 MHz, 25 °C) δ 37.8 (2 CH$_2$NH$_3$), 45.4 and 45.5 (2 CHAr, 2 CHHet), 54.2 (2 CH$_2$N), 67.6 (2 CH$_2$OAr), 67.7 (2 CH$_2$OAr), 68.5 (4 CH$_2$CH$_2$OAr), 69.5 (2 CH$_2$O), 69.6 (4 CH$_2$O), 69.9 (6 CH$_2$O), 112.0 (2 5′-C), 113.4 (2 2′-C), 118.8 (2 8-C), 120.3 (2 6′-C), 120.6 (2 3-C), 128.0 (2 5-C), 128.6 (2 4a-C), 129.3 (2 6-C), 130.1 (2 1′-C), 135.2 (2 7-C), 136.7 (2 8a-C), 147.0 (2 4′-C), 147.1 (2 3′-C), 149.3 (2 2-C), 160.2 (2 4-C) ppm; UV−vis (MeCN−water, 10:1, v/v) λ_{max} (ε) = 238 (58200), 285 (10300), 319 nm (12800 M^{-1}·cm^{-1}). Anal. Calcd for $C_{58}H_{76}Cl_4N_4O_{28}$ (1419.05): C, 49.09; H, 5.40; N, 3.95. Found: C, 48.91; H, 5.51; N, 4.15.

4,4′-(c-2,t-4-Di-2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-ylcyclobutane-r-1,t-3-diyl)bis[1-(3-ammoniopropyl)quinolinium] tetraperchlorate (rctt-9g). Cyclobutane *rctt*-**9g** (yellow solid, quantitative yield) was obtained similarly to cyclobutane *rctt*-**9d** using dye **1g** (16.2 mg, 22.4 μmol) and irradiation for 4 h: mp > 280 °C dec; ^{1}H NMR (500.13 MHz, 30 °C) δ 2.17 (m, 2H, 2 C*H*H′CH$_2$NH$_3$), 2.24 (m, 4H, 2 CH*H′*CH$_2$NH$_3$, 2 C*H*H′NH$_3$), 2.69 (m, 2H, 2 CH*H′*NH$_3$), 3.39 (m, 2H, 2 C*H*H′OAr), 3.50−3.77 (m, 32H, 16 CH$_2$O), 3.82 (m, 4H, 2 CH*H′*OAr, 2 C*H*″H‴OAr), 3.95 (m, 2H, 2 CH″*H*‴OAr), 4.91 (m, 2H, 2 C*H*H′N), 5.32 (m, 2H, 2 CH*H′*N), 5.41 (dd, ^3J = 9.5 Hz, ^3J = 8.3 Hz, 2H, 2 C*H*Ar), 5.73 (dd, ^3J = 9.5 Hz, ^3J = 8.3 Hz, 2H, 2 C*H*Het), 6.57 (d, ^3J = 8.0 Hz, 2H, 2 5′-H), 6.58 (br s, 2H, 2 2′-H), 6.99 (br d, ^3J = 8.0 Hz, 2H, 2 6′-H), 7.25 (br s, 6H, 2 NH$_3$), 8.09 (m, 2H, 2 6-H), 8.26 (m, 2H, 2 7-H), 8.39 (d, ^3J = 6.3 Hz, 2H, 2 3-H), 8.52 (d, ^3J = 9.0 Hz, 2H, 2 8-H), 9.03 (d, ^3J = 8.5 Hz, 2H, 2 5-H), 9.39 (d, ^3J = 6.3 Hz, 2H, 2 2-H) ppm; ^{13}C NMR (125.76 MHz, 30 °C) δ 26.9 (2 CH$_2$CH$_2$NH$_3$), 36.0 (2 CH$_2$NH$_3$), 43.4 (2 CHHet), 44.9 (2 CHAr), 54.0 (2 CH$_2$N), 67.1 (2 CH$_2$OAr), 67.3 (2 CH$_2$OAr), 68.1 (2 CH$_2$O), 68.2 (2 CH$_2$O), 68.6 (2 CH$_2$O), 68.7 (2 CH$_2$O), 69.2 (4 CH$_2$O), 69.6 (2 CH$_2$O), 69.6 (2 CH$_2$O), 111.1 (2 5′-C), 111.8 (2 2′-C), 118.7 (2 8-C), 120.5 (2 3-C), 121.4 (2 6′-C), 128.2 (2 5-C), 128.4 (2 4a-C), 129.3 (2 6-C), 130.2 (2 1′-C), 135.1 (2 7-C), 136.2 (2 8a-C), 145.7 (2 4′-C), 145.9 (2 3′-C), 148.0 (2 2-C), 160.0 (2 4-C) ppm; UV−vis (MeCN) λ_{max} (ε) = 238 (67200), 288 (10500), 319 (13800 M^{-1}·cm^{-1}); IR (KBr) ν = 3437 cm^{-1} (br, NH$_3$). Anal. Calcd for $C_{60}H_{80}Cl_4N_4O_{28}$ (1447.10): C, 49.80; H, 5.57; N, 3.87. Found: C, 49.94; H, 5.49; N, 3.88.

^{1}H NMR Titration. MeCN-d_3 (water content <0.05%, v/v) was used as the solvent. The stability constants of the dimeric complexes of dyes **1** and complexes of dyes **2** with $EtNH_3ClO_4$ were determined by analyzing the shifts of the proton signals of the dye ($\Delta\delta_H$) depending on the concentration of the added salt $EtNH_3ClO_4$. The total dye concentration did not change, being equal to 1×10^{-3}, 2×10^{-3}, or 5×10^{-3} M, and the salt concentration was varied starting from zero (the maximum $EtNH_3ClO_4$/dye concentration ratio was ~48). The $\Delta\delta_H$ values were measured to an accuracy of 0.001 ppm. The stability constants of the complexes were calculated by the HYPNMR program[14] and are shown in Table 1.

Photolysis of Dye 1c. UV−vis spectra of dye **1c** (MeCN, $C_{1c} = 5 \times 10^{-5}$ M, V = 3 mL, 1 cm quartz cell, ambient temperature) and its photolyzates were recorded in the range of 200−600 nm with an increment of 0.5 nm (see Figure S106 in the Supporting Information). Xenon lamp filtered light (λ = 350−420 nm) was used for irradiation, and the distance to the light source was 10 cm; the solution was stirred during irradiation.

Photolysis of Dye 1g. UV−vis spectra of dye **1g** (MeCN, $C_{1g} = 5 \times 10^{-5}$ M, V = 3 mL, 1 cm quartz cell, ambient temperature) and its photolyzates were recorded in the range of 200−650 nm with an increment of 1 nm (see Figure 2). Xenon lamp filtered light (λ > 410 nm) was used for irradiation, and the distance to the light source was 10 cm; the solution was stirred during irradiation.

Comparative Photolysis of Dyes 1b−d,g−i, 2a, and 8: General Method. A solution of dye (15 μmol) in MeCN (spectroscopic grade, 15 mL) placed in a glass flask was irradiated with unfiltered light from a 60 W incandescent lamp (distance to the light source 15 cm) for 4−40 h. An aliquot (1 mL) of the solution was thoroughly evaporated in vacuo in the dark, and the solid residue was analyzed by ^{1}H NMR spectroscopy (in DMSO-d_6), comparing the integral intensities of the signals. The data on the degree of conversion into the cyclobutane derivative are given in Table 2.

Photolysis of Dye 2b and Cyclobutanes 9d,g: General Method. UV−vis spectra of compounds **2b** and **9d,g** (MeCN, $C_{2b} = 2 \times 10^{-5}$ M, $C_{9d} = 1 \times 10^{-5}$ M, $C_{9g} = 2.5 \times 10^{-5}$ M, V = 3 mL, 1 cm quartz cell, ambient temperature) and their photolyzates were recorded in the range of 200−650 nm with an increment of 1 nm (see Figure 4 and Figures S108 and S109 in the Supporting Information). Xenon lamp filtered light (λ = 280−320 nm) was used for irradiation, and the distance to the light source was 10 cm; the solutions were stirred during irradiation.

X-ray Crystal Structure Determinations and Crystal Data. The crystals of styryl dyes **1** and **2** were grown from MeCN or MeCN−water solutions, which were slowly saturated with benzene or dioxane by the vapor diffusion method at ambient temperature in the dark. The single crystals of all compounds were coated with perfluorinated oil and mounted on a CCD diffractometer [graphite monochromatized Mo Kα radiation (λ = 0.71073 Å), ω scan mode] under a stream of cold nitrogen. The sets of experimental reflections were measured, and the structures were solved by direct methods and refined with anisotropic thermal parameters for all non-hydrogen atoms (except for oxygen atoms O(12), ..., O(20) of the disordered perchlorate anion Cl(1)O$_4$ in structure **1b**, which were refined isotropically). In the cases of bromide-containing structures **1a**·3H$_2$O, (**1a**/**9a**)·3H$_2$O, and **1e**·0.5C$_4$H$_8$O$_2$·2H$_2$O, absorption corrections were applied using the SADABS method. The hydrogen atoms were fixed at calculated positions at carbon atoms and then refined with an isotropic approximation for **2c**·1.5C$_6$H$_6$ or by using a riding model for other structures. Hydrogen atoms of the NH$_3^+$ groups in all structures and hydrogen atoms of the solvent water molecules in structures **1a**·3H$_2$O and **1e**·0.5C$_4$H$_8$O$_2$·2H$_2$O were calculated geometrically and refined by using a riding model. In structure (**1a**/**9a**)·3H$_2$O, hydrogen atoms of the solvent water molecule H$_2$O(1W) were calculated geometrically and refined by using a riding model. Refinement of hydrogen atoms of the other water molecules in this strucrure was unstable.

*Data for **1a**·3H$_2$O:* $C_{25}H_{42}Br_2N_2O_9$, M = 674.43, monoclinic, space group $C2/c$ (No. 15), orange block, a = 35.487(2) Å, b = 9.7899(6) Å, c = 18.4307(12) Å, β = 112.139(2)°, V = 5930.9(6) Å^3, T = 120(2) K, Z = 8, μ = 2.785 mm^{-1}, ρ_{calcd} = 1.511 g cm^{-3}, $2\theta_{max}$ = 58.0°, 20084 reflections measured, 7815 unique (R_{int} = 0.0502), R_1 = 0.0555 (4452 reflections with $I > 2\sigma(I)$), R_2 = 0.1474 (all data), goodness-of-fit on F^2 of 0.993, 534 parameters, min/max residual electron density −0.94/1.31 $\bar{e}$ Å^{-3}. Both the conjugated moiety and peripheral part of the crown ether moiety of the dye cation are disordered over two positions with occupancy ratios of 0.58:0.42 and 0.52:0.48, respectively. SADI and ISOR commands were applied to some atoms of the disordered groups to constrain their geometric and anisotropic thermal parameters.

*Data for (**1a**/**9a**)·3H$_2$O:* $C_{50}H_{84}Br_4N_4O_{18}$, M = 1348.85, monoclinic, space group $C2/c$ (No. 15), orange block, a = 35.2762(12) Å, b = 9.8049(3) Å, c = 18.5204(8) Å, β = 112.254(2)°, V = 5928.7(4) Å^3, T = 120(2) K, Z = 4, μ = 2.786 mm^{-1}, ρ_{calcd} = 1.511 g cm^{-3}, $2\theta_{max}$ = 58.0°, 41455 reflections measured, 7873 unique (R_{int} = 0.0796), R_1 = 0.0846 (4357 reflections with $I > 2\sigma(I)$), R_2 = 0.2657 (all data), goodness-of-fit on F^2 of 0.996, 466 parameters, min/max residual electron density −1.43/2.09 $\bar{e}$ Å^{-3}. The experimental reflections were collected from the same crystal of **1a**·3H$_2$O irradiated with visible light from a 60 W incandescent lamp for 10 days. In the obtained structure, the *s-anti*-conformer of initial dye **1a** and cyclobutane derivative *rctt*-**9a**, which forms from *s-syn*-**1a** as a result of the SCSC process, are present simultaneously with an occupancy ratio of 0.36:0.64. The peripheral part of the crown ether moiety is still disordered over two positions with an occupancy ratio of 0.53:0.47. SADI and ISOR commands were applied to some atoms of the disordered fragments.

*Data for **1b**:* $C_{25}H_{36}Cl_2N_2O_{14}$, M = 659.46, monoclinic, space group $P2_1/c$ (No. 14), yellow block, a = 10.316(2) Å, b = 15.932(3) Å, c = 18.450(3) Å, β = 101.066(7)°, V = 2975.9(10) Å^3, T = 120(2) K, Z = 4, μ = 0.290 mm^{-1}, ρ_{calcd} = 1.472 g cm^{-3}, $2\theta_{max}$ = 58.0°, 24644 reflections measured, 7805 unique (R_{int} = 0.0899), R_1 = 0.0743 (3415 reflections with $I > 2\sigma(I)$), R_2 = 0.2055 (all data), goodness-of-fit on F^2 of 0.945, 445 parameters, min/max residual electron density −0.33/0.61 $\bar{e}$ Å^{-3}. The perchlorate anion $Cl(1)O_4$ is disordered over three rotation positions with equal occupancies. The anion $Cl(2)O_4$ is also disordered over two close positions with occupancy ratios of 0.51:0.49. Atom C(21) of the crown ether chain and atom C(25) of the ammonioethyl substituent are both disordered over two positions with occupancy ratios of 0.85:0.15 and 0.80:0.20. SADI and ISOR commands were applied to constrain the geometries and anisotropic thermal parameters of the disordered fragments.

*Data for **9b**:* $C_{50}H_{72}Cl_4N_4O_{28}$, M = 1318.92, monoclinic, space group $P2_1/c$ (No. 14), yellowish block, a = 10.8853(3) Å, b = 16.0031(4) Å, c = 17.3331(5) Å, β = 101.216(1)°, V = 2961.73(14) Å^3, T = 120(2) K, Z = 2, μ = 0.292 mm^{-1}, ρ_{calcd} = 1.479 g cm^{-3}, $2\theta_{max}$ = 58.0°, 26298 reflections measured, 7782 unique (R_{int} = 0.0488), R_1 = 0.0643 (5137 reflections with $I > 2\sigma(I)$), R_2 = 0.1733 (all data), goodness-of-fit on F^2 of 1.007, 434 parameters, min/max residual electron density −0.30/0.62 $\bar{e}$ Å^{-3}. The experimental data were collected from the same crystal of **1b** irradiated with visible light from a 60 W incandescent lamp for 20 h. The anion $Cl(2)O_4$ is disordered over two close positions with an occupancy ratio of 0.53:0.47. SADI and ISOR commands were applied to constrain this anion.

*Data for **1e**·0.5$C_4H_8O_2$·2H_2O:* $C_{31}H_{46}Br_2N_2O_9$, M = 750.52, triclinic, space group $P\ \bar{1}$ (No. 2), red-orange block, a = 11.4310(11) Å, b = 11.6678(11) Å, c = 14.7274(14) Å, α = 104.737(2)°, β = 95.770(2)°, γ = 114.086(2)°, V = 1687.2(3) Å^3, T = 120(2) K, Z = 2, μ = 2.456 mm^{-1}, ρ_{calcd} = 1.477 g cm^{-3}, $2\theta_{max}$ = 58.0°, 19380 reflections measured, 8811 unique (R_{int} = 0.0402), R_1 = 0.0593 (5974 reflections with $I > 2\sigma(I)$), R_2 = 0.1786 (all data), goodness-of-fit on F^2 of 1.038, 468 parameters, min/max residual electron density −0.81/1.62 $\bar{e}$ Å^{-3}. The solvate dioxane molecule is situated at the symmetry center. One of the two independent bromide anions is disordered over two close positions with an occupancy ratio of 0.95:0.05. A peripheral part of the crown ether fragment is disordered over two positions with an occupancy ratio of 0.74:0.26. SADI and ISOR commands were applied to some atoms of the disordered crown ether fragment.

*Data for **1f**:* $C_{29}H_{38}Cl_2N_2O_{14}$, M = 709.51, triclinic, space group $P\bar{1}$ (No. 2), orange needles, a = 11.425(3) Å, b = 11.981(3) Å, c = 12.650(3) Å, α = 101.734(11)°, β = 99.896(12)°, γ = 109.094(11)°, V = 1548.0(7) Å^3, T = 120(2) K, Z = 2, μ = 0.285 mm^{-1}, ρ_{calcd} = 1.522 g cm^{-3}, $2\theta_{max}$ = 54.0°, 18418 reflections measured, 6701 unique (R_{int} = 0.2313), R_1 = 0.1233 (2334 reflections with $I > 2\sigma(I)$), R_2 = 0.3272 (all data), goodness-of-fit on F^2 of 0.925, 471 parameters, min/max residual electron density −0.64/0.65 $\bar{e}$ Å^{-3}. The fine-needle structure of the studied crystal decreases its reflective ability and, hence, considerably decreases the accuracy of the X-ray diffraction experiment. One of the two independent perchlorate anions is disordered over two close positions with an occupancy ratio of 0.67:0.33. SADI and ISOR commands were applied to constrain this anion.

*Data for **2c**·1.5C_6H_6:* $C_{38}H_{45}ClNO_{10}$, M = 711.20, monoclinic, space group $P2_1/c$ (No. 14), orange plate, a = 12.0370(9) Å, b = 12.9351(9) Å, c = 23.7840(18) Å, β = 103.709(3)°, V = 3597.7(5) Å^3, T = 120(2) K, Z = 4, μ = 0.165 mm^{-1}, ρ_{calcd} = 1.313 g cm^{-3}, $2\theta_{max}$ = 50.0°, 18727 reflections measured, 6313 unique (R_{int} = 0.1134), R_1 = 0.0704 (3326 reflections with $I > 2\sigma(I)$), R_2 = 0.1212 (all data), goodness-of-fit on F^2 of 0.973, 630 parameters, min/max residual electron density −0.29/0.30 $\bar{e}$ Å^{-3}. One of two independent solvate benzene molecules is situated at the symmetry center.

All the calculations were performed using the SHELXTL-Plus[19] and Olex-2[20] software. CCDC 1017989 (**1a**·3H_2O), 1017990 [(**1a**/**9a**)·3H_2O], 1017991 (**1b**), 1017992 (**1e**·0.5$C_4H_8O_2$·2H_2O), 1017993 (**1f**), 1017994 (**2c**·1.5C_6H_6), and 1017995 (**9b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR, ^{1}H−^{1}H COSY and NOESY, ^{1}H−^{13}C correlation (HSQC and HMBC), and UV−vis spectra, crystal packings, and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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