Synthesis, structure, and stereospecific cross-[2+2] photocycloaddition of pseudodimeric complexes based on ammonioalkyl derivatives of styryl dyes†

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New 4-pyridine-derived styryl dyes having an ammonioalkyl *N*-substituent in the pyridine moiety and various substituents in the benzene moiety were synthesized. The formation of pseudodimeric complexes of ammonioalkyl styryl dye derivatives with 18-crown-6-containing styryl dyes of the 4-pyridine, 4-quinoline, and 2-benzothiazole series was studied by ^{1}H NMR in MeCN-*d*$_3$. It was found that the stability of supramolecular complexes is mainly determined by the monotopic interaction of the ammonioalkyl group with the crown ether moiety *via* hydrogen bonding. The components of pseudodimeric complexes undergo stereospecific cross-[2+2] photocycloaddition reaction to give unsymmetrical *rctt* isomers of cyclobutane derivatives owing to the *syn*-head-to-tail arrangement of components in the initial complex. The efficiency of photoreaction is affected by the *N*-substituent length, the nature of the substituent in the benzene ring of the ammonioalkyl component, and the nature of the heterocyclic residue of the crown-containing component. The structures of dyes, pseudodimeric complexes, and the cyclobutane derivative were studied by X-ray diffraction.

Introduction

Development of promising methods for the self-assembly of organic molecules *via* various non-covalent interactions such as coordination, hydrogen bonding, Coulomb, ion–dipole, stacking, and hydrophobic interactions has been the subject of numerous studies in supramolecular chemistry.[1] The self-assembly of photoactive compounds to supramolecular assemblies can considerably affect their photophysical and photochemical properties, as this concentrates the sites responsible for these properties; interaction of these sites located at short distances often gives rise to new

useful properties of molecular assemblies not inherent in single molecules.[2]

It is well known[3] that benzo-18-crown-6 ether and its derivatives efficiently bind primary ammonium ions *via* hydrogen bonding. This feature underlies the supramolecular self-assembly of some photoactive compounds in which the benzo-18-crown-6 ether moiety can be a part of the conjugated system. The first studies along this line were concerned with the properties of crown azobenzenes, which are capable of reversible *E–Z* photoisomerization.[4] 18-Crown-6-substituted unsaturated compounds such as cinnamic acid, stilbene, and styryl heterocycle derivatives are more promising.[5] The C=C double bond contained in their chromophores can be involved in photoinduced *E–Z* isomerization, [2+2] cycloaddition and electrocyclization reactions. There are only a few examples of using photoactive 18-crown-6-substituted unsaturated compounds in self-assembly involving the RNH$_3^+$ ions;[6] they were mainly reported by our research group.[5c,d]

Previously, we demonstrated[7] that the *E* isomer of a 18-crown-6-containing 2-benzothiazole styryl dye having a long ammoniohexyl spacer in the heterocyclic residue, in a MeCN solution, spontaneously forms stable dimeric complexes (log K_d = 6.1 [M^{-1}]) with the *anti*-head-to-tail arrangement of chromophores. Upon exposure to light, this dye is converted almost completely to a cation-capped *Z* isomer stabilized by intramolecular coordination of

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† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra, UV-vis spectra, emission spectra, crystal packings, and X-ray crystallographic data. CCDC 1430268–1430272. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5nj03500g
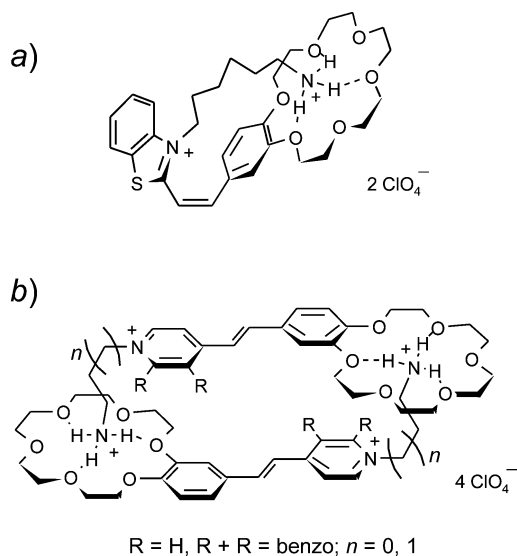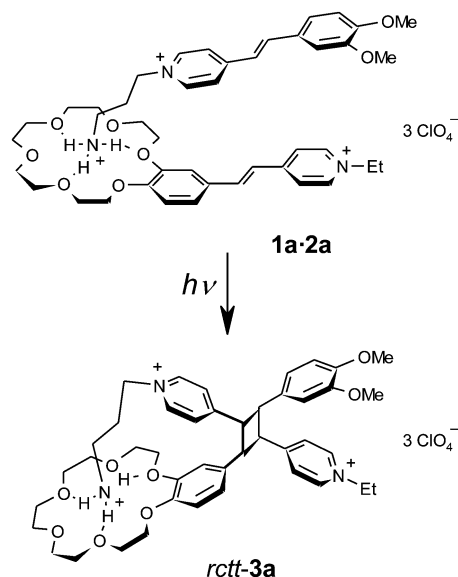
Chart 1 Structure of 18-crown-6-containing styryl dye complexes based on hydrogen bonding.

Scheme 1 Formation of cyclobutane *rctt*-**3a** from pseudodimeric complex of two styryl dyes.

the ammonium group to the crown ether moiety (Chart 1a). The *E–Z* isomerization is accompanied by a pronounced hypsochromic shift of the long-wavelength absorption band (LWAB).

The crown-containing 4-pyridine- and 4-quinoline-derived styryl dyes, which have rather short ammonioalkyl *N*-substituents, dimerize spontaneously according to the *syn*-head-to-tail pattern both in solution and in the solid phase (Chart 1b).[8] In MeCN, the dimeric complexes are very stable, $\log K_d$ = 7.1–8.0 [M^{-1}], due to the homoditopic binding of the terminal ammonium groups *via* hydrogen bonds with the 18-crown-6 ether fragments and stacking interactions of the conjugated moieties. In the dimeric complexes, the C=C double bonds are proximate and anti-parallel, which promote an effective stereospecific auto-[2+2] photo-cycloaddition (auto-PCA, *i.e.*, two identical ethylene molecules take part in the PCA) to give only the *rctt* isomer of cyclobutane derivatives. Transition from the dimeric complexes to cyclobutane derivatives is accompanied by a sharp change in the spectral characteristics of compounds caused by the disruption of the conjugated chain in the chromophore moieties.

We suggested that the components of the styryl dye dimers can be held together even by monotopic interaction between the ammonioalkyl group and the crown ether moiety. Preliminary investigations showed[9] that two different 4-pyridine-derived dyes, one having an ammoniopropyl substituent (**1a**) and the other having a crown ether moiety (**2a**), actually form a pseudodimeric complex. Complex **1a·2a** is preorganized towards cross-[2+2] photocyclo-addition (here "cross-PCA" means that two different ethylene com-pounds react with each other[10]), *i.e.*, the chromophore groups of the components are mainly located above each other owing to the stacking interaction of the dye conjugated systems. Irradiation of a solution containing an equimolar mixture of dyes **1a** and **2a** afforded the only *rctt* isomer of the unsymmetrical cyclobutane derivative **3a** (Scheme 1). This opens up broad prospects for varying the structures of both the ammonioalkyl styryl dye derivative and the crown styryl dye derivative and, hence, for fine tuning their spectral properties.
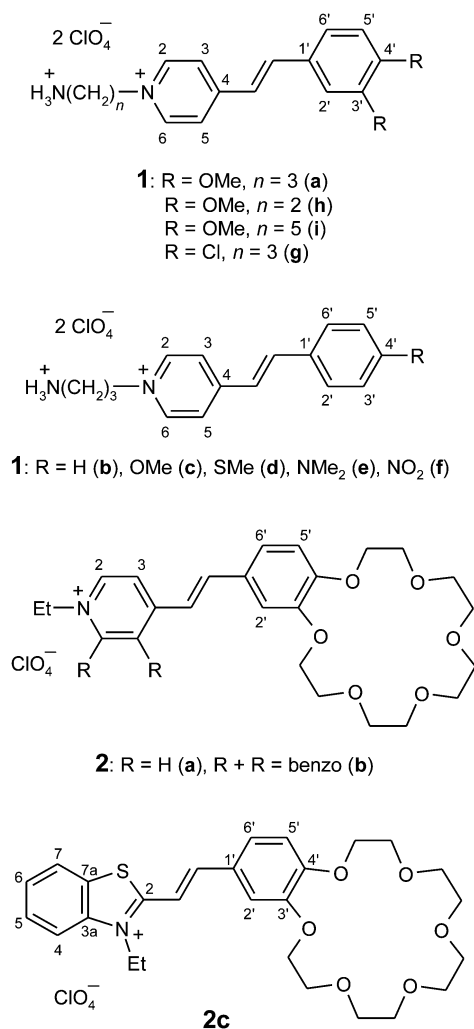
It is noteworthy that the examples of cross-PCA reactions that usually accompany auto-PCA and/or afford mixtures of cyclobutane isomers have been reported.[5d,6b,10,11] In recent years, the regio- and stereoselectivities of cross-PCA reactions have been increased by using the protocol of encapsulation of the reactant molecules in the cavities of zeolites and macroheterocyclic cavitands (cyclo-dextrins, cucurbiturils, nanocages[12]) or by forming appropriate crystal packings.[13]

The purpose of this study was to develop a method for the synthesis of a series of 4-pyridine-derived styryl dyes **1b–i**, having *N*-ammonioalkyl substituents of different length in the heterocyclic residue and various substituents in the benzene ring. We studied how these factors influence the structure and stability of the pseudodimeric complexes formed by these dyes with 18-crown-6-containing 4-pyridine-derived styryl dye **2a** and the efficiency and stereoselectivity of cross-PCA in these complexes. For comparison, the heterocyclic residue in the crown component was also varied (4-quinoline- **2b** and 2-benzothiazole-derived **2c** dyes) (Chart 2). The stability of the complexes was determined by ^{1}H NMR titration and the stereochemistry of the resulting cyclobutane derivatives was elucidated by NMR spectroscopy. The structures of some dyes, complexes, and cyclobutane derivatives were determined by X-ray diffraction analysis.
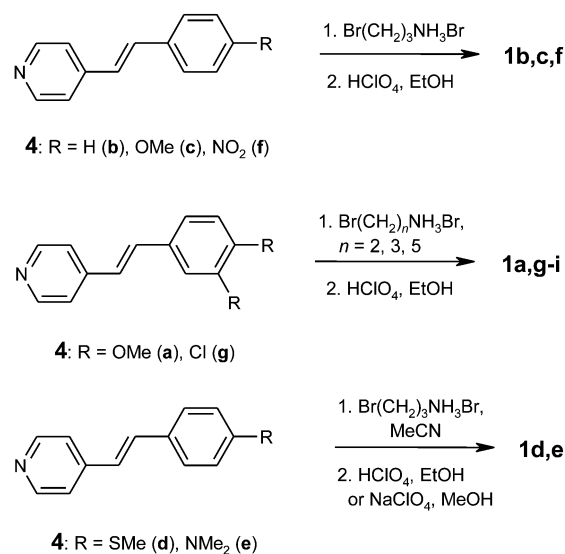
Results and discussion

Synthesis of dyes

The syntheses of **1a**,[9] **1b**,[14] **1g**,[15] **2a**,[16] **2b**,[17] and **2c**[7] were reported in our previous publications. Dyes **1c,f,h,i** were prepared by fusing together the respective neutral 4-styrylpyridines **4a,c,f**[18] with ω-bromoalkylammonium bromides and subsequent anion exchange for perchlorate by treatment with concentrated HClO$_4$ in ethanol (Scheme 2). In the synthesis of dyes **1d,e**, quterniza-tion of **4d,e** (R = SMe, NMe$_2$) with 3-bromopropylammonium

1: R = OMe, n = 3 (**a**)
R = OMe, n = 2 (**h**)
R = OMe, n = 5 (**i**)
R = Cl, n = 3 (**g**)

1: R = H (**b**), OMe (**c**), SMe (**d**), NMe$_2$ (**e**), NO$_2$ (**f**)

2: R = H (**a**), R + R = benzo (**b**)

2c

Chart 2 Structure of dyes **1a–i** and **2a–c**.

4: R = H (**b**), OMe (**c**), NO$_2$ (**f**)

4: R = OMe (**a**), Cl (**g**)

4: R = SMe (**d**), NMe$_2$ (**e**)

Scheme 2 Synthesis of dyes **1a–i**.

induce a bathochromic shift of the peak by up to 134 nm with respect to the unsubstituted dye (**1b**, λ_{max} = 348 nm in MeCN), whereas the LWAB of dyes with electron-withdrawing substituents (NO$_2$, Cl) undergoes only a slight hypsochromic shift ($\Delta\lambda_{max}$ up to −3 nm) with respect to the LWAB of **1b**. The position of the LWAB maximum in the series of crown-containing dyes depends on the electron-withdrawing properties of the heterocyclic residue. The intramolecular charge transfer is facilitated for compounds **2b** and **2c** with more electron-withdrawing quinolinium and benzothiazolium residues (λ_{max} = 434 and 431 nm, respectively) as compared with the less electron-withdrawing pyridinium residue (for **2a** λ_{max} = 399 nm). Dyes **1a–e,g–i** and **2c** slightly fluoresce in MeCN solutions (see the Experimental section and Fig. S22 in the ESI†). Dye **1f** containing the NO$_2$ group is non-fluorescent.

Complex formation of dyes

Previously, we showed[16] that crown-containing dye **2a** with a chromophoric group similar to that of dyes **1a,h,i** shows also similar spectral characteristics. Indeed, in an MeCN solution, dyes **1a** and **2a** have LWAB with λ_{max} = 403 and 399 nm, respectively. Studies in acetonitrile solutions demonstrated that all styryl dyes **1a–i** having ammonioalkyl substituents can form pseudodimeric complexes with **2a–c** (Scheme 3). The formation of complexes **1·2** is accompanied by a slight increase in the electronic transition energy for dye **2**, because the interaction between the ammonium cation and the crown ether moiety involving hydrogen bonding weakens the electron-donating properties of the benzocrown ether moiety. The absorption of dyes **1** is barely affected by the formation of complexes **1·2**.[15]

The formation of pseudodimeric complexes is clearly seen from comparison of the ^{1}H NMR spectra of free components and equimolar mixtures. For example, in a solution in MeCN-d_3, the signals of ethylene and most aromatic protons of mixed dyes **1b** and **2a** are shifted upfield to $\Delta\delta_H$ = −0.09 ppm relative to free

bromide was carried out under milder conditions (boiling MeCN) in order to avoid quaternization of sulfur or nitrogen of the dimethylamino-group with excess alkylating agent. In the preparation of **1e**, the ion exchange was accomplished by treatment of the corresponding dye dibromide with a methanol solution of NaClO$_4$ in order to preclude the protonation of NMe$_2$.

The structures of the products were determined by ^{1}H and ^{13}C NMR spectroscopy and electronic spectroscopy methods and confirmed by elemental analysis data (^{1}H and ^{13}C NMR spectra and UV-vis and emission spectra of dyes **1a–i** and **2c** are shown in Fig. S1–S22 in the ESI†). All dyes **1** and **2** have the E configuration, judging by the spin–spin coupling constant $^3J_{HC=CH}$ = 15.7–16.5 Hz.

The chromophores of dyes **1a–i** and **2a–c** are donor–acceptor type conjugated systems.[19] The long-wavelength band in the absorption spectra of these compounds refers to intramolecular electronic transition accompanied by charge transfer from the benzene moiety to the quaternized heterocyclic residue. The nature of substituents in the benzene ring of compounds **1a–i** considerably affects the position of the LWAB maximum. Electron-donating substituents (OMe, SMe, NMe$_2$) in the para position to the ethylene bond
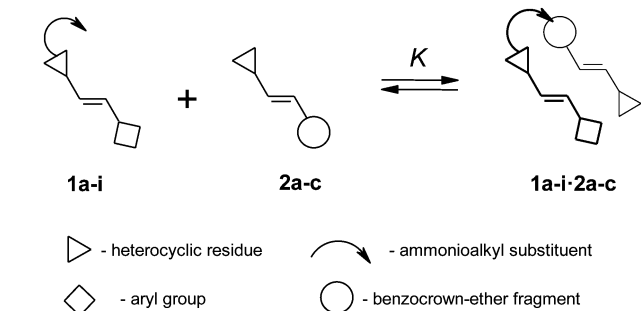
Scheme 3 Complex formation between dyes **1a−i** and **2a−c**.

1b and **2a** (Fig. 1; the proton numbering is shown in Chart 2). Previously, we showed[20] that complexation of dye **2a** with the EtNH$_3^+$ ions results, conversely, in a slight downfield shift of all proton signals of **2a**. Indeed, the signals for crown ether CH$_2$O groups of **2a** shift downfield by up to $\Delta\delta_H = 0.07$ ppm upon mixing with **1b**, which confirms the hydrogen bonding of the ammonium group with the crown ether. Meanwhile, the (CH$_2$)$_3$NH$_3^+$ signals of dye **1b** and ethyl group signals of dye **2a** shift upfield upon mixing by up to $\Delta\delta_H = -0.15$ ppm (Fig. 2). The observed upfield shift for mixed dyes **1b** and **2a** can be attributed only to the preferred arrangement of the planar conjugated moieties of the dyes approximately one above the other in complex **1b·2a** (for example, see Scheme 1) and, hence, to substantial anisotropic effects in this complex. Similar changes were observed for mixtures of other dyes **1** with dyes **2** (Fig. S23–S31 in the ESI†).

Quantitative determination of the stability of complexes of ammonioalkyl dye derivatives **1b–i** with crown dyes **2a–c** was performed by ^{1}H NMR titration in a MeCN-d_3 solution. The complex formation is described by the following equilibrium:

$$\mathbf{1b-i} + \mathbf{2a-c} \; \underset{}{\overset{K}{\rightleftarrows}} \; \mathbf{1b-i} \cdot \mathbf{2a-c}$$
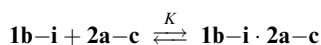
where K/M^{-1} is the stability constant of the pseudodimeric complex.

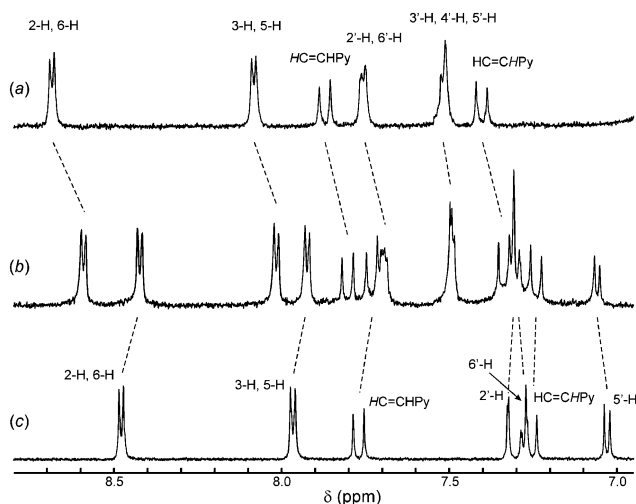

Fig. 1 ^{1}H NMR spectra (aromatic proton region) of (a) dye **1b**, (b) a 1:1 mixture of dyes **1b** and **2a**, and (c) dye **2a** ($C_{dye} = 1 \times 10^{-3}$ M), MeCN-d_3, 30 °C.
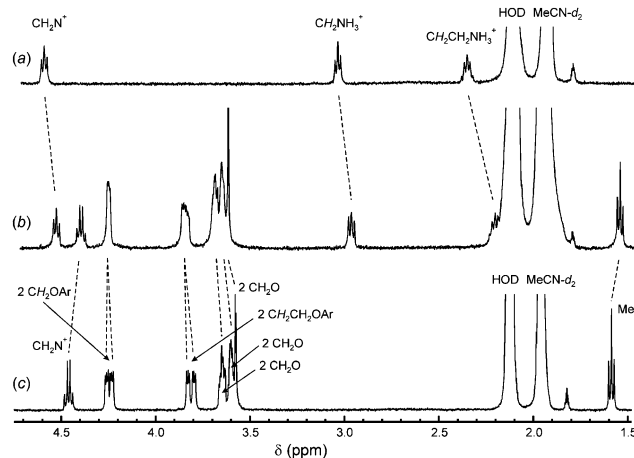

Fig. 2 ^{1}H NMR spectra (aliphatic proton region) of (a) dye **1b**, (b) a 1:1 mixture of dyes **1b** and **2a**, and (c) dye **2a** ($C_{dye} = 1 \times 10^{-3}$ M), MeCN-d_3, 30 °C.

The stability constants of complexes **1·2** were determined using HYPNMR[21] software by analyzing the variation of proton signal positions of dye **2** as functions of the concentration of dye **1** added. The results are summarized in Table 1.

As compared with the dimeric complexes of styryl dyes shown in Chart 1b, the stability of pseudodimeric complexes decreases by more than 3 orders of magnitude. Evidently, the cause is the presence of ditopic NH$_3^+$···18-crown-6 interactions in the dimeric complexes and only monotopic interactions in complexes **1·2**. The stability of pseudodimeric complexes varies over a rather narrow range of values, $\log K = 3.1$–3.7, which implies the highest contribution to the stability of hydrogen bonding between the primary ammonium group and the 18-crown-6 ether moiety. The most stable complexes are formed by dyes **1a,e,g,h** and **2b,c**, which contain more extended conjugated systems, that additionally stabilize pseudodimeric complexes owing to stacking interactions (secondary interaction of the p$_z$-orbitals of the conjugated systems) between spatially proximate components. Noteworthy in this respect is that the least stable complex is formed by dye **1b** devoid of substituents in the benzene ring. The nature of substituents (donor or acceptor) in the benzene ring of dyes **1** has little influence on the stability of complexes. The length of the ammonioalkyl chain in dyes **1** also affects only slightly the stability of complexes with dye **2a**. Only a minor stability decrease can be noted on going from **1a,h** (ammoniopropyl and ammonioethyl) to

Table 1 Effective stability constants of pseudodimeric complexes of dyes **1a−i** with dyes **2a−c**[a]

Complex	$\log K$	Complex	$\log K$
1a·2b	3.7	**1d·2a**	3.3
1a·2c	3.6	**1f·2a**	3.3
1a·2a	3.5[b]	**1i·2a**	3.3
1h·2a	3.5	**1c·2a**	3.3
1e·2a	3.4	**1b·2a**	3.1
1g·2a	3.4		

[a] ^{1}H NMR titration, MeCN-d_3, 30 ± 1 °C. The errors for determination of constants K are ±30%. [b] From ref. 7.

1i (ammoniopentyl). Apparently, the long *N*-substituent in dye **1i** weakens the stacking interactions in the complex with **2a** due to the remote spatial positions of the conjugated moieties of the components.

Pseudodimeric complexes were obtained in the solid state by slow crystallization of equimolar mixtures of the components (see the Experimental section and Fig. S32–S39 in the ESI†). The composition of most complexes is 1 : 1 (^{1}H NMR monitoring and elemental analysis data). The only exception is the complex formed by dyes **1a** and **2a**, which proved to have 1.5 : 1 composition (a reproducible result from several crystallizations). Apparently, the fine-grained crystalline phase formed consists of a co-crystallizate of complex **1a·2a** with free **1a**.

X-ray diffraction study of dyes and complexes

The X-ray diffraction investigations of dyes **1a**, **2a**, and **2b** have been previously reported.[8,16,22] It was ascertained that in the crystals, the organic cations of these dyes form centrosymmetric *syn*-head-to-tail dimeric pairs with extensive stacking interactions of conjugated moieties. In the dimeric pairs, the C=C bonds occupy proximate positions at ~3.6–4.0 Å distances and are strictly antiparallel. These conditions proved to be favourable for the solid-phase auto-PCA, which proceeded with retention of single crystals for **1a** and **2a**.[16,22] Note, however, that in solution, these compounds do not undergo the auto-PCA reaction.

We succeeded in growing single crystals of free dyes **1f** and **2c**, which were studied by X-ray diffraction; the structures are shown in Fig. 3.

The independent part of the unit cell of **2c** contains a dioxane molecule of solvation and three water molecules. This structure was determined with high accuracy, which allowed the location of hydrogen atoms of water molecules in electron density maps. Two water molecules, $H_2O(1W)$ and $H_2O(2W)$, are arranged above and below the mean plane of the macrocyclic moiety and form weak directional or bifurcate hydrogen bonds with their oxygen atoms.‡ The $H_2O(3W)$ water molecule connects, *via* hydrogen bonding,§ the $H_2O(1WA)$ and $H_2O(2W)$ molecules of two neighbouring subunits separated by a translation. Thus, a continuous chain of hydrogen-bonded atoms is present in the **2c·$C_4H_8O_2$·$3H_2O$** crystal (see Fig. S40 in the ESI†).

Note that a solvation water molecule hydrogen-bonded to the crown ether moiety was also found in the crystal structure of dye **2a**.[16] This coordination of the water molecule hampers complex formation between the crown ether moiety and the ammonium groups of dyes **1**; therefore, a considerable content of water in acetonitrile solution can markedly decrease the stability constants of complexes **1·2**.

‡ In **2c·$C_4H_8O_2$·$3H_2O$**, the hydrogen bond parameters are as follows: the O(1W)H···O(4), O(1W)H···O(5), O(1W)H···O(6), O(2W)H···O(3), O(2W)H···O(1), and O(2W)H···O(6) distances are 1.99(5), 2.44(7), 2.42(7), 1.99(4), 2.46(5), and 2.49(5) Å, respectively, and the angles at the H atoms are 152(4)°, 121(5)°, 168(5)°, 167(3)°, 145(5)°, and 151(6)°, respectively.

§ Hydrogen bond parameters are as follows: the O(3W)H···O(1WA) and O(3W)H···O(2W) distances are 2.00(4) and 1.77(5) Å and the angles are 174(4)° and 165(4)°.
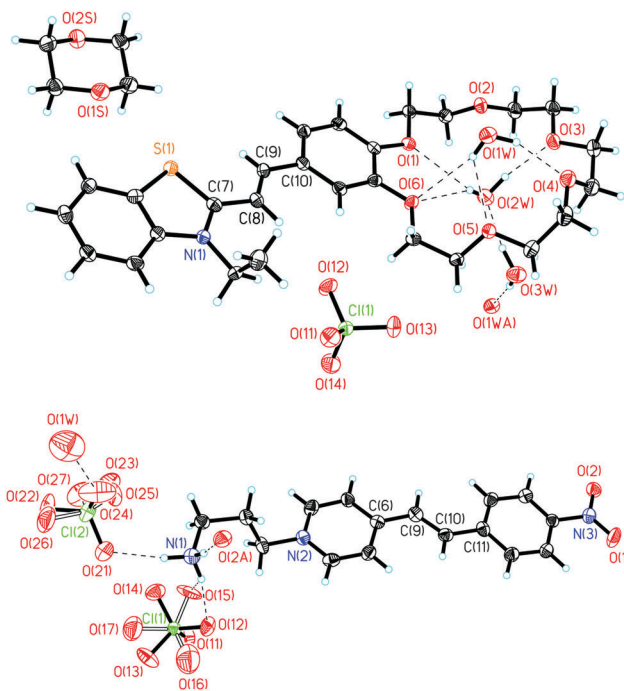
Fig. 3 Structures **2c·$C_4H_8O_2$·$3H_2O$** (top) and **1f·$0.25H_2O$** (bottom). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen bonds are drawn with dash lines. The additional letters "A" indicate that atoms belong to symmetrically related sites.

The chromophore of dye **2c** is generally planar: the dihedral angle between the benzothiazole residue and benzene ring planes is only 3.8°. The ethylene group is relatively localized: the C(8)=C(9) bond length is 1.335(4) Å, whereas the lengths of the neighbouring formally single bonds, C(7)–C(8) and C(9)–C(10), are increased to 1.440(4) and 1.458(4) Å. This is a typical bond length distribution in styryl dyes,[8,16–18,22] which does not prevent efficient conjugation throughout the whole chromophore. Note that for the PCA reaction to occur, the ethylene bond in the chromophore should be substantially localized.

The molecular cations of dye **2c** form centrosymmetric dimeric pairs arranged in the *syn*-head-to-tail fashion, which are stacked (Fig. S40 in the ESI†). The C=C double bonds in the dimeric pair approach each other to a distance of 3.77 Å and are strictly antiparallel. This packing of styryl dyes is favourable for the solid-phase auto-PCA, which has been confirmed previously[16,18] for dye **2a** and related 2-benzothiazole styryl dye devoid of the crown ether moiety. However, prolonged visible light irradiation of the crystals of **2c·$C_4H_8O_2$·$3H_2O$** did not bring about a change in their structure. Apparently, the numerous hydrogen bonds, mentioned above, make the crystal structure more rigid, which prevents the ethylene bond atoms from moving toward each other as needed to form a cyclobutane derivative.

In the crystal of **1f·$0.25H_2O$**, both independent perchlorate anions are disordered over two sites each *via* rotation about one of the Cl–O bonds.

The chromophore of dye **1f** is planar, which is confirmed by the dihedral angle of 5.4° between the pyridine and benzene ring planes. The ethylene bond is also rather localized: the

distances in the C(6)–C(9)=C(10)–C(11) moiety are 1.469(7), 1.324(7), and 1.465(7) Å, respectively. The ammoniopropyl *N*-substituent has a *trans*, *gauche* conformation, although the steric and Coulomb interactions require that this substituent be in all-transoid conformation. Evidently, the Coulomb interactions are partially counterbalanced by the weak hydrogen bonding of the ammonium group with the anions.¶

The cations of dye **1f** are arranged in loose slanted stacks formed in the head-to-head fashion in which the conjugated moieties are projected only by the nitrostyrene groups (Fig. S41 in the ESI†). The ethylene-bond carbon atoms of adjacent cations in the stack are separated by distances of 4.20–4.86 Å and, moreover, these bonds are non-parallel. The solid-phase auto-PCA reaction cannot occur in this packing for geometrical reasons, which accounts for the stability of the crystals of **1f**·0.25H$_2$O on prolonged irradiation.

We also prepared single crystals for two pseudodimeric complexes, **1d**·**2a** and **1f**·**2a**.

The structure of the major components of complex **1f**·**2a**·0.5C$_6$H$_6$·2H$_2$O is shown in Fig. 4. The independent part of the unit cell was found to contain the organic cations of dyes **1f** and **2a**, four disordered perchlorate anions, and molecules of solvation.

The conjugated moiety of dye **2a** is disordered over two sites, *i.e.*, the crystal contains simultaneously the *s-anti* and *s-syn* conformers of **2a** (see Chart 3). This is due to so-called "pedal" isomerization of the ethylene bond in the crystals of stilbene-type compounds,[23] which is typical of styryl dyes.[18]

Complex **1f**·**2a** is a pseudodimeric pair of dye cations arranged in the head-to-tail fashion. The ammonium group of **1f** is coordinated to the crown ether moiety of **2a** *via* the formation of directional hydrogen bonds with its oxygen atoms.‖ The conjugated moiety of dye **2a** is nearly planar: the dihedral angles between the pyridine and benzene rings in the predominant and minor *s*-conformers are 10.5° and 7.0°, respectively. The chromophore of ammonium dye **1f** is somewhat incurved (without twisting), the pyridine residue/benzene ring dihedral angle being 13.3°. The conjugated moieties of both dyes are projected onto each other and lie in roughly parallel planes: the dihedral angle between them is only 6.6°.

However, the conjugated moieties of dyes **1f** and **2a** in the crystalline pseudodimeric complex were found to be rather far from each other. For example, the C(6′)···C(10″) and C(7′)···(9″) distances are 6.85 and 6.81 Å, respectively. Such a structure of the pseudodimer is a consequence of the given crystal packing. The complexes form very loose stacks extended along the *ab* direction in which the conjugated moieties of dyes **1f** and **2a** alternate in pairs (see Fig. 4). Therefore, proximate positions are found for the molecular cations of dyes **1f** and **2a** from
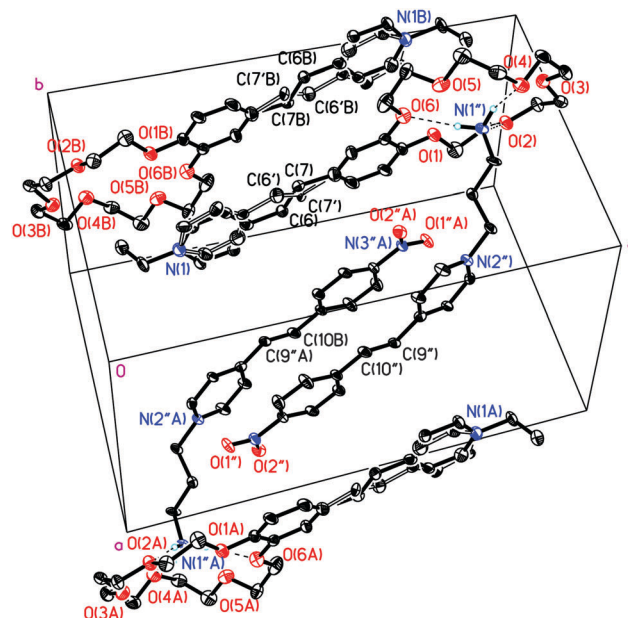

Fig. 4 Stack of cations forming pseudodimeric complexes in structure **1f**·**2a**·0.5C$_6$H$_6$·2H$_2$O. Thermal ellipsoids are drawn at the 40% probability level. Most of the hydrogen atoms are omitted for clarity. Hydrogen bonds are drawn with dash lines. The additional letters "A" and "B" indicate that atoms belong to symmetrically related sites.
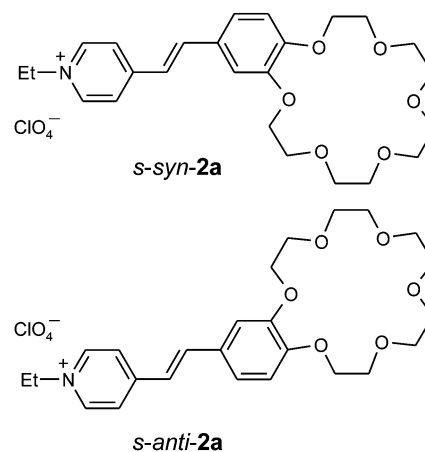

Chart 3 Conformers of dye **2a**.

neighbouring complexes, which are arranged in the head-to-head fashion with a considerable shift, so that only the nitro group of **1f** and the benzene ring of **2a** are projected onto each other. The distances between the ethylene moieties of these cations are too long for cross-PCA: the C(6′)···C(9″A) and C(7′)···C(10B) distances are 6.08 and 5.69 Å. In a stack, two neighbouring cations of dye **1f** are arranged in the *syn*-head-to-tail fashion in parallel planes with an interplanar spacing of ∼3.6 Å. However, despite the considerable degree of overlapping of their conjugated systems, auto-PCA is impossible because of a large distance between the ethylene moieties: the C(9″)···C(10B) and C(10″)···C(9″A) distances are 5.26 Å. The two cations of dye **2a** adjoining each other in the stacks are also

¶ For the N(1)H···O(12), N(1)H···O(15), and N(1)H···O(21) bonds in structure **1f**·0.25H$_2$O, the distances are 2.04, 2.10, and 2.01 Å, while the angles at hydrogen atoms are 164°, 123°, and 162°. Also, the ammonium group is hydrogen-bonded to the NO$_2$ group of the neighbouring molecular cation: the N(1)H···O(2A) contact has a length of 2.20 Å and an angle of 169°.

‖ In structure **1f**·**2a**·0.5C$_6$H$_6$·2H$_2$O, the length of the N(1″)H···O(2,4,6) contacts varies in the range of 1.95–2.10 Å and the angles at H atoms are 148–164°.

arranged in the head-to-tail fashion in parallel planes at ~3.4 Å distance, thus enabling stacking interactions of the conjugated moieties. The cations of **2a** are substantially shifted relative to each other; therefore their ethylene bonds are not projected. The distances between the carbon atoms of the disordered ethylene moieties, C(6)···C(7B) and C(7)···C(6B), C(6′)···C(7′B) and C(7′)···C(6′B), are 4.20 and 4.02 Å, respectively. This geometry is unsuitable for auto-PCA of the crown-containing dye. Indeed, visible light irradiation of the crystal **1f·2a·0.5C₆H₆·2H₂O** for eight days did not induce any structural change.

Complex **1d·2a** forms very unstable loose crystals, which weakly reflect X-rays and, therefore, the accuracy of X-ray experiments proved to be relatively low for all studied samples. We still decided to include these results into the article only to demonstrate a different structure of a pseudodimeric complex as compared with the above-described structure of **1f·2a**. Therefore, we do not dwell on fine structure details for the components of complex **1d·2a** but consider only their general geometry and relative positions in the crystal.

The independent part of the unit cell of **1d·2a·0.7C₆H₆·0.7H₂O** was found to contain two cations of dye **1d**, two cations of dye **2a**, six ClO_4^- anions, three benzene molecules of solvation, and six water molecules. The vast majority of the unit cell components are strongly disordered, which partly explains the weak reflecting ability of the crystal (see the Experimental section).

The molecular cations of dyes **1d** and **2a** form two independent head-to-tail pseudodimeric complexes, which are stacked along the *b* axis of the crystal (Fig. 5). In the stacks, the planar conjugated moieties of the neighbouring cations are projected onto each other and are roughly parallel with interplanar spacings of ~3.4–3.7 Å, *i.e.*, the stacking interactions are substantial throughout the whole stack. Unlike **1f·2a·0.5C₆H₆·2H₂O**, the cations that form complexes **1d·2a** are spatially proximate, although in both structures, the ammoniopropyl *N*-substituents assume the all-transoid conformation. This emphasizes the structure flexibility of the pseudodimeric complexes. In **1d·2a·0.7C₆H₆·0.7H₂O**, the dihedral angles between the mean planes of the conjugated moieties of pseudodimer components are only ~8–9°. Due to the pedal disorder, their ethylene groups can be roughly antiparallel or crossed and spaced apart by ~3.7–4.4 Å. The ethylene groups in cations of the same type adjacent in the stack are spaced apart by ~4.2–4.6 Å, which implies that there are no conditions for auto-PCA to occur. Thus, **1d·2a·0.7C₆H₆·0.7H₂O** clearly demonstrates the typical structure of pseudodimeric complexes, which is also retained in solutions (according to ¹H NMR data). This structure of the complexes provides the conditions for selective cross-PCA in solutions in which the component mobility markedly increases but molecules of the same type do not form stable dimers.

Cross-[2+2] photocycloaddition of pseudodimeric complexes

Previously, we found[16,17,22] that dyes **1a**, **2a**, and **2b** in the solid phase (crystals and polycrystalline films) undergo auto-PCA upon exposure to visible light to give centrosymmetric *rctt* isomers of cyclobutane derivatives. This is possible owing to the topochemical control of the crystal lattice which favours the formation of dimeric pairs of the dyes. In these dimers, the planar molecular dye cations
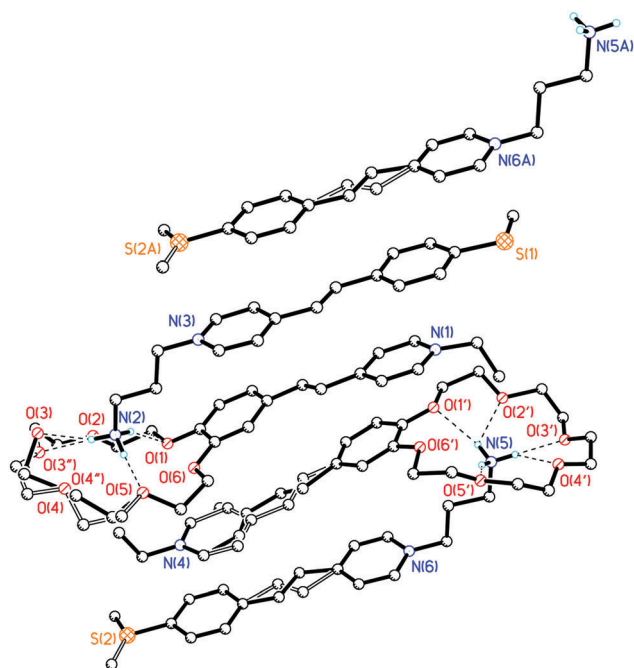

Fig. 5 Stack of cations forming pseudodimeric complexes in structure **1d·2a·0.7C₆H₆·0.7H₂O**. Most of the hydrogen atoms are omitted for clarity. Hydrogen bonds are drawn with dash lines. The additional letters "A" indicate that atoms belong to symmetrically related sites.

are located above each other according to the *syn*-head-to-tail pattern; therefore, the C=C double bonds are antiparallel and spaced apart by only ~3.5–4.0 Å. According to Schmidt's criterion,[24] these conditions are favourable for solid-phase PCA. Meanwhile, in solutions, dyes **1a**, **2a**, and **2b** underwent only geometric *E–Z* isomerization. In this case, the PCA is evidently hampered by the short lifetime of the excited states of the molecules, potential participants of the photoreaction, and long distances between them.

Visible light irradiation of solutions of free dyes **1a–i** in MeCN results, in most cases, in relatively fast decrease in LWAB intensity (down to 33–81% of the initial value) and a slight hypsochromic shift of the absorption maximum, which is caused by *E–Z* isomerization of the dyes (see Fig. S42–S49 in the ESI†). Previously,[16] we observed a similar behaviour of dye **2a** (see also Fig. S50, ESI†). An exception is dye **1e** containing the NMe₂ group for which the LWAB intensity decreases only slightly (to 96% of the initial value, Fig. S46, ESI†). Apparently, the high electron-donating properties of the substituent nitrogen as compared with other heteroatoms lead to a much higher degree of conjugation in the chromophore of **1e** and, hence, to fast thermal *Z–E* isomerization.[25] Dyes having chromophores similar to that of **1e** are also prone to non-radiative transition from the excited state to the ground state *via* the twisted internal charge transfer (TICT) excited state.[26]

As an example, Fig. 6 shows the changes for a solution of dye **1f**. It is noteworthy that after the photostationary equilibrium has been attained in solution of any dye **1**, further long-term irradiation does not induce any spectral changes.

It was ascertained above that in solutions of MeCN, dyes **1** and **2** form relatively stable pseudodimeric complexes in which
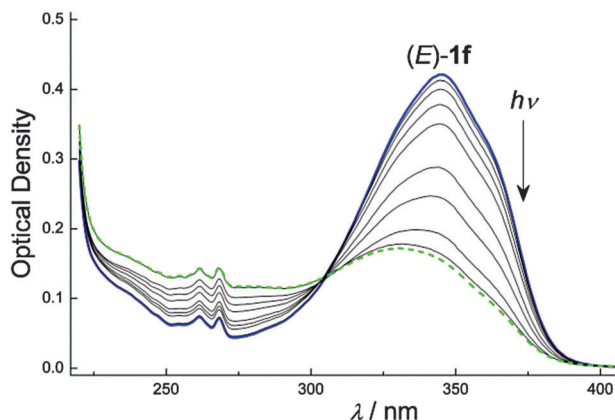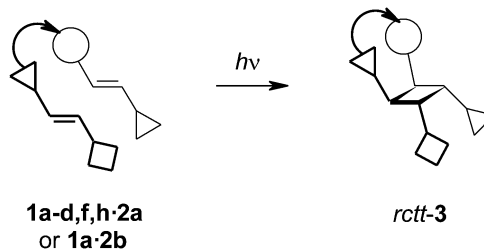
Fig. 6 Irradiation of the solution of dye **1f** for 0, 1, 3, 6, 10, 20, 30, 50, 80, and 110 min (MeCN, $C\mathbf{1f} = 1.11 \times 10^{-4}$ M, 0.1 cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source $\sim$15 cm). The green dash curve is a photostationary mixture consisting of E and Z isomers of **1f**.

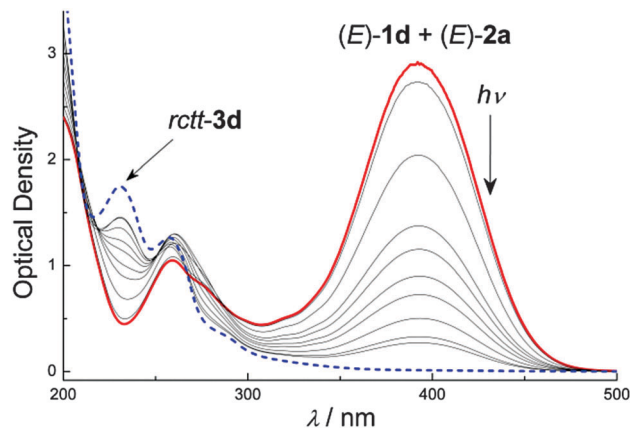Scheme 4 Formation of cyclobutane derivatives *rctt*-**3**.

Fig. 7 Irradiation of solution of an equimolar mixture of dyes **1d** and **2a** for 0, 1, 6, 20, 40, and 80 min and 2, 4, 8, and 16 h (MeCN, $C_{1d} = C_{2a} = 5 \times 10^{-4}$ M, 0.1 cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source $\sim$15 cm). The blue dash curve is the spectrum of cyclobutane *rctt*-**3d** (MeCN, $C_{3d} = 5 \times 10^{-4}$ M, 0.1 cm quartz cell).

the conjugated moieties are spatially proximate owing to stacking interactions (see Schemes 1 and 3). Thus, complexes **1·2** are preorganized towards cross-PCA.

Visible light irradiation of solutions of equimolar mixtures of dyes **1a–d,f,h** with **2a** and **1a** with **2b** resulted in a more pronounced decrease in the long-wavelength absorption intensity as compared with free components (Fig. S51–S55 in the ESI†). The disappearance of absorption in the region of >330 nm is caused by the disruption of the conjugated system in the chromophores of both pseudodimer components as a result of cross-PCA to give 1,2,3,4-tetrasubstituted cyclobutanes **3** (Scheme 4).

This is exemplified in Fig. 7, which shows data on the irradiation of a solution containing an equimolar mixture of dyes **1d** and **2a**. In the beginning of irradiation, the absorption intensity at about 400 nm rapidly decreases (in $\sim$30 min), which is caused by the fast E–Z isomerization of both dyes. This is followed by slower changes caused by cross-PCA. However, in none of the cases, the absorption at about 400 nm disappears completely even after >100 h due to insufficiently high stability constants of complexes **1·2** (see Table 1). As the dyes are consumed in cross-PCA, their concentration decreases and, hence, the content of the complexed dyes decreases. For comparison, Fig. 7 also shows the absorption spectrum of single *rctt*-**3d**, which was isolated by crystallization (see below). This compound barely absorbs light at λ > 330 nm.

The variation of the absorbance at 397 nm for solutions of equimolar mixtures of dye **2a** with dyes **1a,h,i** depending on the irradiation time is shown in Fig. 8. It can be clearly seen that cross-PCA occurs most rapidly in complex **1a·2a** and is somewhat slower in **1h·2a**. In the case of complex **1i·2a**, the decrease in the long-wavelength absorption reaches $\sim$65% of the initial value, *i.e.*, E–Z isomerization is the major process. Thus, the study of the effect of N-substituent length on the efficiency of cross-PCA demonstrated that the ammoniopropyl spacer has the length of choice, whereas in the system with the ammoniopentyl N-substituent, this photoreaction barely occurs. Apparently, the too long spacer is unfavourable as regards the requirement of

spatial proximity of the C=C bonds in the pseudodimeric complex **1i·2a**, which is necessary for PCA. The shortest ammonioethyl spacer apparently makes the pseudodimeric complex molecule too rigid as compared with longer and more flexible N-ammonioalkyl substituents, which prevents the ethylene bonds in the complex based on **1h** from approaching each other. A similar dependence of the auto-PCA rate on the length of the N-substituent has been demonstrated[8] by styryl dyes shown in Chart 1b.

In the complexes formed by **1e,g** with **2a**, the spectral variations depending on the irradiation time are similar to those for **1i·2a** (Fig. S56 and S57 in the ESI†). That is, in the case of ammoniopropyl dyes with two electron-withdrawing substituents (Cl) or with the most electron-donating substituent (NMe$_2$) in the benzene ring, cross-PCA is either very slow and gives cyclobutane derivatives in only trace amounts or does not proceed at all. The absence of PCA with dye **1e** is apparently due to the efficient formation of the TICT excited state.

Varying the heterocyclic residue in the crown-containing dye has a considerable effect on the cross-PCA rate. Indeed, in complex **1a·2b**, photocycloaddition occurs much more slowly than in complex **1a·2a**: in 290 h, the degree of conversion to the corresponding cyclobutane derivative is 51% (^{1}H NMR monitoring; Fig. S58 in the ESI†). Complex **1a·2c** is not converted to the cyclobutane derivative at all. Apparently, the large quinoline or benzothiazole residues sterically prevent the ethylene moieties in complexes **1a·2b,c** from approaching each other, which is necessary
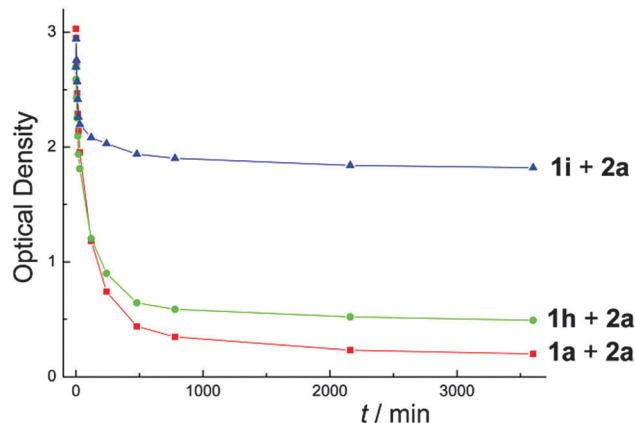
Fig. 8 Dependence of the absorbance at 397 nm on the time of irradiation of solutions of equimolar mixtures of dye **2a** with dyes **1a**, **1h**, and **1i** (MeCN, $C_{1a,h,i} = C_{2a} = 5 \times 10^{-4}$ M, 0.1 cm quartz cell).

for the formation of cyclobutanes **3**. Moreover, an additional obstacle to the proximity of ethylene bonds can be caused by the closely located *N*-ethyl substituent in the benzothiazole residue.

^{1}H NMR examination of the photolysis products of dye mixtures **1a–i**/**2a–c** confirmed the conclusions drawn from UV-vis spectroscopy data concerning the reactivity of pseudo-dimeric complexes. Thus, cross-PCA reaction efficiently occurs in the complexes formed by 4-pyridine-derived dyes having a relatively short ammoniopropyl *N*-substituent and electron-donating substituents OMe and SMe (or without substituents) in the benzene ring.

In all of the above cases where the cross-PCA reaction is relatively efficient, only one stereoisomer of cyclobutane **3** is formed. Apart from the signals of minor *E* and *Z* isomers of the initial compounds **1a–d,f,h** and **2a,b**, the ^{1}H NMR spectra of photolysis products exhibit a new set of signals at about 5 ppm, which is characteristic of cyclobutane derivatives of a similar structure.[8,14,16,18,22] While comparing these signals with analogous signals of the previously studied isomer *rctt*-**3a**,[9] we concluded that all of the obtained cyclobutanes have a *rctt* stereochemistry and, hence, they are formed from pseudodimeric complexes **1·2** in which the dyes were arranged in the *syn*-head-to-tail fashion (see Schemes 1 and 5). The signals of all cyclobutane protons of *rctt*-**3a** overlap little with each other; therefore, they all are doublets of doublets (ABCD type spin system). For cyclobutanes *rctt*-**3b–d**, the a-H and d-H proton signals considerably overlap; therefore, the multiplicity pattern for all signals of the cyclobutane moiety is more complex (*i.e.*, it is a high-order ^{1}H NMR spectrum), which complicates the determination of spin–spin coupling constants (Fig. 9, atom numbering is shown in Scheme 5).

From photolysis products of complexes **1b–d·2a** in which cross-PCA is most effective and can proceed to a >95% conversion to cyclobutane derivatives, compounds *rctt*-**3b–d** were isolated in 92–95% yields by fractional crystallization. Their structures were characterized by ^{1}H and ^{13}C NMR spectroscopy and UV-vis spectrometry and confirmed by elemental analysis data (^{1}H and ^{13}C NMR spectra and UV-vis spectra of compounds

rctt-**3**: R = H (**b**), OMe (**c**), SMe (**d**)
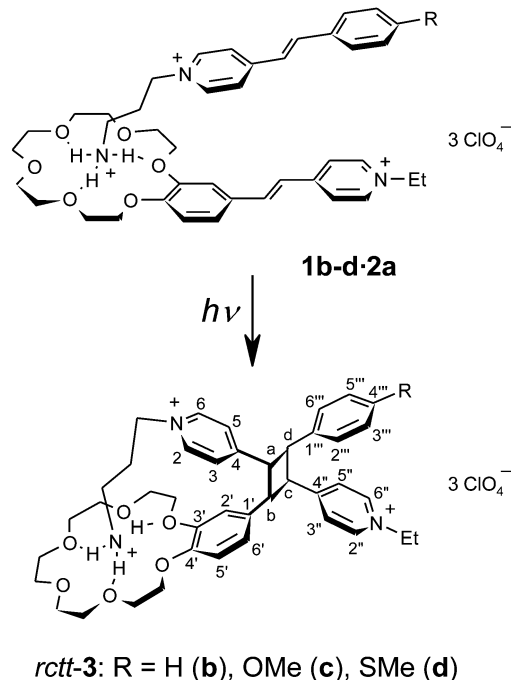
Scheme 5 Synthesis of cyclobutane derivatives *rctt*-**3b–d**.

rctt-**3b–d** are shown in Fig. S61–S67 in the ESI†). The ^{13}C NMR spectra of *rctt*-**3b–d** exhibit four signals in the characteristic 43–47 ppm range, which correspond to the unsymmetrically substituted cyclobutane ring. The positions of these signals are similar to the positions of cyclobutane carbon signals of *rctt*-**3a** prepared previously (*cf.* Fig. S60 in the ESI†). In the case of cyclobutane derivatives formed from complexes **1f·2a**, **1h·2a**, and **1a·2b**, the photolysis products containing these cyclobutanes were substantially contaminated by mixtures of geometric isomers of the initial dyes; therefore, we were unable to isolate these cyclobutanes in a pure state.

X-ray diffraction study of cyclobutane derivatives

A colourless crystal of cyclobutane derivative *rctt*-**3c** was studied by X-ray diffraction; Fig. 10 shows the structure of its major component (see the packing in Fig. S68 in the ESI†).

The cyclobutane derivative **3c** identified in the crystal is the *rctt* isomer. It should have been formed from the *syn*-head-to-tail pseudodimeric complex **1c·2a**. This is direct evidence supporting our conclusion based on ^{1}H NMR spectroscopy data about the prevailing structure of pseudodimeric complexes and the stereochemistry of cyclobutanes **3** they form.

In *rctt*-**3c**·2C$_6$H$_6$·0.75MeCN·0.25H$_2$O, the NH$_3^+$ group of the *N*-ammoniopropylpyridinium moiety is coordinated intra-molecularly by the benzocrown ether moiety that occupies the *cis*-position to it *via* the formation of three hydrogen bonds.** The pyridine and phenyl substituents, which are *cis*-arranged in the cyclobutane ring, are not parallel due to the attachment to sp[3]-hybridized carbon atoms: the dihedral angles between the

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** In structure *rctt*-**3c**·2C$_6$H$_6$·0.75MeCN·0.25H$_2$O, the N(2)H···O(2,4,5) distances are 2.00–2.21 Å and the angles at the H atoms are 130–158°.
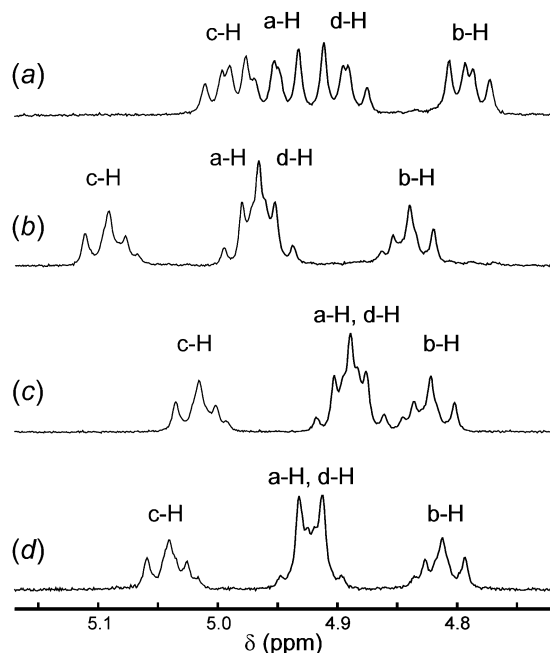
Fig. 9 ^{1}H NMR spectra (cyclobutane proton region) of compounds (a) *rctt*-**3a**, (b) *rctt*-**3b**, (c) *rctt*-**3c**, and (d) *rctt*-**3d**, DMSO-d_6, 30 °C.

planes of the indicated rings are 38.8° and 55.7°. It is typical that the $C_5H_4N(3)$/benzocrown pair is less twisted, obviously, due to the "constricting" action of the complex formation between the ammonium group and the macroheterocycle.
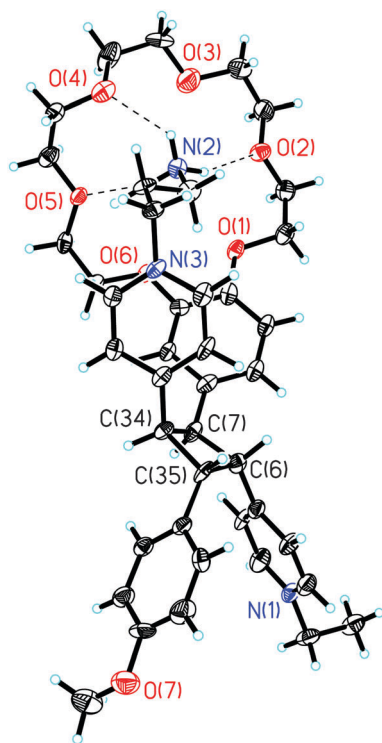

Fig. 10 Structure of the main component in *rctt*-**3c**·$2C_6H_6$·0.75MeCN· 0.25H_2O. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen bonds are drawn with dash lines.

The cyclobutane ring has a non-planar conformation: the torsion angles in the C(6)–C(7)–C(34)–C(35) ring are −10.7°, 10.6°, −10.8°, and 10.6°. The distances in this ring are 1.563(11), 1.593(11), 1.565(11), and 1.572(12) Å. The endocyclic angles in the cyclobutane ring are 88.8(6)–90.2(6)°. These values are typical of 1,2,3,4-tetrasubstituted cyclobutanes that we studied earlier.[8,14,16,18,22]

Conclusions

We developed a synthesis of a series of new 4-pyridine-derived styryl dyes with *N*-ammonioalkyl spacers of various lengths and various substituents in the benzene ring. In MeCN solutions, these dyes form stable pseudodimeric complexes with 18-crown-6-containing styryl dyes mainly due to monotopic hydrogen bonding of the terminal ammonium group of one dye with the macrocycle O atoms of the other dye. Additional contribution to the stability of complexes is made by the stacking interactions of the planar conjugated moieties of the dyes. Therefore, pseudo-dimer components are mainly arranged according to the head-to-tail pattern, their ethylene bonds being spatially proximate. These complexes are preorganized towards stereospecific cross-[2+2] photocycloaddition (cross-PCA) reaction to give the only *rctt* isomer of cyclobutane derivatives out of 38 theoretically possible isomers (considering the possible auto-PCA and cross-PCA reactions in a mixture of two dyes). The structural characteristics of the dyes that benefit more efficient cross-PCA were elucidated. The targeted design of pseudodimeric complexes of styryl dyes may provide for the elaboration of new promising optical data recording systems operating with high efficiency in the specified spectral range.

Experimental section

General

The melting points were measured using a Mel-Temp II apparatus in a capillary and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX500 instrument in DMSO-d_6 and MeCN-d_3 using the solvent as the internal reference (δ_H 2.50 and 1.96, respectively; δ_C 39.43 for DMSO-d_6); *J* values are given in Hz. 2D NOESY spectra and ^{1}H–^{13}C correlation spectra (HSQC and HMBC) were used to assign the proton and carbon signals (see Chart 2 and Scheme 5 for atom numbering in compounds **1**–**3**); the mixing time in the NOESY experiments was 300 μs. Absorption and emission spectra were recorded on a Cary 4000 spectrophotometer (Agilent) and a RF-5301PC spectrofluorimeter (Shimadzu) in the range of 200–600 nm and 320–750 nm, respectively, with an increment of 1 nm in MeCN (spectroscopic grade, the water content ≤0.03% v/v, Cryochrom, Russian Federation) at ambient temperature using 1 cm quartz cells. Elemental analyses were performed at the microanalytical laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds (Moscow, Russian Federation); the samples for elemental analysis were dried *in vacuo* at 80 °C. All of the obtained compounds containing perchlorate anions are non-explosive.

Preparation

Styryl dyes 2a,[16] 2b,[17] neutral 4-styrylpyridines 4a–g,[18] and 5-bromopentylammonium bromide[27] were synthesized according to published procedures.

Dye 1a was obtained according to a published procedure;[9] λ_{max}^{abs}(MeCN)/nm 403 (ε/dm³ mol⁻¹ cm⁻¹ 33 600); λ_{max}^{fl}(MeCN)/nm 550.

Dye 1b was obtained according to a published procedure;[14] λ_{max}^{abs}(MeCN)/nm 348 (ε/dm³ mol⁻¹ cm⁻¹ 29 600); λ_{max}^{fl}(MeCN)/nm 367.

Dye 1g was obtained according to a published procedure;[15] λ_{max}^{abs}(MeCN)/nm 346 (ε/dm³ mol⁻¹ cm⁻¹ 37 400); λ_{max}^{fl}(MeCN)/nm 438.

Dye 2c was obtained according to a published procedure;[7] λ_{max}^{abs}(MeCN)/nm 431 (ε/dm³ mol⁻¹ cm⁻¹ 41 700); λ_{max}^{fl}(MeCN)/nm 535; δ_C(125.76 MHz; DMSO-d_6; 30 °C) 14.0 (Me), 44.2 (CH₂N), 68.3 (4′-CH₂OAr), 68.4 (4′-CH₂CH₂OAr), 68.5 (3′-CH₂OAr, 3′-CH₂CH₂OAr), 69.6 (CH₂O), 69.7 (3 × CH₂O), 69.8 (CH₂O), 69.9 (CH₂O), 110.4 (HC = CHHet), 112.6 (5′-C), 112.9 (2′-C), 116.3 (4-C), 124.2 (7-C), 125.8 (6′-C), 126.8 (1′-C), 127.9 (7a-C), 128.1 (6-C), 129.3 (5-C), 140.8 (3a-C), 148.4 (3′-C), 149.6 (HC = CHHet), 152.5 (4′-C) and 171.6 (2-C).

Cyclobutane rctt-3a was obtained according to a published procedure;[9] λ_{max}^{abs}(MeCN)/nm 231 and 281 (ε/dm³ mol⁻¹ cm⁻¹ 34 400 and 6300); δ_C(125.76 MHz; DMSO-d_6; 30 °C) 16.2 (MeCH₂), 28.1 (CH₂CH₂NH₃), 35.7 (CH₂NH₃), 43.5 (d-CH), 44.6 (c-CH), 45.7 (b-CH), 46.6 (a-CH), 55.3 (3‴-MeO), 55.47 (CH₂Me), 55.52 (4‴-MeO), 57.2 (CH₂N), 67.1 (4′-CH₂OAr), 67.3 (3′-CH₂OAr), 68.3 (CH₂CH₂OAr), 68.4 (CH₂CH₂OAr), 68.6 (2 × CH₂O), 69.1 (CH₂O), 69.2 (CH₂O), 69.6 (CH₂O), 69.7 (CH₂O), 111.2 (5‴-C), 111.4 (2′-C, 5′-C), 112.1 (2‴-C), 119.8 (6‴-C), 120.5 (6′-C), 127.1 (3-C, 5-C), 127.2 (3″-C, 5″-C), 130.0 (1‴-C), 130.4 (1′-C), 143.2 (2-C, 6-C, 2″-C, 6″-C), 145.6 (4′-C), 146.4 (3′-C), 147.6 (4‴-C), 148.4 (3‴-C), 160.2 (4″-C) and 160.6 (4-C).

Synthesis of dyes 1c,f–i (general procedure)

A mixture of 4-styrylpyridine 4a,c,f (1.25 mmol) and 3-bromo-propylammonium bromide (0.82 g, 3.75 mmol) or 2-bromoethyl-ammonium bromide (0.77 g, 3.75 mmol) or 5-bromopentyl-ammonium bromide (0.31 g, 1.25 mmol) was heated at 140–160 °C (oil bath) in the dark for 4–6 h. After cooling to room temperature, the reaction mixture was triturated with hot abs. EtOH (5 cm³) and then cooled to −10 °C. The insoluble substance was filtered off, washed with cold abs. EtOH (2 × 3 cm³) and CHCl₃ (2 × 3 cm³) and dried in air to give dibromide of the dye. This dibromide was dissolved in a mixture of abs. EtOH (5 cm³) and water (minimal quantity) with heating, and 70% aq HClO₄ (0.31 cm³, 3.6 mmol) was added to this solution. After cooling to −10 °C, the precipitate thus formed was filtered off, washed with cold abs. EtOH (2 × 2 cm³), and dried in air in the dark to give dye 1c,f,h,i.

1-(3-Ammoniopropyl)-4-[(E)-2-(4-methoxyphenyl)vinyl]pyridinium diperchlorate (1c) was obtained in 61% yield as a yellow powder: mp 185–188 °C (dec.) (Found: C, 43.55; H, 4.57; N, 5.76. Calc. for C₁₇H₂₂Cl₂N₂O₉ (469.27): C, 43.51; H, 4.73; N, 5.97%); λ_{max}^{abs}(MeCN)/nm 388 (ε/dm³ mol⁻¹ cm⁻¹ 36400); λ_{max}^{fl}(MeCN)/nm 500; δ_H(500.13 MHz; DMSO-d_6; 25 °C) 2.18 (2 H, m, CH₂CH₂NH₃), 2.85 (2 H, m, CH₂NH₃), 3.84 (3 H, s, MeO), 4.54 (2 H, t, ³J 7.0, CH₂N), 7.08 (2 H, d, ³J 8.6, 3′-H, 5′-H),

7.38 (1 H, d, ³J 16.4, HC = CHPy), 7.72 (3 H, br s, NH₃), 7.73 (2 H, d, ³J 8.6, 2′-H, 6′-H), 8.00 (1 H, d, ³J 16.4, HC = CHPy), 8.21 (2 H, d, ³J 6.6, 3-H, 5-H) and 8.86 (2 H, d, ³J 6.6, 2-H, 6-H); δ_C(125.76 MHz; DMSO-d_6; 30 °C) 28.4 (CH₂CH₂NH₃), 35.7 (CH₂NH₃), 55.3 (MeO), 56.6 (CH₂N), 114.6 (3′-C, 5′-C), 120.6 (HC = CHPy), 123.4 (3-C, 5-C), 127.7 (1′-C), 130.0 (2′-C, 6′-C), 141.0 (HC = CHPy), 144.0 (2-C, 6-C), 153.5 (4-C) and 161.2 (4′-C).

1-(3-Ammoniopropyl)-4-[(E)-2-(4-nitrophenyl)vinyl]pyridinium diperchlorate (1f) was obtained in 48% yield as a light beige powder: mp 269–270 °C (dec.) (Found: C, 39.83; H, 3.74; N, 8.42. Calc. for C₁₆H₁₉Cl₂N₃O₁₀ (484.24): C, 39.69; H, 3.95; N, 8.68%); λ_{max}^{abs}(MeCN)/nm 345 (ε/dm³ mol⁻¹ cm⁻¹ 37 800); δ_H(500.13 MHz; DMSO-d_6; 25 °C) 2.19 (2 H, m, CH₂CH₂NH₃), 2.86 (2 H, m, CH₂NH₃), 4.59 (2 H, t, ³J 7.1, CH₂N), 7.73 (3 H, br s, NH₃), 7.78 (1 H, d, ³J 16.5, HC = CHPy), 8.01 (2 H, d, ³J 9.1, 2′-H, 6′-H), 8.14 (1 H, d, ³J 16.5, HC = CHPy), 8.35 (2 H, d, ³J 6.9, 3-H, 5-H), 8.36 (2 H, d, ³J 9.1, 3′-H, 5′-H) and 9.00 (2 H, d, ³J 6.9, 2-H, 6-H); δ_C(125.76 MHz; DMSO-d_6; 30 °C) 28.4 (CH₂CH₂NH₃), 35.7 (CH₂NH₃), 57.1 (CH₂N), 124.2 (3′-C, 5′-C), 124.7 (3-C, 5-C), 127.4 (HC = CHPy), 128.9 (2′-C, 6′-C), 138.1 (HC = CHPy), 141.4 (1′-C), 144.6 (2-C, 6-C), 147.8 (4′-C) and 152.1 (4-C).

1-(2-Ammonioethyl)-4-[(E)-2-(3,4-dimethoxyphenyl)vinyl]pyridi-nium diperchlorate (hydrate) (1h) was obtained in 67% yield as a yellow powder: mp 235–237 °C (dec.) (Found: C, 39.47; H, 4.85; N, 5.83. Calc. for C₁₇H₂₂Cl₂N₂O₁₀·1.5H₂O (512.29): C, 39.86; H, 4.92; N, 5.47%); λ_{max}^{abs}(MeCN)/nm 407 (ε/dm³ mol⁻¹ cm⁻¹ 34 300); λ_{max}^{fl}(MeCN)/nm 550; δ_H(500.13 MHz; DMSO-d_6; 30 °C) 3.49 (2 H, m, CH₂NH₃), 3.84 (3 H, s, 4′-MeO), 3.86 (3 H, s, 3′-MeO), 4.69 (2 H, m, CH₂N), 7.09 (1 H, d, ³J 8.3, 5′-H), 7.32 (1 H, dd, ³J 8.3, ⁴J 1.2, 6′-H), 7.40 (1 H, d, ⁴J 1.2, 2′-H), 7.44 (1 H, d, ³J 16.2, HC = CHPy), 7.95 (3 H, br s, NH₃), 8.01 (1 H, d, ³J 16.2, HC = CHPy), 8.21 (2 H, d, ³J 6.6, 3-H, 5-H) and 8.80 (2 H, d, ³J 6.6, 2-H, 6-H); δ_C(125.76 MHz; DMSO-d_6; 30 °C) 38.8 (CH₂NH₃), 55.57 (MeO), 55.59 (MeO), 56.6 (CH₂N), 110.1 (2′-C), 111.7 (5′-C), 120.7 (HC = CHPy), 123.3 (3-C, 5-C, 6′-C), 127.9 (1′-C), 141.7 (HC = CHPy), 144.5 (2-C, 6-C), 149.1 (3′-C), 151.3 (4′-C) and 154.0 (4-C).

1-(5-Ammoniopentyl)-4-[(E)-2-(3,4-dimethoxyphenyl)vinyl]-pyridinium diperchlorate (1i) was obtained in 17% yield as a yellow powder: mp 207–210 °C (Found: C, 45.61; H, 5.36; N, 5.18. Calc. for C₂₀H₂₈Cl₂N₂O₁₀ (527.35): C, 45.55; H, 5.35; N, 5.31%); λ_{max}^{abs}(MeCN)/nm 400 (ε/dm³ mol⁻¹ cm⁻¹ 31 800); λ_{max}^{fl}(MeCN)/nm 546; δ_H(500.13 MHz; DMSO-d_6; 25 °C) 1.31 (2 H, m, CH₂CH₂CH₂NH₃), 1.57 (2 H, m, CH₂CH₂NH₃), 1.93 (2 H, m, CH₂CH₂N), 2.79 (2 H, m, CH₂NH₃), 3.83 (3 H, s, 4′-MeO), 3.85 (3 H, s, 3′-MeO), 4.46 (2 H, t, ³J 7.5, CH₂N), 7.08 (1 H, d, ³J 8.6, 5′-H), 7.30 (1 H, dd, ³J 8.6, ⁴J 1.8, 6′-H), 7.38 (1 H, d, ⁴J 1.8, 2′-H), 7.41 (1 H, d, ³J 16.2, HC = CHPy), 7.60 (3 H, br s, NH₃), 7.97 (1 H, d, ³J 16.2, HC = CHPy), 8.17 (2 H, d, ³J 6.8, 3-H, 5-H) and 8.87 (2 H, d, ³J 6.8, 2-H, 6-H); δ_C(125.76 MHz; DMSO-d_6; 30 °C) 22.3 (CH₂CH₂CH₂NH₃), 26.3 (CH₂CH₂NH₃), 29.7 (CH₂CH₂N), 38.5 (CH₂NH₃), 55.5 (3′-MeO), 55.6 (4′-MeO), 59.3 (CH₂N), 110.0 (2′-C), 111.7 (5′-C), 120.7 (HC = CHPy), 123.1 (6′-C), 123.2 (3-C, 5-C), 127.9 (1′-C), 141.2 (HC = CHPy), 143.9 (2-C, 6-C), 149.0 (3′-C), 151.1 (4′-C) and 153.2 (4-C).

1-(3-Ammoniopropyl)-4-(E)-2-[4-(methylthio)phenyl]vinylpyr-idinium diperchlorate (1d). A mixture of compound 4d (0.15 g, 0.66 mmol), 3-bromopropylammonium bromide (0.17 g, 0.78 mmol),

and dry MeCN (10 cm^3) was heated at 80 °C with stirring in the dark for 30 h. After cooling to room temperature, an insoluble substance was filtered off, washed with dry MeCN (3 cm^3), and dried in air to give crude dibromide of the dye (0.19 g) as a tawny powder. The dibromide was dissolved in abs. EtOH (3 cm^3) with heating, and 70% aq HClO$_4$ (0.14 cm^3, 1.62 mmol) was added to the solution. After cooling to room temperature, the precipitate thus formed was filtered off, washed with abs. EtOH (2 × 2 cm^3) and Et$_2$O (5 cm^3), and dried in air in the dark to give dye **1d** (0.15 g, overall yield 47%) as a tawny powder: mp 207–210 °C (Found: C, 42.11; H, 4.61; N, 5.63. Calc. for C$_{17}$H$_{22}$Cl$_2$N$_2$O$_8$S (485.34): C, 42.07; H, 4.57; N, 5.77%); λ_{max}^{abs}(MeCN)/nm 400 (ε/dm^3 mol^{-1} cm^{-1} 30 700); λ_{max}^{fl}(MeCN)/nm 558; δ_H(500.13 MHz; DMSO-d_6; 25 °C) 2.17 (2 H, m, CH$_2$CH$_2$NH$_3$), 2.54 (3 H, s, MeS), 2.84 (2 H, m, CH$_2$NH$_3$), 4.54 (2 H, t, ^3J 6.8, CH$_2$N), 7.37 (2 H, d, ^3J 8.4, 3′-H, 5′-H), 7.50 (1 H, d, ^3J 16.4, HC = CHPy), 7.70 (2 H, d, ^3J 8.4, 2′-H, 6′-H), 7.73 (3 H, br s, NH$_3$), 8.01 (1 H, d, ^3J 16.4, HC = CHPy), 8.24 (2 H, d, ^3J 6.8, 3-H, 5-H) and 8.90 (2 H, d, ^3J 6.8, 2-H, 6-H); δ_C(125.76 MHz; DMSO-d_6; 27 °C) 14.1 (MeS), 28.4 (CH$_2$CH$_2$NH$_3$), 35.7 (CH$_2$NH$_3$), 56.7 (CH$_2$N), 122.0 (HC = CHPy), 123.7 (3-C, 5-C), 125.7 (3′-C, 5′-C), 128.6 (2′-C, 6′-C), 131.4 (1′-C), 140.6 (HC = CHPy), 142.0 (4′-C), 144.1 (2-C, 6-C) and 153.2 (4-C).

1-(3-Ammoniopropyl)-4-(E)-2-[4-(dimethylamino)phenyl]vinyl-pyridinium diperchlorate (1e). A mixture of compound **4e** (0.22 g, 0.97 mmol), 3-bromopropylammonium bromide (0.26 g, 1.17 mmol), and dry MeCN (15 cm^3) was heated at 80 °C with stirring in the dark for 60 h. After cooling to room temperature, an insoluble substance was filtered off, washed with CHCl$_3$ (3 × 10 cm^3), abs. EtOH (2 × 3 cm^3), and benzene (10 cm^3), and dried in air to give crude dibromide of the dye (0.38 g) as a reddish-brown powder. The dibromide was dissolved in MeOH (15 cm^3) with heating, and a solution of NaClO$_4$ (0.25 g, 2.05 mmol) in MeOH (3 cm^3) was added to the dye solution. After cooling to −10 °C, the pre-cipitate thus formed was quickly filtered off and dried in air to give dye **1e** (0.20 g, overall yield 43%) as a dark red powder: mp 201–204 °C (Found: C, 44.70; H, 5.33; N, 8.94. Calc. for C$_{18}$H$_{25}$Cl$_2$N$_3$O$_8$ (482.31): C, 44.82; H, 5.23; N, 8.71%); λ_{max}^{abs}(MeCN)/nm 482 (ε/dm^3 mol^{-1} cm^{-1} 42500); λ_{max}^{fl}(MeCN)/nm 634; δ_H(500.13 MHz; DMSO-d_6; 24 °C) 2.15 (2 H, m, CH$_2$CH$_2$NH$_3$), 2.83 (2 H, m, CH$_2$NH$_3$), 3.03 (6 H, s, Me$_2$N), 4.47 (2 H, t, ^3J 7.0, CH$_2$N), 6.80 (2 H, d, ^3J 9.0, 3′-H, 5′-H), 7.19 (1 H, d, ^3J 16.0, HC = CHPy), 7.60 (2 H, d, ^3J 9.0, 2′-H, 6′-H), 7.71 (3 H, br s, NH$_3$), 7.94 (1 H, d, ^3J 16.0, HC = CHPy), 8.09 (2 H, d, ^3J 6.9, 3-H, 5-H) and 8.74 (2 H, d, ^3J 6.9, 2-H, 6-H); δ_C(125.76 MHz; DMSO-d_6; 25 °C) 28.4 (CH$_2$CH$_2$NH$_3$), 35.7 (CH$_2$NH$_3$), 39.6 (Me$_2$N), 56.1 (CH$_2$N), 111.9 (3′-C, 5′-C), 117.0 (HC = CHPy), 122.5 (3-C, 5-C, 1′-C), 130.2 (2′-C, 6′-C), 142.4 (HC = CHPy), 143.4 (2-C, 6-C), 151.9 (4′-C) and 154.0 (4-C).

Complexes between dyes 1a–d,f,g and 2a–c (general method). A solution of a mixture of dye **1** (15 μmol) and dye **2** (15 μmol) in MeCN (∼4 cm^3) was slowly (for 2–3 weeks) saturated with a vapour of benzene or a benzene–dioxane mixture (∼2:1, v/v) at room temperature in the dark. The precipitate thus formed was decanted and dried in air to give an appropriate complex **1·2** as a yellow (for dye **2a**) or orange (for dyes **2b,c**) powder. The stoichiometry

of the complex was proved by ^{1}H NMR (in DMSO-d_6; in this solvent, all complexes decompose to give a mixture of free dyes; see Fig. S32–S39 in the ESI†).

Complex (**1a**)$_{1.5}$·**2a** (hydrate) was obtained in 63% yield; water release >115 °C, mp 230–235 °C (dec.) (Found: C, 47.12; H, 5.10; N, 3.89. Calc. for 1.5C$_{18}$H$_{24}$Cl$_2$N$_2$O$_{10}$·C$_{25}$H$_{34}$ClNO$_{10}$·1.5H$_2$O (1319.96): C, 47.32; H, 5.57; N, 4.25%).

Complex **1b·2a** was obtained in 82% yield; mp 98–100 °C (dec.) (Found: C, 50.14; H, 5.61; N, 4.19. Calc. for C$_{16}$H$_{20}$Cl$_2$N$_2$O$_8$·C$_{25}$H$_{34}$ClNO$_{10}$ (983.23): C, 50.08; H, 5.54; N, 4.27%).

Complex **1c·2a** (hydrate) was obtained in 88% yield; glass transition >110 °C (Found: C, 49.50; H, 5.71; N, 4.11. Calc. for C$_{17}$H$_{22}$Cl$_2$N$_2$O$_9$·C$_{25}$H$_{34}$ClNO$_{10}$·0.5H$_2$O (1022.27): C, 49.35; H, 5.62; N, 4.11%).

Complex **1d·2a** was obtained in 85% yield; mp 141–143 °C (dec.) (Found: C, 49.09; H, 5.54; N, 4.07. Calc. for C$_{17}$H$_{22}$Cl$_2$N$_2$O$_8$S·C$_{25}$H$_{34}$ClNO$_{10}$ (1029.33): C, 49.01; H, 5.48; N, 4.08%).

Complex **1f·2a** was obtained in 64% yield; mp 139–142 °C (Found: C, 47.67; H, 5.21; N, 5.38. Calc. for C$_{16}$H$_{19}$Cl$_2$N$_3$O$_{10}$·C$_{25}$H$_{34}$ClNO$_{10}$ (1028.23): C, 47.89; H, 5.20; N, 5.45%).

Complex **1g·2a** was obtained in 90% yield;[15] glass transition ∼155 °C, mp > 177 °C (dec.).

Complex **1a·2b** (hydrate) was obtained in 95% yield; mp 178–182 °C (Found: C, 50.67; H, 5.60; N, 3.73. Calc. for C$_{18}$H$_{24}$Cl$_2$N$_2$O$_{10}$·C$_{29}$H$_{36}$ClNO$_{10}$·H$_2$O (1111.36): C, 50.79; H, 5.62; N, 3.78%).

Complex **1a·2c** was obtained in 63% yield; mp 168–172 °C (Found: C, 49.06; H, 5.28; N, 3.86. Calc. for C$_{18}$H$_{24}$Cl$_2$N$_2$O$_{10}$·C$_{27}$H$_{34}$ClNO$_{10}$S (1099.37): C, 49.16; H, 5.32; N, 3.82%).

Synthesis of cyclobutane derivatives rctt-3b–d (general procedure)

A solution of a mixture of dye **1b–d** (27 μmol) and dye **2a** (14.8 mg, 27 μmol) in dry MeCN (16 cm^3) in a glass flask was irradiated with light from an incandescent lamp (power 60 W) from a distance of ∼15 cm for 200 h. The reaction mixture was concentrated in vacuo to a volume of ∼5–6 cm^3, and this solution was slowly saturated with vapour of a benzene–dioxane mixture (∼2:1, v/v) at room temperature (for 1–2 weeks). The fine-grained crystalline precipitate thus formed was decanted and dried in air to give compound rctt-**3b–d** as a yellowish powder.

1-(3-Ammoniopropyl)-4-r-[2-c-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)-3-t-(1-ethylpyr-idinium-4-yl)-4-t-phenylcyclobutyl]pyridinium triperchlorate (rctt-3b) was obtained in 95% yield: mp > 154 °C (dec.) (Found: C, 51.54; H, 5.75; N, 3.96. Calc. for C$_{41}$H$_{54}$Cl$_3$N$_3$O$_{18}$·0.5C$_6$H$_6$ (1022.29): C, 51.69; H, 5.62; N, 4.11%); λ_{max}^{abs}(MeCN)/nm 225, ∼258sh and ∼285 sh (ε/dm^3 mol^{-1} cm^{-1} 29 700, 10 700 and 4700); δ_H(500.13 MHz; DMSO-d_6; 25 °C) 1.40 (3 H, t, ^3J 7.3, Me), 2.12 (2 H, m, CH$_2$CH$_2$N), 2.28–2.43 (2 H, m, CH$_2$NH$_3$), 3.62 (4 H, s, 2 × CH$_2$O), 3.65 (4 H, m, 2 × CH$_2$O), 3.71 (4 H, m, 2 × CH$_2$O), 3.79 (4 H, m, 2 × CH$_2$CH$_2$OAr), 3.92 (2 H, m, 3′-CH$_2$OAr), 4.08 (2 H, m, 4′-CH$_2$OAr), 4.48 (2 H, q, ^3J 7.3, CH$_2$Me), 4.55 (2 H, t, ^3J 5.9, CH$_2$N), 4.84 (1 H, m, b-CH), 4.97 (2 H, m, a-CH, d-CH), 5.09 (1 H, m, c-CH), 6.53 (1 H, d, ^4J 1.4, 2′-H), 6.93 (1 H, d, ^3J 8.6, 5′-H), 7.03 (1 H, dd, ^3J 8.6, ^4J 1.4, 6′-H), 7.15 (1 H, br t, ^3J 7.0, 4‴-H), 7.20 (3 H, br s, NH$_3$), 7.24 (2 H, t, ^3J 7.5, 3‴-H, 5‴-H), 7.28 (2 H, br d,

^3J 7.3, 2$'''$-H, 6$'''$-H), 7.94 (2 H, d, ^3J 6.8, 3$''$-H, 5$''$-H), 7.97 (2 H, d, ^3J 6.8, 3-H, 5-H), 8.82 (2 H, d, ^3J 6.8, 2-H, 6-H) and 8.88 (2 H, d, ^3J 6.8, 2$''$-H, 6$''$-H); δ_C(125.76 MHz; DMSO-d_6; 30 $^\circ$C) 16.2 (Me), 28.1 (CH$_2$CH$_2$NH$_3$), 35.6 (CH$_2$NH$_3$), 43.5 (d-CH), 44.2 (c-C), 45.9 (b-CH), 46.5 (a-CH), 55.4 (CH$_2$Me), 57.1 (CH$_2$N), 67.1 (4$'$-CH$_2$OAr), 67.3 (3$'$-CH$_2$OAr), 68.2 (CH$_2$CH$_2$OAr), 68.4 (CH$_2$CH$_2$OAr), 68.6 (2 × CH$_2$O), 69.1 (CH$_2$O), 69.2 (CH$_2$O), 69.6 (CH$_2$O), 69.7 (CH$_2$O), 111.6 (2$'$-C), 111.7 (5$'$-C), 120.5 (6$'$-C), 126.8 (4$'''$-C), 127.0 (3$''$-C, 5$''$-C), 127.3 (3-C, 5-C), 127.8 (2$'''$-C, 6$'''$-C), 128.3 (3$'''$-C, 5$'''$-C), 130.3 (1$'$-C), 137.7 (1$'''$-C), 143.18 (2-C, 6-C), 143.24 (2$''$-C, 6$''$-C), 145.7 (4$'$-C), 146.4 (3$'$-C), 159.9 (4$''$-C) and 160.5 (4-C).

1-(3-Ammoniopropyl)-4-r-[2-c-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)-3-t-(1-ethyl-pyridinium-4-yl)-4-t-(4-methoxyphenyl)cyclobutyl]pyridinium triper-chlorate ($rctt$-3c) was obtained in 92% yield: mp 261–262 $^\circ$C (dec.) (Found: C, 51.29; H, 5.81; N, 3.94. Calc. for C$_{42}$H$_{56}$Cl$_3$N$_3$O$_{19}$·0.5C$_6$H$_6$ (1052.32): C, 51.36; H, 5.65; N, 3.99%); λ_{max}^{abs}(MeCN)/nm 230 and ~280sh (ε/dm^3 mol^{-1} cm^{-1} 38 600 and 5700); δ_H(500.13 MHz; DMSO-d_6; 30 $^\circ$C) 1.42 (3 H, t, ^3J 7.3, MeCH$_2$), 2.11 (2 H, m, CH$_2$CH$_2$N), 2.29–2.44 (2 H, m, CH$_2$NH$_3$), 3.62 (4 H, s, 2 × CH$_2$O), 3.65 (4 H, m, 2 × CH$_2$O), 3.67 (3 H, s, MeO), 3.71 (4 H, m, 2 × CH$_2$O), 3.79 (4 H, m, 2 × CH$_2$CH$_2$OAr), 3.92 (2 H, m, 3$'$-CH$_2$OAr), 4.08 (2 H, m, 4$'$-CH$_2$OAr), 4.50 (2 H, q, ^3J 7.3, CH$_2$Me), 4.55 (2 H, t, ^3J 6.0, CH$_2$N), 4.82 (1 H, m, b-CH), 4.89 (2 H, m, a-CH, d-CH), 5.02 (1 H, m, c-CH), 6.52 (1 H, d, ^4J 1.5, 2$'$-H), 6.79 (2 H, d, ^3J 8.7, 3$'''$-H, 5$'''$-H), 6.93 (1 H, d, ^3J 8.4, 5$'$-H), 7.02 (1 H, dd, ^3J 8.4, ^4J 1.5, 6$'$-H), 7.20 (2 H, d, ^3J 8.7, 2$'''$-H, 6$'''$-H), 7.21 (3 H, br s, NH$_3$), 7.91 (2 H, d, ^3J 6.7, 3$''$-H, 5$''$-H), 7.94 (2 H, d, ^3J 6.7, 3-H, 5-H), 8.80 (2 H, d, ^3J 6.7, 2-H, 6-H) and 8.88 (2 H, d, ^3J 6.7, 2$''$-H, 6$''$-H); δ_C(125.76 MHz; DMSO-d_6; 30 $^\circ$C) 16.2 (MeCH$_2$), 28.1 (CH$_2$CH$_2$NH$_3$), 35.7 (CH$_2$NH$_3$), 42.9 (d-CH), 44.3 (c-CH), 45.8 (b-CH), 46.9 (a-CH), 54.9 (MeO), 55.5 (CH$_2$Me), 57.2 (CH$_2$N), 67.1 (4$'$-CH$_2$OAr), 67.2 (3$'$-CH$_2$OAr), 68.2 (CH$_2$CH$_2$OAr), 68.4 (CH$_2$CH$_2$OAr), 68.5 (2 × CH$_2$O), 69.1 (CH$_2$O), 69.2 (CH$_2$O), 69.6 (CH$_2$O), 69.7 (CH$_2$O), 111.5 (2$'$-C), 111.7 (5$'$-C), 113.7 (3$'''$-C, 5$'''$-C), 120.4 (6$'$-C), 127.0 (3$''$-C, 5$''$-C), 127.2 (3-C, 5-C), 129.0 (2$'''$-C, 6$'''$-C), 129.5 (1$'''$-C), 130.3 (1$'$-C), 143.2 (2-C, 6-C), 143.3 (2$''$-C, 6$''$-C), 145.6 (4$'$-C), 146.4 (3$'$-C), 158.0 (4$'''$-C), 160.1 (4$''$-C) and 160.6 (4-C).

1-(3-Ammoniopropyl)-4-r-2-c-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)-3-t-(1-ethylpyr-idinium-4-yl)-4-t-[4-(methylthio)phenyl]cyclobutylpyridinium tri-perchlorate ($rctt$-3d) was obtained in 93% yield: mp 258–259 $^\circ$C (dec.) (Found: C, 49.16; H, 5.37; N, 4.07. Calc. for C$_{42}$H$_{56}$Cl$_3$-N$_3$O$_{18}$S (1029.33): C, 49.01; H, 5.48; N, 4.08%); λ_{max}^{abs}(MeCN)/nm 231, 258 and ~280sh (ε/dm^3 mol^{-1} cm^{-1} 35 000, 25 300 and 8300); δ_H(500.13 MHz; DMSO-d_6; 30 $^\circ$C) 1.42 (3 H, t, ^3J 7.3, MeCH$_2$), 2.11 (2 H, m, CH$_2$CH$_2$N), 2.29–2.43 (2 H, m, CH$_2$NH$_3$), 2.39 (3 H, s, MeS), 3.62 (4 H, s, 2 × CH$_2$O), 3.65 (4 H, m, 2 × CH$_2$O), 3.71 (4 H, m, 2 × CH$_2$O), 3.79 (4 H, m, 2 × CH$_2$CH$_2$OAr), 3.92 (2 H, m, 3$'$-CH$_2$OAr), 4.08 (2 H, m, 4$'$-CH$_2$OAr), 4.51 (2 H, q, ^3J 7.3, CH$_2$Me), 4.55 (2 H, t, ^3J 5.9, CH$_2$N), 4.82 (1 H, m, b-CH), 4.92 (2 H, m, a-CH, d-CH), 5.04 (1 H, m, c-CH), 6.53 (1 H, d, ^4J 1.7, 2$'$-H), 6.93 (1 H, d, ^3J 8.4, 5$'$-H), 7.02 (1 H, dd, ^3J 8.4, ^4J 1.7, 6$'$-H), 7.12 (2 H, d, ^3J 8.4, 3$'''$-H, 5$'''$-H), 7.21 (3 H, br s, NH$_3$), 7.22 (2 H, d, ^3J 8.4, 2$'''$-H, 6$'''$-H), 7.93 (2 H, d, ^3J 6.7, 3$''$-H, 5$''$-H), 7.94 (2 H, d, ^3J 6.7, 3-H, 5-H), 8.81 (2 H, d, ^3J 6.7, 2-H, 6-H) and 8.89 (2 H, d, ^3J 6.7, 2$''$-H, 6$''$-H); δ_C(125.76 MHz; DMSO-d_6; 30 $^\circ$C) 14.5 (MeS), 16.1 (MeCH$_2$), 28.1 (CH$_2$CH$_2$NH$_3$), 35.6 (CH$_2$NH$_3$), 43.0 (d-CH), 44.2 (c-CH), 45.9 (b-CH), 46.6 (a-CH), 55.5 (CH$_2$Me), 57.2 (CH$_2$N), 67.1 (4$'$-CH$_2$OAr), 67.2 (3$'$-CH$_2$OAr), 68.2 (CH$_2$CH$_2$-OAr), 68.4 (CH$_2$CH$_2$OAr), 68.5 (2 × CH$_2$O), 69.1 (CH$_2$O), 69.2 (CH$_2$O), 69.6 (CH$_2$O), 69.7 (CH$_2$O), 111.6 (2$'$-C), 111.7 (5$'$-C), 120.4 (6$'$-C), 125.8 (3$'''$-C, 5$'''$-C), 127.0 (3$''$-C, 5$''$-C), 127.2 (3-C, 5-C), 128.4 (2$'''$-C, 6$'''$-C), 130.2 (1$'$-C), 134.3 (1$'''$-C), 136.7 (4$'''$-C), 143.2 (2-C, 6-C), 143.3 (2$''$-C, 6$''$-C), 145.7 (4$'$-C), 146.4 (3$'$-C), 159.8 (4$''$-C) and 160.4 (4-C).

^{1}H NMR titration

MeCN-d_3 (water content <0.05% v/v, FGUP RNTs Prikladnaya Khimiya, St. Petersburg, Russian Federation) was used as the solvent. The stability constants of the complexes of dyes 1a–i with dyes 2a–c were determined by analyzing the shifts of the proton signals of dyes 2a–c ($\Delta\delta_H$) depending on the concentration of the added dye 1a–i. The total concentrations of dyes 2a–c did not change being equal to ~1 × 10^{-3} M, and the dye 1a–i concentra-tions were varied starting from zero (the maximum 1 to 2 concen-tration ratio was ~3). The $\Delta\delta_H$ values were measured to an accuracy of 0.001 ppm. The stability constants of the complexes were calcu-lated using the HYPNMR program[21] and are shown in Table 1.

Irradiation of dyes 1a–i (general procedure)

UV-vis spectra of dyes 1a–i (MeCN, C_{dye} ≈ 1 × 10^{-4} M, 0.1 cm quartz cells, ambient temperature) and their photolysis products were recorded in the range 200–600 nm with an increment of 0.5 nm (Fig. 6 and Fig. S42–S50 in the ESI†). The unfiltered light of a 60 W incandescent lamp was used for irradiation, the distance to the light source was ~15 cm. The solutions were not degassed prior to irradiation, as an electrocyclic reaction of the dyes, which could result in the formation of dihydrophenan-threne analogues, does not occur.

Irradiation of pseudodimeric complexes 1·2 (general procedure)

UV-vis spectra of a mixture of dye 1a–i with dye 2a or dye 1a with dye 2b,c (MeCN, $C_1 = C_2 = 5 × 10^{-4}$ M, 0.1 cm quartz cell, ambient temperature) and their photolysis products were recorded in the range of 200–600 nm with an increment of 0.5 nm (Fig. 7 and Fig. S51–S57 in the ESI†). The unfiltered light of a 60 W incandescent lamp was used for irradiation, the distance to the light source was ~15 cm. The solutions were not degassed before irradiation.

X-ray crystallography

The crystals of styryl dyes 1f and 2c, complexes 1d·2a and 1f·2a, and cyclobutane $rctt$-3c were grown from MeCN solutions, which were slowly saturated with benzene or a benzene–dioxane mixture (~2:1, v/v) by the vapour diffusion method at ambient tempera-ture in the dark. The single crystals of all compounds were coated with perfluorinated oil and mounted on a Bruker SMART-CCD diffractometer [graphite monochromatized Mo-Kα radia-tion (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54178 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 the disordered benzene molecule in structure $rctt$-$3c$·$2C_6H_6$·$0.75MeCN$·$0.25H_2O$ and whole structure $1d$·$2a$·$0.7C_6H_6$·$0.7H_2O$, which were refined isotropically). In the case of $1f$·$0.25H_2O$, absorption correction was applied using the SADABS method. The hydrogen atoms were fixed at calculated positions at carbon atoms and then refined with an isotropic approximation for $2c$·$C_4H_8O_2$·$3H_2O$ or by using a "riding" model for other structures. The hydrogen atoms of the NH_3^+ groups in all structures were calculated geometrically and refined by using the "riding" model. The hydrogen atoms of the water molecules of solvation in $2c$·$C_4H_8O_2$·$3H_2O$ were found from the Fourier syntheses and then refined isotropically. In other hydrated structures, water hydrogen atoms were not located.

Crystal data for $1f$·$0.25H_2O$: $C_{16}H_{19.5}Cl_2N_3O_{10.25}$, M = 488.74, orthorhombic, space group $Pbcn$ (no. 60), yellowish plate, a = 16.3977(5) Å, b = 8.3891(3) Å, c = 29.1772(9) Å, V = 4013.7(2) Å^3, T = 100(2) K, Z = 8, μ = 3.501 mm^{-1}, ρ_{calc} = 1.618 g cm^{-3}, $2\theta_{max}$ = 114.59°, 11 130 reflections measured, 2475 unique (R_{int} = 0.0614), R_1 = 0.0588 (1891 reflections with $I > 2\sigma(I)$), wR_2 = 0.1179 (all data), goodness-of-fit on F^2 = 1.035, 342 parameters, min/max residual electron density = $-0.307/0.397$ e̅ Å^{-3}. The $H_2O(1W)$ water molecule of solvation lies in a two-fold axis with the occupancy of 0.25. Both independent perchlorate anions are disordered over two sites with occupancy ratios of 0.89 : 0.11 and 0.56 : 0.44. ISOR command was applied to oxygen atoms of the disordered anions in order to constrain their anisotropic thermal parameters.

Crystal data for $2c$·$C_4H_8O_2$·$3H_2O$: $C_{31}H_{48}ClNO_{15}S$, M = 742.21, triclinic, space group $P\bar{1}$ (no. 2), red block, a = 7.9257(5) Å, b = 11.4270(7) Å, c = 19.6257(10) Å, α = 100.100(2)°, β = 100.108(2)°, γ = 93.581(2)°, V = 1714.74(17) Å^3, T = 120(2) K, Z = 2, μ = 0.245 mm^{-1}, ρ_{calc} = 1.437 g cm^{-3}, $2\theta_{max}$ = 56.998°, 10 164 reflections measured, 8476 unique (R_{int} = 0.0335), R_1 = 0.0578 (4386 reflections with $I > 2\sigma(I)$), wR_2 = 0.1381 (all data), goodness-of-fit on F^2 = 0.875, 634 parameters, min/max residual electron density = $-0.489/0.378$ e̅ Å^{-3}. No constraints were applied.

Crystal data for $1d$·$2a$·$0.7C_6H_6$·$0.7H_2O$: $C_{46.2}H_{61.6}Cl_3N_3O_{18.7}S$, M = 1096.59, monoclinic, space group $C2/c$ (no. 15), yellow block, a = 37.878(8) Å, b = 16.492(3) Å, c = 35.710(7) Å, β = 106.404(3)°, V = 21399(8) Å^3, T = 120(2) K, Z = 16, μ = 0.284 mm^{-1}, ρ_{calc} = 1.361 g cm^{-3}, $2\theta_{max}$ = 54.000°, 100 229 reflections measured, 23352 unique (R_{int} = 0.2225), R_1 = 0.1843 (6415 reflections with $I > 2\sigma(I)$), wR_2 = 0.5145 (all data), goodness-of-fit on F^2 = 1.180, 764 parameters, min/max residual electron density = $-1.216/1.285$ e̅ Å^{-3}. The reflections were collected from a weakly reflecting crystal (mean $I/\sigma(I)$ = 1.09). For this reason the final parameters are characterized by low accuracy. Unfortunately, we failed to obtain better crystals and better structural data. Nevertheless, we include this structure in this article without discussing subtle details of the geometry just in order to show one more arrangement of two styryl dye cations within a pseudodimeric complex. The peripheral part of the crown ether fragment of one of the two independent dye $2a$ cations is disordered over

two conformations with the occupancy ratio of 0.67 : 0.33. The conjugated fragment of the second dye $2a$ cation is disordered according to "pedal" isomerization and the s-conformer occupancy ratio is 0.53 : 0.47. The ethylene moiety of one of the two independent dye $1d$ cations is also "pedal"-disordered with the occupancy ratio of 0.62 : 0.38. The MeS group of this cation is disordered over two sites with the same occupancy ratio. Each of the six independent perchlorate anions $Cl(1)O_4$,...,$Cl(6)O_4$ are disordered over two sites with the occupancy ratios of 0.54 : 0.46, 0.56 : 0.44, 0.73 : 0.27, 0.59 : 0.41, 0.59 : 0.41, and 0.61 : 0.39, respectively. One of the three independent benzene molecules is situated at the symmetry centre. Another benzene molecule is placed in the two-fold axis and is disordered over two sites via rotation in the own plane with the occupancy ratio of 0.72 : 0.28. The third benzene molecule has the occupancy of 0.40 and alternates with water molecules $H_2O(2W)$,...,$H_2O(6W)$. All water molecules of solvation have occupancies of 0.30 or 0.20. SADI commands were applied in order to constrain the disordered fragments. For the reason of low accuracy of structure $1d$·$2a$·$0.7C_6H_6$·$0.7H_2O$ we do not discuss its structural details, but consider only the general view, that is, the connectivity scheme that surely is realistic.

Crystal data for $1f$·$2a$·$0.5C_6H_6$·$2H_2O$: $C_{44}H_{60}Cl_3N_4O_{22}$, M = 1103.31, triclinic, space group $P\bar{1}$ (no. 2), yellow needle, a = 10.7742(7) Å, b = 12.9619(9) Å, c = 19.5026(14) Å, α = 74.870(3)°, β = 74.856(3)°, γ = 80.051(3)°, V = 2521.9(3) Å^3, T = 120(2) K, Z = 2, μ = 0.267 mm^{-1}, ρ_{calc} = 1.453 gcm^{-3}, $2\theta_{max}$ = 51.998°, 14 526 reflections measured, 9469 unique (R_{int} = 0.0752), R_1 = 0.0715 (4080 reflections with $I > 2\sigma(I)$), wR_2 = 0.1942 (all data), goodness-of-fit on F^2 = 0.873, 794 parameters, min/max residual electron density = $-0.423/0.499$ e̅ Å^{-3}. The benzene molecule of solvation is situated at the symmetry centre. The perchlorate anion $Cl(2)O_4$ and the conjugated moiety of the dye $2a$ cation are disordered over two sites with the occupancy ratios of 0.74 : 0.26 and 0.70 : 0.30, respectively. The anions $Cl(3)O_4$ and $Cl(4)O_4$ are situated near the symmetry centres with equal occupancies of 0.50. SADI and ISOR commands were applied to constrain these disordered groups.

Crystal data for $rctt$-$3c$·$2C_6H_6$·$0.75MeCN$·$0.25H_2O$: $C_{55.5}H_{70.75}Cl_3N_{3.75}O_{19.25}$, M = 1204.75, orthorhombic, space group $Pca2_1$ (no. 29), colourless plate, a = 14.0228(9) Å, b = 18.0075(11) Å, c = 22.8626(14) Å, V = 5773.2(6) Å^3, T = 120(2) K, Z = 4, μ = 0.237 mm^{-1}, ρ_{calc} = 1.386 g cm^{-3}, $2\theta_{max}$ = 56.000°, 57 119 reflections measured, 13 902 unique (R_{int} = 0.2335), R_1 = 0.0818 (5745 reflections with $I > 2\sigma(I)$), wR_2 = 0.1730 (all data), goodness-of-fit on F^2 = 0.898, 717 parameters, min/max residual electron density = $-0.323/0.510$ e̅ Å^{-3}. One of the two independent benzene molecules is disordered over two close sites with the occupancy ratio of 0.52 : 0.48. The MeCN, $H_2O(1W)$, and $H_2O(2W)$ molecules of solvation are situated in one and the same site with the occupancies of 0.75, 0.14, and 0.11, respectively. ISOR command was applied to these molecules to constrain their anisotropic thermal parameters.

All the calculations were performed using the SHELXL[28] and Olex-2[29] software. CCDC reference numbers 1430268 ($1f$·$0.25H_2O$), 1430269 ($2c$·$C_4H_8O_2$·$3H_2O$), 1430270 ($1d$·$2a$·$0.7C_6H_6$·$0.7H_2O$), 1430271 ($1f$·$2a$·$0.5C_6H_6$·$2H_2O$), and 1430272 ($rctt$-$3c$·$2C_6H_6$·$0.75MeCN$·$0.25H_2O$).

Acknowledgements

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