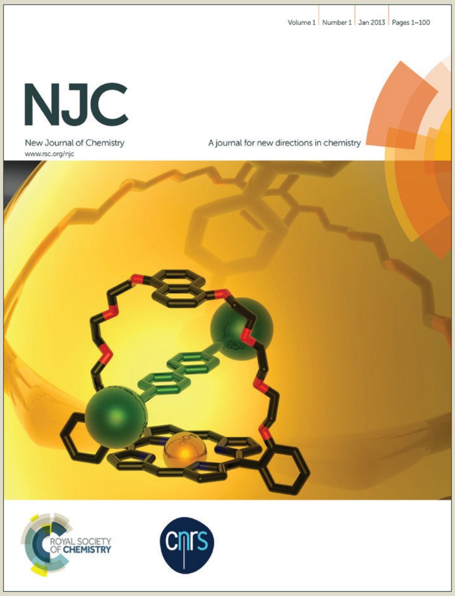
NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/njc

Please do not adjust margins

Journal Name

ARTICLE

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Sergey P. Gromov,*[a,b] Artem I. Vedernikov,[a] Sergey K. Sazonov,[a] Lyudmila G. Kuz'mina,[c] Natalia A. Lobova,[a] Yuri A. Strelenko[d] and Judith A. K. Howard[e]

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 monotopic interaction of the ammonioalkyl group with the crown ether moiety via hydrogen bonding. Components of pseudodimeric complexes undergo stereospecific cross-[2 + 2] photocycloaddition reaction to give unsymmetrical *rctt* isomer 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 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 self-assembly of organic molecules via various non-covalent interactions such as coordination, hydrogen bonding, and 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 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. On exposure to light, this dye is converted almost completely to cation-capped *Z* isomer stabilized by intramolecular coordination of 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).

---

[a] *Photochemistry Center, Russian Academy of Sciences, ul. Novatorov 7A-1, Moscow 119421, Russian Federation. E-mail: spgromov@mail.ru.*
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory 1-3, Moscow 119991, Russian Federation.*
[c] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskiy prosp. 31, Moscow 119991, Russian Federation.*
[d] *N. D. Zelinskiy Institute of Organic Chemistry, Russian Academy of Sciences, Leninskiy prosp. 47, Moscow 119991, Russian Federation.*
[e] *Chemistry Department, Durham University, South Road, Durham DH1 3LE, United Kingdom.*

† Electronic Supplementary Information (ESI) available: ^{1}H and ^{13}C NMR spectra, UV–vis spectra, emission spectra, crystal packings, and X-ray crystallographic data in CIF format. See DOI: 10.1039/x0xx00000x

New Journal of Chemistry Accepted Manuscript

Please do not adjust margins

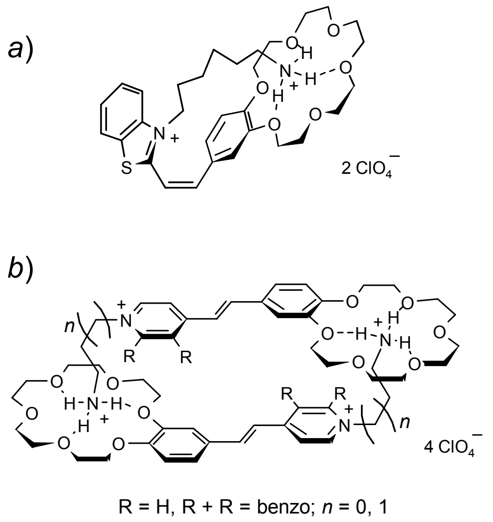
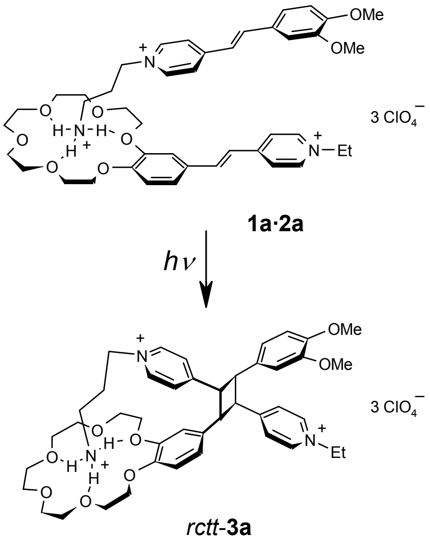


Chart 1 Structure of 18-crown-6-containing styryl dye complexes based on hydrogen bonding.

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, logK_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 antiparallel, which promotes an effective stereospecific auto-[2 + 2] photocycloaddition (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 disruption of the conjugated chain in the chromophore moieties.

We suggested that 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] photocycloaddition (here "cross-PCA" means that two different ethylene compounds 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 of their spectral properties.



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

It is noteworthy that 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 (cyclodextrins, 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.

New Journal of Chemistry Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

New Journal of Chemistry Accepted Manuscript

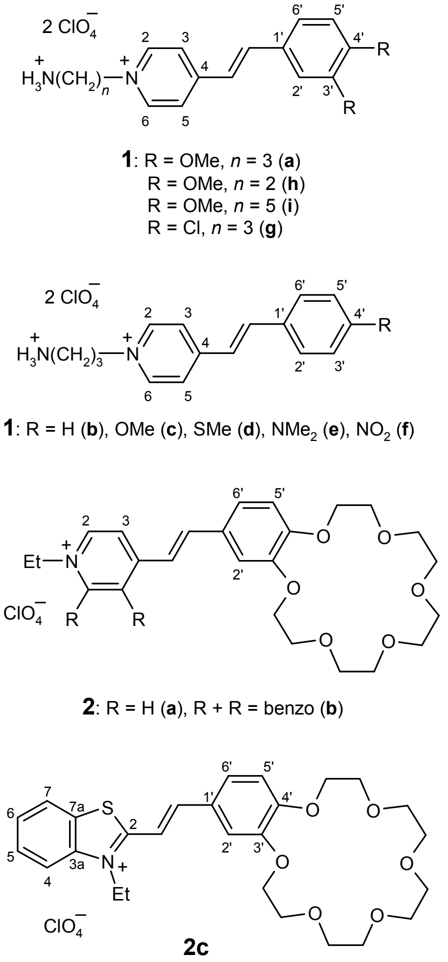
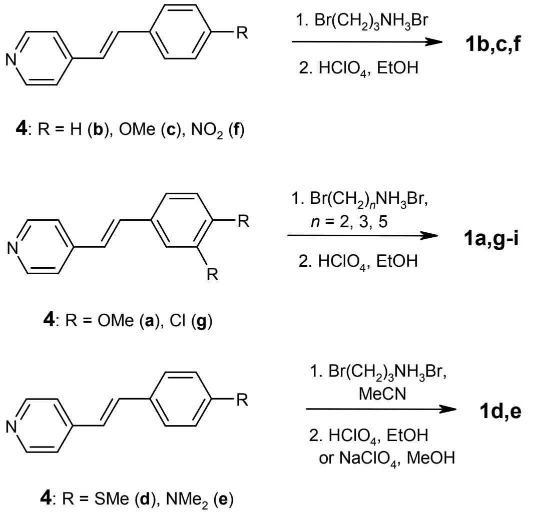


Chart 2 Structure of dyes **1a–i** and **2a–c**.

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**, quaternization of **4d,e** (R = SMe, NMe_2) with 3-bromopropylammonium 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.



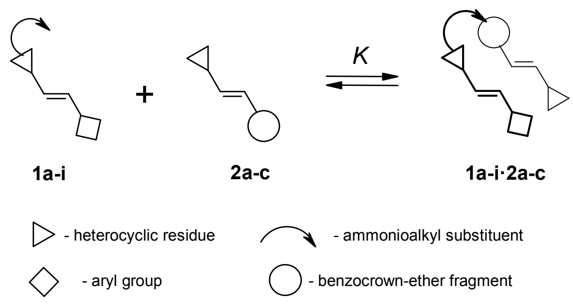
Scheme 2 Synthesis of dyes **1a–i**.

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 Figs 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 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 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 Experimental section and Fig. S22 in the ESI). Dye **1f** containing the NO_2 group is non-fluorescent.

Please do not adjust margins

New Journal of Chemistry Accepted Manuscript



Scheme 3 Complex formation between dyes **1a–i** and **2a–c**.

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 **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_2O groups of **2a** shift downfield by up to $\Delta\delta_H$ = 0.07 ppm upon mixing with **1b**, which confirms hydrogen bonding of the ammonium group with the crown ether. Meanwhile, the $(CH_2)_3NH_3^+$ signals of dye **1b** and ethyl group signals of dye **2a** shift upfield on 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** (Figs 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:

$$\mathbf{1b\text{–}i} + \mathbf{2a\text{–}c} \xrightleftharpoons{K} \mathbf{1b\text{–}i{\cdot}2a\text{–}c}$$

where K/M^{-1} is the stability constant of the pseudodimeric complex.

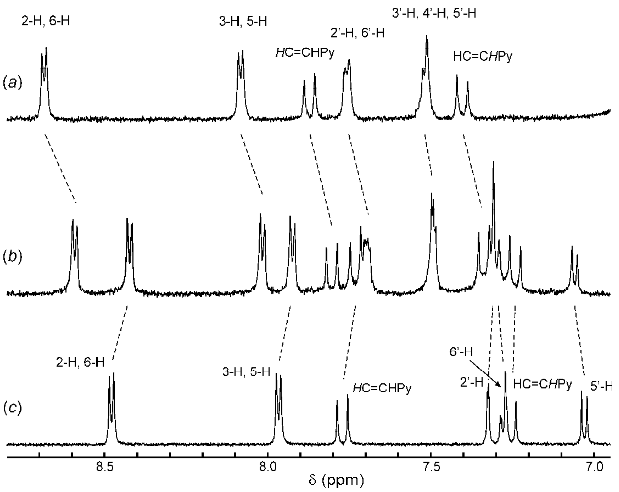


Fig. 1 ^{1}H NMR spectra (aromatic proton region) of (*a*) dye **1b**, (*b*) a 1:1 mixture of dyes **1b** and **2a**, and (*c*) dye **2a** (C_{dye} = 1×10^{-3} M), MeCN-d_3, 30 °C.

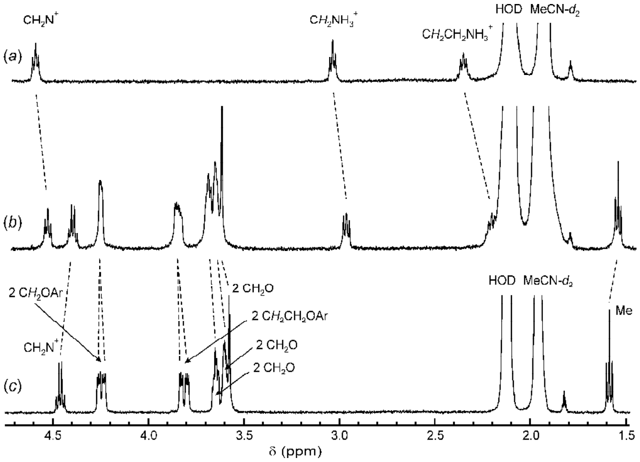


Fig. 2 ^{1}H NMR spectra (aliphatic proton region) of (*a*) dye **1b**, (*b*) a 1:1 mixture of dyes **1b** and **2a**, and (*c*) dye **2a** (C_{dye} = 1×10^{-3} M), MeCN-d_3, 30 °C.

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.

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

This journal is © The Royal Society of Chemistry 20xx

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 stability of hydrogen bonding between the primary ammonium group and 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 **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 Experimental section and Figs 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.

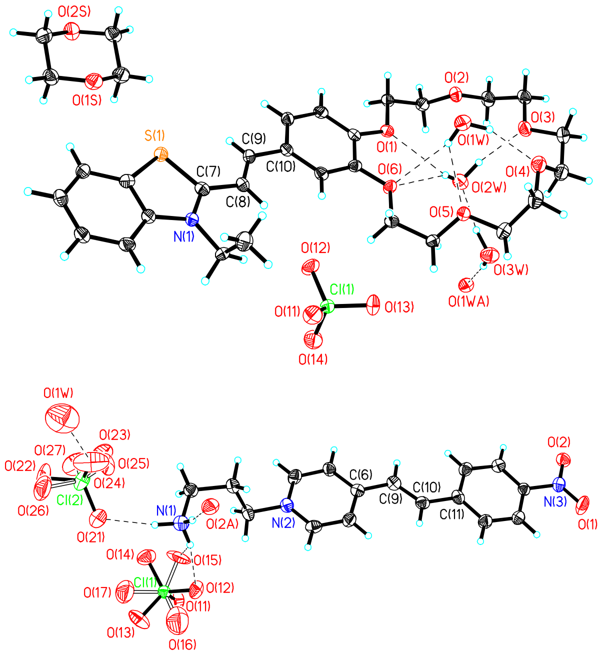


Fig. 3 Structures **2c**·$C_4H_8O_2$·$3H_2O$ (top) and **1f**·$0.25H_2O$ (bottom). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen bonds are drawn with dash lines. The additional letters "A" indicate that atoms belong to symmetrically related sites.

The 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 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 its 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**.

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

New Journal of Chemistry Accepted Manuscript

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**·$0.25H_2O$ 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**·$0.5C_6H_6$·$2H_2O$ 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]

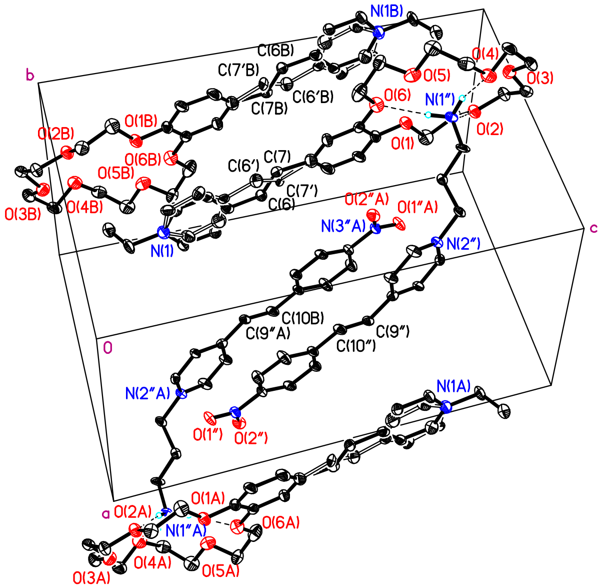


Fig. 4 Stack of cations forming pseudodimeric complexes in structure **1f**·**2a**·$0.5C_6H_6$·$2H_2O$. Thermal ellipsoids are drawn at the 40% probability level. Most of hydrogen atoms are omitted for clarity. Hydrogen bonds are drawn with dash lines. The additional letters "A" and "B" indicate that atoms belong to symmetrically related sites.

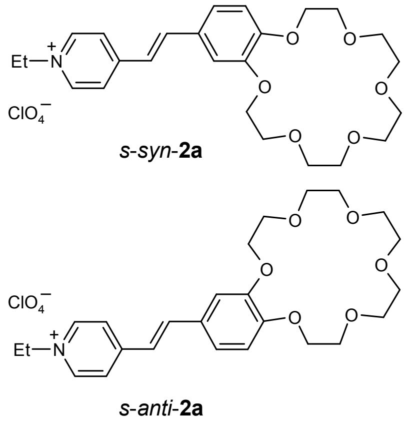


Chart 3 Conformers of dye **2a**.

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

New Journal of Chemistry Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

C(7′)…C(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 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 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**·0.5C_6H_6·2H_2O 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**·0.7C_6H_6·0.7H_2O 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 weak reflecting ability of the crystal (see Experimental section).

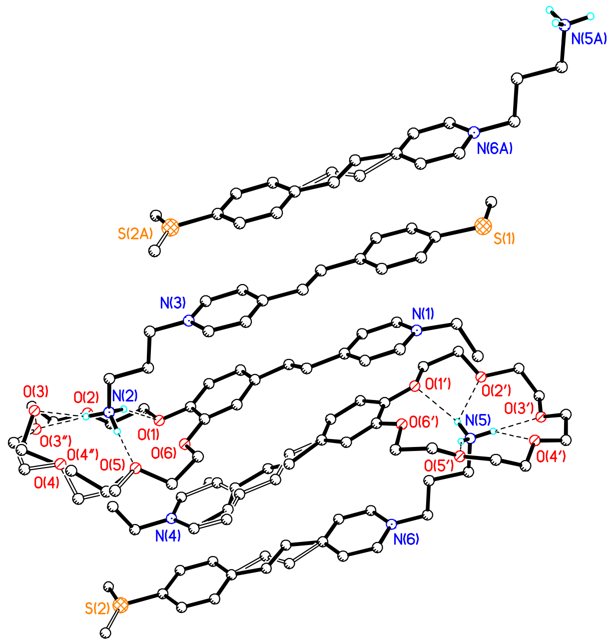


Fig. 5 Stack of cations forming pseudodimeric complexes in structure **1d**·**2a**·0.7C_6H_6·0.7H_2O. Most of hydrogen atoms are omitted for clarity. Hydrogen bonds are drawn with dash lines. The additional letters “A” indicate that atoms belong to symmetrically related sites.

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**·0.5C_6H_6·2H_2O, 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**·0.7C_6H_6·0.7H_2O, 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**·0.7C_6H_6·0.7H_2O clearly demonstrates the typical structure of pseudodimeric complexes, which is also retained in solutions (according to ^{1}H 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 on exposure to visible light to give centrosymmetric *rctt* isomers of cyclobutane derivatives. This is possible owing to the

New Journal of Chemistry Accepted Manuscript

topochemical control of the crystal lattice which favours the formation of dimeric pairs of the dyes. In these dimers, the planar molecular dye cations 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 Figs S42–S49 in the ESI). Previously,[16] we observed a similar behaviour of dye **2a** (see also Fig. S50). An exception is dye **1e** containing the NMe_2 group for which the LWAB intensity decreases only slightly (to 96% of the initial value, Fig. S46). Apparently, high electron-donating properties of the substituent nitrogen as compared with other heteroatoms lead to 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) exited state.[26]

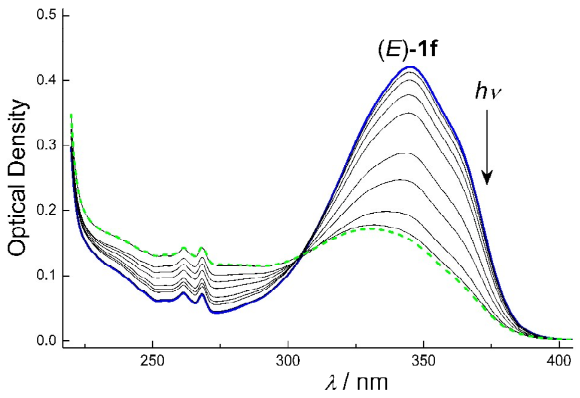
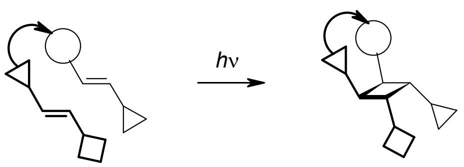


Fig. 6 Irradiation of solution of dye **1f** for 0, 1, 3, 6, 10, 20, 30, 50, 80, and 110 min (MeCN, $C_{1f} = 1.11\times10^{-4}$ M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm). The green dash curve is a photostationary mixture consisting of *E* and *Z* isomers of **1f**.



1a-d,f,h·2a
or **1a·2b**

rctt-**3**

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

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 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 (Figs S51–S55 in the ESI). The disappearance of absorption in the region of >330 nm is caused by 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 equimolar mixture of dyes **1d** and **2a**. In the beginning of irradiation, the absorption intensity at about 400 nm rapidly decreases (in ~ 30 min), which is caused by 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 $\lambda > 330$ nm.

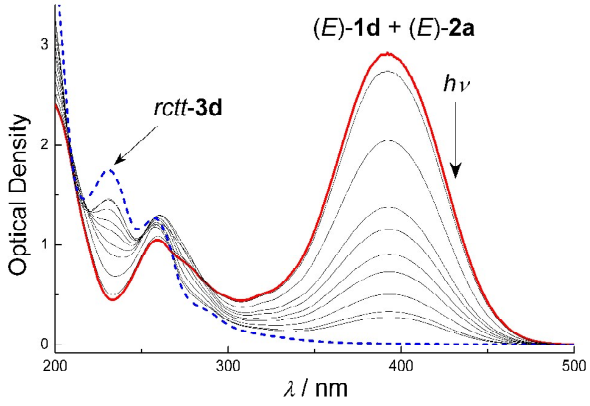


Fig. 7 Irradiation of solution of an equimolar mixture of dyes **1d** and **2a** for 0, 1, 6, 20, 40, and 80 min and 2, 4, 8, and 16 h (MeCN, $C_{1d} = C_{2a} = 5\times10^{-4}$ M, 0.1-cm quartz cell, unfiltered light from a 60 W incandescent lamp, distance to the light source ~ 15 cm). The blue dash curve is the spectrum of cyclobutane *rctt*-**3d** (MeCN, $C_{3d} = 5\times10^{-4}$ M, 0.1-cm quartz cell).

New Journal of Chemistry Accepted Manuscript

New Journal of Chemistry Accepted Manuscript

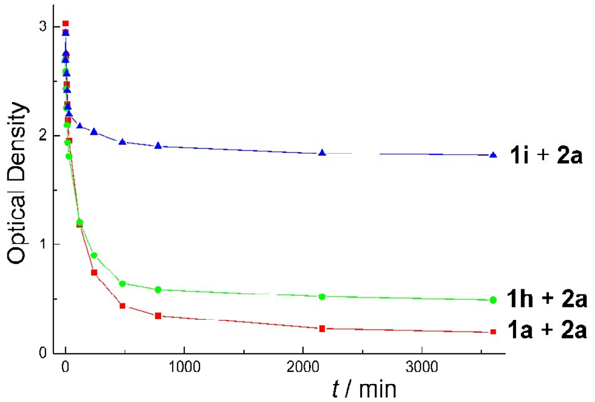


Fig. 8 Dependence of the absorbance at 397 nm on the time of irradiation of solutions of equimolar mixtures of dye **2a** with dyes **1a**, **1h**, and **1i** (MeCN, $C_{1a,h,i} = C_{2a} = 5\times10^{-4}$ M, 0.1-cm quartz cell).

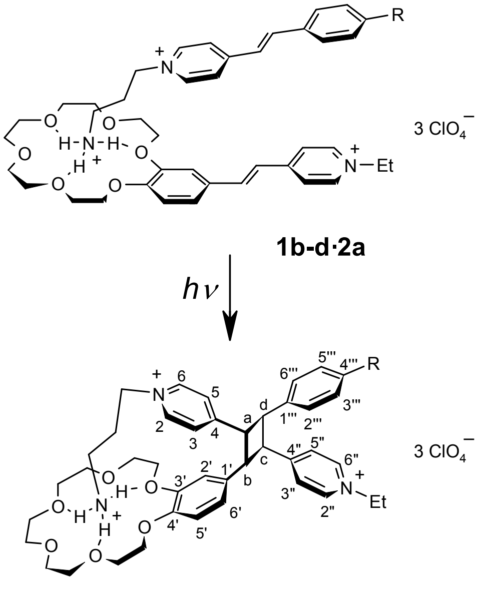
The variation of the absorbance at 397 nm for solutions of equimolar mixtures of dye **2a** with dyes **1a,h,i** depending on the irradiation time is shown in Fig. 8. It can be clearly seen that cross-PCA occurs most rapidly in complex **1a**·**2a** and is somewhat slower in **1h**·**2a**. In the case of complex **1i**·**2a**, the decrease in the long-wavelength absorption reaches ~ 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 *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** (Figs S56, 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 efficient formation of the TICT exited 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 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 pseudodimeric complexes. Thus, cross-PCA reaction efficiently occurs in the complexes formed by 4-pyridine-derived dyes having relatively short ammoniopropyl *N*-substituent and electron-donating substituents OMe, 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).



rctt-**3**: R = H (**b**), OMe (**c**), SMe (**d**)

Scheme 5 Synthesis of cyclobutane derivatives *rctt*-**3b–d**.

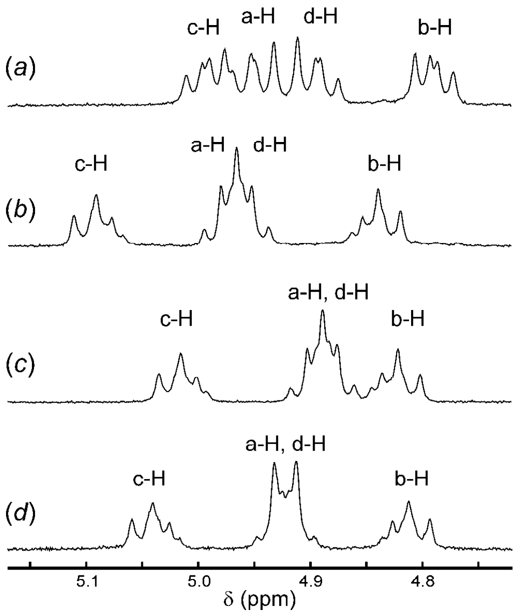


Fig. 9 ^{1}H NMR spectra (cyclobutane proton region) of compounds (*a*) *rctt*-**3a**, (*b*) *rctt*-**3b**, (*c*) *rctt*-**3c**, and (*d*) *rctt*-**3d**, DMSO-d_6, 30 °C.

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*-**3b–d** are shown in Figs 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 derivative. 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.

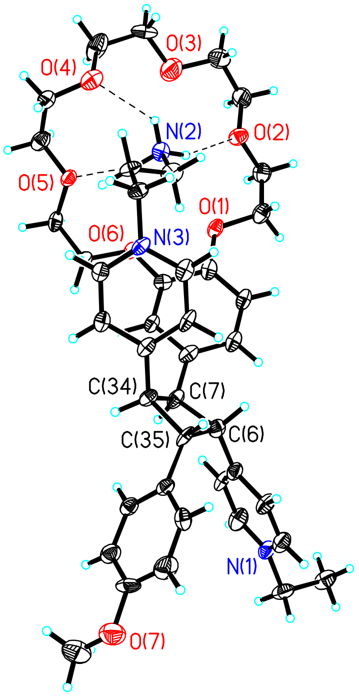


Fig. 10 Structure of the main component in *rctt*-**3c**·2C_6H_6·0.75MeCN·0.25H_2O. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen bonds are drawn with dash lines.

In *rctt*-**3c**·2C_6H_6·0.75MeCN·0.25H_2O, the NH_3^+ group of the *N*-ammoniopropylpyridinium moiety is coordinated intramolecularly by the benzocrown ether moiety that occupies *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 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.

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

New Journal of Chemistry Accepted Manuscript

made by the stacking interactions of the planar conjugated moieties of the dyes. Therefore, pseudodimer 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 with 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.

Preparations

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] $\lambda_{max}{}^{abs}$(MeCN)/nm 403 (ε/dm^3 mol^{-1} cm^{-1} 33600); $\lambda_{max}{}^{fl}$(MeCN)/nm 550.

Dye **1b** was obtained according to a published procedure;[14] $\lambda_{max}{}^{abs}$(MeCN)/nm 348 (ε/dm^3 mol^{-1} cm^{-1} 29600); $\lambda_{max}{}^{fl}$(MeCN)/nm 367.

Dye **1g** was obtained according to a published procedure;[15] $\lambda_{max}{}^{abs}$(MeCN)/nm 346 (ε/dm^3 mol^{-1} cm^{-1} 37400); $\lambda_{max}{}^{fl}$(MeCN)/nm 438.

Dye **2c** was obtained according to a published procedure;[7] $\lambda_{max}{}^{abs}$(MeCN)/nm 431 (ε/dm^3 mol^{-1} cm^{-1} 41700); $\lambda_{max}{}^{fl}$(MeCN)/nm 535; δ_C(125.76 MHz; DMSO-d_6; 30 °C) 14.0 (Me), 44.2 (CH_2N), 68.3 (4′-CH_2OAr), 68.4 (4′-CH_2CH_2OAr), 68.5 (3′-CH_2OAr, 3′-CH_2CH_2OAr), 69.6 (CH_2O), 69.7 (3 × CH_2O), 69.8 (CH_2O), 69.9 (CH_2O), 110.4 (HC=*C*HHet), 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 (H*C*=CHHet), 152.5 (4′-C) and 171.6 (2-C).

Cyclobutane *rctt*-**3a** was obtained according to a published procedure;[9] $\lambda_{max}{}^{abs}$(MeCN)/nm 231 and 281 (ε/dm^3 mol^{-1} cm^{-1} 34400 and 6300); δ_C(125.76 MHz; DMSO-d_6; 30 °C) 16.2 (*Me*CH_2), 28.1 ($CH_2CH_2NH_3$), 35.7 (CH_2NH_3), 43.5 (d-CH), 44.6 (c-CH), 45.7 (b-CH), 46.6 (a-CH), 55.3 (3′′′-MeO), 55.47 (*C*H_2Me), 55.52 (4′′′-MeO), 57.2 (CH_2N), 67.1 (4′-CH_2OAr), 67.3 (3′-CH_2OAr), 68.3 (CH_2CH_2OAr), 68.4 (CH_2CH_2OAr), 68.6 (2 × CH_2O), 69.1 (CH_2O), 69.2 (CH_2O), 69.6 (CH_2O), 69.7 (CH_2O), 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-bromopropylammonium bromide (0.82 g, 3.75 mmol) or 2-bromoethylammonium bromide (0.77 g, 3.75 mmol) or 5-bromopentylammonium 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 cm^3) and then cooled to –10 °C. The insoluble substance was filtered off, washed with cold abs. EtOH (2 × 3 cm^3) and $CHCl_3$ (2 × 3 cm^3) and dried in air to give dibromide of the dye. This dibromide was dissolved in a mixture of abs. EtOH (5 cm^3) and water (minimal quantity) with heating, and 70% aq $HClO_4$ (0.31 cm^3, 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 cm^3), 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 $C_{17}H_{22}Cl_2N_2O_9$ (469.27): C, 43.51; H, 4.73; N, 5.97%); $\lambda_{max}{}^{abs}$(MeCN)/nm 388 (ε/dm^3 mol^{-1} cm^{-1} 36400); $\lambda_{max}{}^{fl}$(MeCN)/nm 500; δ_H(500.13 MHz; DMSO-d_6; 25 °C) 2.18 (2 H, m, CH_2CH$_2$NH$_3$), 2.85 (2 H, m, CH_2NH$_3$), 3.84 (3 H, s, MeO), 4.54 (2 H, t, ^{3}*J* 7.0, CH$_2$N), 7.08 (2 H, d, ^{3}*J* 8.6, 3′-H, 5′-H), 7.38 (1 H, d, ^{3}*J* 16.4, HC=C*H*Py), 7.72 (3 H, br s, NH$_3$), 7.73 (2 H, d, ^{3}*J* 8.6, 2′-H, 6′-H), 8.00 (1 H, d, ^{3}*J* 16.4, *H*C=CHPy), 8.21 (2 H, d, ^{3}*J* 6.6, 3-H, 5-H) and 8.86 (2 H, d, ^{3}*J* 6.6, 2-H, 6-H); δ_C(125.76 MHz; DMSO-d_6; 30 °C) 28.4 ($CH_2CH_2NH_3$), 35.7 (CH_2NH_3), 55.3 (MeO), 56.6 (CH_2N), 114.6 (3′-C, 5′-C), 120.6 (HC=*C*HPy), 123.4 (3-C, 5-C), 127.7 (1′-C), 130.0 (2′-C, 6′-C), 141.0 (H*C*=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 $C_{16}H_{19}Cl_2N_3O_{10}$ (484.24): C, 39.69; H, 3.95; N, 8.68%); $\lambda_{max}{}^{abs}$(MeCN)/nm 345 (ε/dm^3 mol^{-1} cm^{-1} 37800); δ_H(500.13 MHz; DMSO-d_6; 25 °C)

New Journal of Chemistry Accepted Manuscript

Please do not adjust margins

2.19 (2 H, m, CH_2CH$_2$NH$_3$), 2.86 (2 H, m, CH_2NH$_3$), 4.59 (2 H, t, ^3J 7.1, CH$_2$N), 7.73 (3 H, br s, NH$_3$), 7.78 (1 H, d, ^3J 16.5, HC=C*H*Py), 8.01 (2 H, d, ^3J 9.1, 2′-H, 6′-H), 8.14 (1 H, d, ^3J 16.5, *H*C=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 (*C*H$_2$CH$_2$NH$_3$), 35.7 (CH$_2$NH$_3$), 57.1 (CH$_2$N), 124.2 (3′-C, 5′-C), 124.7 (3-C, 5-C), 127.4 (HC=*C*HPy), 128.9 (2′-C, 6′-C), 138.1 (H*C*=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]pyridinium 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 $C_{17}H_{22}Cl_2N_2O_{10}\cdot1.5H_2O$ (512.29): C, 39.86; H, 4.92; N, 5.47%); λ_{max}^{abs}(MeCN)/nm 407 (ε/dm^3 mol^{-1} cm^{-1} 34300); λ_{max}^{fl}(MeCN)/nm 550; δ_H(500.13 MHz; DMSO-d_6; 30 °C) 3.49 (2 H, m, CH_2NH$_3$), 3.84 (3 H, s, 4′-MeO), 3.86 (3 H, s, 3′-MeO), 4.69 (2 H, m, CH$_2$N), 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=C*H*Py), 7.95 (3 H, br s, NH$_3$), 8.01 (1 H, d, ^3J 16.2, *H*C=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 (CH$_2$NH$_3$), 55.57 (MeO), 55.59 (MeO), 56.6 (CH$_2$N), 110.1 (2′-C), 111.7 (5′-C), 120.7 (HC=*C*HPy), 123.3 (3-C, 5-C, 6′-C), 127.9 (1′-C), 141.7 (H*C*=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 $C_{20}H_{28}Cl_2N_2O_{10}$ (527.35): C, 45.55; H, 5.35; N, 5.31%); λ_{max}^{abs}(MeCN)/nm 400 (ε/dm^3 mol^{-1} cm^{-1} 31800); λ_{max}^{fl}(MeCN)/nm 546; δ_H(500.13 MHz; DMSO-d_6; 25 °C) 1.31 (2 H, m, CH_2CH$_2$CH$_2$NH$_3$), 1.57 (2 H, m, CH_2CH$_2$NH$_3$), 1.93 (2 H, m, CH_2CH$_2$N), 2.79 (2 H, m, CH_2NH$_3$), 3.83 (3 H, s, 4′-MeO), 3.85 (3 H, s, 3′-MeO), 4.46 (2 H, t, ^3J 7.5, CH$_2$N), 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=C*H*Py), 7.60 (3 H, br s, NH$_3$), 7.97 (1 H, d, ^3J 16.2, *H*C=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 (*C*H$_2$CH$_2$CH$_2$NH$_3$), 26.3 (*C*H$_2$CH$_2$NH$_3$), 29.7 (*C*H$_2$CH$_2$N), 38.5 (CH$_2$NH$_3$), 55.5 (3′-MeO), 55.6 (4′-MeO), 59.3 (CH$_2$N), 110.0 (2′-C), 111.7 (5′-C), 120.7 (HC=*C*HPy), 123.1 (6′-C), 123.2 (3-C, 5-C), 127.9 (1′-C), 141.2 (H*C*=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]vinyl}pyridinium 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 $C_{17}H_{22}Cl_2N_2O_8S$ (485.34): C, 42.07; H, 4.57; N, 5.77%); λ_{max}^{abs}(MeCN)/nm 400 (ε/dm^3 mol^{-1} cm^{-1} 30700); λ_{max}^{fl}(MeCN)/nm 558; δ_H(500.13 MHz; DMSO-d_6; 25 °C) 2.17 (2 H, m, CH_2CH$_2$NH$_3$), 2.54 (3 H, s, MeS), 2.84 (2 H, m, CH_2NH$_3$), 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=C*H*Py), 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, *H*C=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 (*C*H$_2$CH$_2$NH$_3$), 35.7 (CH$_2$NH$_3$), 56.7 (CH$_2$N), 122.0 (HC=*C*HPy), 123.7 (3-C, 5-C), 125.7 (3′-C, 5′-C), 128.6 (2′-C, 6′-C), 131.4 (1′-C), 140.6 (H*C*=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 precipitate 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 $C_{18}H_{25}Cl_2N_3O_8$ (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_2CH$_2$NH$_3$), 2.83 (2 H, m, CH_2NH$_3$), 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=C*H*Py), 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, *H*C=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 (*C*H$_2$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=*C*HPy), 122.5 (3-C, 5-C, 1′-C), 130.2 (2′-C, 6′-C), 142.4 (H*C*=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 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 Figs 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

New Journal of Chemistry Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

$1.5C_{18}H_{24}Cl_2N_2O_{10}\cdot C_{25}H_{34}ClNO_{10}\cdot 1.5H_2O$ (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 $C_{16}H_{20}Cl_2N_2O_8\cdot C_{25}H_{34}ClNO_{10}$ (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 $C_{17}H_{22}Cl_2N_2O_9\cdot C_{25}H_{34}ClNO_{10}\cdot 0.5H_2O$ (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 $C_{17}H_{22}Cl_2N_2O_8S\cdot C_{25}H_{34}ClNO_{10}$ (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 $C_{16}H_{19}Cl_2N_3O_{10}\cdot C_{25}H_{34}ClNO_{10}$ (1028.23): C, 47.89; H, 5.20; N, 5.45%).

Complex ***1g*·*2a*** was obtained in 90% yield;[15] glass transition ~ 155 °C, >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 $C_{18}H_{24}Cl_2N_2O_{10}\cdot C_{29}H_{36}ClNO_{10}\cdot H_2O$ (1111.36): C, 50.79; H, 5.62; N, 3.78%).

Complex ***1a*·*2c*** was obtained in 63% yield; 168–172 °C (Found: C, 49.06; H, 5.28; N, 3.86. Calc. for $C_{18}H_{24}Cl_2N_2O_{10}\cdot C_{27}H_{34}ClNO_{10}S$ (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 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-ethylpyridinium-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 $C_{41}H_{54}Cl_3N_3O_{18}\cdot 0.5C_6H_6$ (1022.29): C, 51.69; H, 5.62; N, 4.11%); λ_{max}^{abs}(MeCN)/nm 225, ~ 258sh and ~ 285sh (ε/dm^3 mol^{-1} cm^{-1} 29700, 10700 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, C*H*$_2$CH$_2$N), 2.28–2.43 (2 H, m, C*H*$_2$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 × C*H*$_2$CH$_2$OAr), 3.92 (2 H, m, 3’-C*H*$_2$OAr), 4.08 (2 H, m, 4’-C*H*$_2$OAr), 4.48 (2 H, q, ^3J 7.3, C*H*$_2$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 °C) 16.2 (Me), 28.1 (*C*H$_2$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 (*C*H$_2$Me), 57.1 (CH$_2$N), 67.1 (4’-*C*H$_2$OAr), 67.3 (3’-*C*H$_2$OAr), 68.2 (*C*H$_2$CH$_2$OAr), 68.4 (*C*H$_2$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-ethylpyridinium-4-yl)-4-t-(4-methoxyphenyl)cyclobutyl]pyridinium triperchlorate (*rctt*-**3c**) was obtained in 92% yield: mp 261–262 °C (dec.) (Found: C, 51.29; H, 5.81; N, 3.94. Calc. for $C_{42}H_{56}Cl_3N_3O_{19}\cdot 0.5C_6H_6$ (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} 38600 and 5700); δ_H(500.13 MHz; DMSO-d_6; 30 °C) 1.42 (3 H, t, ^3J 7.3, *Me*CH$_2$), 2.11 (2 H, m, C*H*$_2$CH$_2$N), 2.29–2.44 (2 H, m, C*H*$_2$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 × C*H*$_2$CH$_2$OAr), 3.92 (2 H, m, 3’-C*H*$_2$OAr), 4.08 (2 H, m, 4’-C*H*$_2$OAr), 4.50 (2 H, q, ^3J 7.3, C*H*$_2$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 °C) 16.2 (*Me*CH$_2$), 28.1 (*C*H$_2$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 (*C*H$_2$Me), 57.2 (CH$_2$N), 67.1 (4’-*C*H$_2$OAr), 67.2 (3’-*C*H$_2$OAr), 68.2 (*C*H$_2$CH$_2$OAr), 68.4 (*C*H$_2$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-ethylpyridinium-4-yl)-4-t-[4-(methylthio)phenyl]cyclobutyl}pyridinium triperchlorate (*rctt*-**3d**) was obtained in 93% yield: mp 258–259 °C (dec.) (Found: C, 49.16; H, 5.37; N, 4.07. Calc. for $C_{42}H_{56}Cl_3N_3O_{18}S$ (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} 35000, 25300 and 8300); δ_H(500.13 MHz; DMSO-d_6; 30 °C) 1.42 (3 H, t, ^3J 7.3, *Me*CH$_2$), 2.11 (2 H, m, C*H*$_2$CH$_2$N), 2.29–2.43 (2 H, m, C*H*$_2$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 × C*H*$_2$CH$_2$OAr), 3.92 (2 H, m, 3’-C*H*$_2$OAr), 4.08 (2 H, m, 4’-C*H*$_2$OAr), 4.51 (2 H, q, ^3J 7.3, C*H*$_2$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,

New Journal of Chemistry Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

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 °C) 14.5 (MeS), 16.1 (*Me*CH_2), 28.1 ($CH_2CH_2NH_3$), 35.6 (CH_2NH_3), 43.0 (d-CH), 44.2 (c-CH), 45.9 (b-CH), 46.6 (a-CH), 55.5 (CH_2Me), 57.2 (CH_2N), 67.1 (4′-CH_2OAr), 67.2 (3′-CH_2OAr), 68.2 (CH_2CH_2OAr), 68.4 (CH_2CH_2OAr), 68.5 (2 × CH_2O), 69.1 (CH_2O), 69.2 (CH_2O), 69.6 (CH_2O), 69.7 (CH_2O), 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** concentrations were varied starting from zero (the maximum **1** to **2** concentration ratio was ~ 3). 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[21] and are shown in Table 1.

Irradiation of dyes 1a–i (general procedure)

UV–vis spectra of dyes **1a–i** (MeCN, $C_{dye} \approx 1\times10^{-4}$ 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 Figs S42–S50 in the ESI). The unfiltered light of a 60 W incandescent lamp was used for the irradiation, the distance to the light source was ~ 15 cm. The solutions were not degassed prior to the irradiation, as an electrocyclic reaction of the dyes, which could result in formation of dihydrophenanthrene analogs, 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, $C_1 = C_2 = 5\times10^{-4}$ 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 Figs S51–S57 in the ESI). The unfiltered light of a 60 W incandescent lamp was used for the irradiation, the distance to the light source was ~ 15 cm. The solutions were not degassed before the 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 vapour diffusion method at ambient temperature 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 radiation (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), *b* = 8.3891(3), *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°, 11130 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 ē 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), *b* = 11.4270(7), *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°, 10164 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 ē 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 *C*2/*c* (no. 15), yellow block, *a* = 37.878(8), *b* = 16.492(3), *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°, 100229 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 ē 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 a low accuracy. Unfortunately, we failed to obtain better crystals and better structural data. Nevertheless, we include this

New Journal of Chemistry Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

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 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), *b* = 12.9619(9), *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 g cm^{-3}, $2\theta_{max}$ = 51.998°, 14526 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 ē $Å^{-3}$. 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 *Pca*2_1 (no. 29), colourless plate, *a* = 14.0228(9), *b* = 18.0075(11), *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°, 57119 reflections measured, 13902 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 ē $Å^{-3}$. 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

Financial support from the Russian Science Foundation (project 14-13-00076) and the Russian Academy of Sciences (in respect of X-ray diffraction studies of the complexes) is gratefully acknowledged. L.G.K. thanks the Royal Society of Chemistry for International Author Grant. The authors are grateful to Mr. Pavel S. Loginov for his help in the synthesis.

Notes and references

‡ 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)°.

§§ For the N(1)H…O(12), N(1)H…O(15), and N(1)H…O(21) bonds in structure **1f**·0.25H_2O, 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_6H_6·2H_2O, 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°.

§§§§ In structure *rctt*-**3c**·2C_6H_6·0.75MeCN·0.25H_2O, 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°.

1 (*a*) *Modern Supramolecular Chemistry*, eds. F. Diederich, P. J. Stang and R. R. Tykwinski, Wiley-VCH, Weinheim, 2008; (*b*) J. Lagona, P. Mukhopadhyay, S. Chakrabarti and L. Isaacs, *Angew. Chem. Int. Ed.*, 2005, **44**, 4844; (*c*) H.-J. Schneider, *Angew. Chem. Int. Ed.*, 2009, **48**, 3924; (*d*) B. Zheng, F. Wang, S. Dong and F. Huang, *Chem. Soc. Rev.*, 2012, **41**, 1621; (*e*) A. C. Fahrenbach, C. J. Bruns, D. Cao and J. F. Stoddart, *Acc. Chem. Res.*, 2012, **45**, 1581; (*f*) K. P. Carter, A. M. Young and A. E. Palmer, *Chem. Rev.*, 2014, **114**, 4564; (*g*) N. H. Evans and P. D. Beer, *Chem. Soc. Rev.*, 2014, **43**, 4658; (*h*) Y. Han, Y. Jiang and C.-F. Chen, *Tetrahedron*, 2015, **71**, 503.

2 (*a*) *Supramolecular Catalysis*, ed. P. W. N. M. Van Leeuwen, Wiley-VCH, Weinheim, 2008; (*b*) B. C. Pemberton, R. Raghunathan, S. Volla and J. Sivaguru, *Chem. Eur. J.*, 2012, **18**, 12178; (*c*) N. Vallavoju and J. Sivaguru, *Chem. Soc. Rev.*, 2014, **43**, 4084; (*d*) B. Bibal, C. Mongin and D. M. Bassani, *Chem. Soc. Rev.*, 2014, **43**, 4179.

3 (*a*) R. M. Izatt, K. Pawlak, J. S. Bradshaw and R. L. Bruening, *Chem. Rev.*, 1991, **91**, 1721; (*b*) A. Späth and B. König, *Beilstein J. Org. Chem.*, 2010, **6**, No. 32; (*c*) O. P. Kryatova, S. V. Kryatov, R. J. Staples and E. V. Rybak-Akimova, *Chem. Commun.*, 2002, 3014.

4 (*a*) S. Shinkai, M. Ishihara, K. Ueda and O. Manabe, *J. Chem. Soc., Perkin Trans. 2*, 1985, 511; (*b*) S. Shinkai, T. Yoshida, O.

New Journal of Chemistry Accepted Manuscript

Please do not adjust margins

Manabe and F. Fuchita, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1431.

5 (*a*) S. Fery-Forgues and F. Al-Ali, *J. Photochem. Photobiol. C*, 2004, **5**, 139; (*b*) S. Kume and H. Nishihara, *Struct. Bond.*, 2007, **123**, 79; (*c*) S. P. Gromov, *Russ. Chem. Bull., Int. Ed.*, 2008, **57**, 1325; (*d*) E. N. Ushakov and S. P. Gromov, *Russ. Chem. Rev.*, 2015, **84**, 787.

6 (*a*) O. A. Fedorova, E. N. Andryukhina, Yu. V. Fedorov, M. A. Panfilov, M. V. Alfimov, G. Jonusauskas, A. Grelard and E. Dufourc, *Org. Biomol. Chem.*, 2006, **4**, 1007; (*b*) E. V. Lukovskaya, A. A. Kosmacheva, O. A. Fedorova, A. A. Bobyleva, A. V. Dolganov, N. E. Shepel’, Yu. V. Fedorov, V. V. Novikov and A. V. Anisimov, *Russ. J. Org. Chem.*, 2014, **50**, 552.

7 A. I. Vedernikov, D. V. Kondratuk, N. A. Lobova, T. M. Valova, V. A. Barachevskii, M. V. Alfimov and S. P. Gromov, *Mendeleev Commun.*, 2007, **17**, 264.

8 S. P. Gromov, A. I. Vedernikov, N. A. Lobova, L. G. Kuz’mina, S. N. Dmitrieva, Yu. A. Strelenko and J. A. K. Howard, *J. Org. Chem.*, 2014, **79**, 11416.

9 A. I. Vedernikov, S. K. Sazonov, P. S. Loginov, N. A. Lobova, M. V. Alfimov and S. P. Gromov, *Mendeleev Commun.*, 2007, **17**, 29.

10 (*a*) M. Yasuda, T. Kishi, C. Goto, H. Satoda, K. Nakabayashi, T. Minami and K. Shima, *Tetrahedron Lett.*, 1992, **33**, 6465; (*b*) J.-P. Zhuang, Y. Zheng and W.-Q. Zhang, *Acta Crystallogr. E*, 2002, **58**, o720; (*c*) Y. Nishioka, T. Yamaguchi, M. Yoshizawa and M. Fujita, *J. Am. Chem. Soc.*, 2007, **129**, 7000; (*d*) D. W. Cho, C. W. Lee, J. G. Park, S. W. Oh, N. K. Sung, H. J. Park, K. M. Kim, P. S. Mariano and U. C. Yoon, *Photochem. Photobiol. Sci.*, 2011, **10**, 1169.

11 (*a*) S. C. Coote, A. Pöthig and T. Bach, *Chem. Eur. J.*, 2015, **21**, 6906; (*b*) Q. Liu, F.-P. Zhu, X.-L. Jin, X.-J. Wang, H. Chen and L.-Z. Wu, *Chem. Eur. J.*, 2015, **21**, 10326.

12 (*a*) V. Ramamurthy and B. Mondal, *J. Photochem. Photobiol. C*, 2015, **23**, 68; (*b*) A. R. Clements and M. Pattabiraman, *J. Photochem. Photobiol. A*, 2015, **297**, 1.

13 K. Biradha and R. Santra, *Chem. Soc. Rev.*, 2013, **42**, 950.

14 A. I. Vedernikov, S. K. Sazonov, L. G. Kuz’mina, J. A. K. Howard, M. V. Alfimov and S. P. Gromov, *Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 1955.

15 E. N. Ushakov, A. I. Vedernikov, S. K. Sazonov, L. G. Kuz’mina, M. V. Alfimov, J. A. K. Howard and S. P. Gromov, *Russ. Chem. Bull., Int. Ed.*, 2015, **64**, 562.

16 A. I. Vedernikov, S. P. Gromov, N. A. Lobova, L. G. Kuz’mina, Yu. A. Strelenko, J. A. K. Howard and M. V. Alfimov, *Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 1954.

17 L. G. Kuz’mina, A. I. Vedernikov, N. A. Lobova, A. V. Churakov, J. A. K. Howard, M. V. Alfimov and S. P. Gromov, *New J. Chem.*, 2007, **31**, 980.

18 A. I. Vedernikov, L. G. Kuz’mina, S. K. Sazonov, N. A. Lobova, P. S. Loginov, A. V. Churakov, Yu. A. Strelenko, J. A. K. Howard, M. V. Alfimov and S. P. Gromov, *Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 1860.

19 E. N. Ushakov, M. V. Alfimov and S. P. Gromov, *Russ. Chem. Rev.*, 2008, **77**, 39.

20 A. I. Vedernikov, E. N. Ushakov, N. A. Lobova, A. A. Kiselev, M. V. Alfimov and S. P. Gromov, *Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 666.

21 C. Frassineti, S. Ghelli, P. Gans, A. Sabatini, M. S. Moruzzi and A. Vacca, *Anal. Biochem.*, 1995, **231**, 374.

22 S. P. Gromov, A. I. Vedernikov, L. G. Kuz’mina, D. V. Kondratuk, S. K. Sazonov, Yu. A. Strelenko, M. V. Alfimov and J. A. K. Howard, *Eur. J. Org. Chem.*, 2010, 2587.

23 (*a*) J. Harada and K. Ogawa, *J. Am. Chem. Soc.*, 2004, **126**, 3539; (*b*) J. Harada and K. Ogawa, *Chem. Soc. Rev.*, 2009, **38**, 2244; (*c*) E. Elacqua, P. Kaushik, R. H. Groeneman, J. C. Sumrak, D.-K. Bučar and L. R. MacGillivray, *Angew. Chem. Int. Ed.*, 2012, **51**, 1037.

24 G. J. M. Schmidt, *J. Pure Appl. Chem.*, 1971, **27**, 647.

25 H. Görner and H. Gruen, *J. Photochem.*, 1985, **28**, 329.

26 (*a*) Z. R. Grabowski, K. Rotkiewicz and W. Rettig, *Chem. Rev.*, 2003, **103**, 3899; (*b*) J.-S. Yang, C.-K. Lin, A. M. Lahoti, C.-K. Tseng, Y.-H. Liu, G.-H. Lee and S.-M. Peng, *J. Phys. Chem. A*, 2009, **113**, 4868.

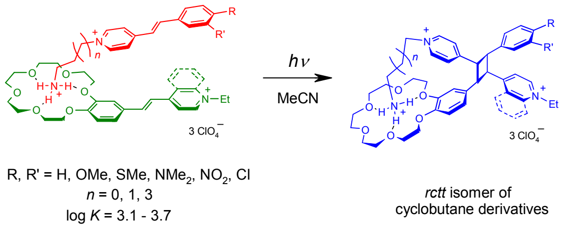
27 W. G. Bardsley, J. S. Ashford and C. M. Hill, *Biochem. J.*, 1971, **122**, 557.

28 G. M. Sheldrick, *Acta Crystallogr. C*, 2015, **71**, 3.

29 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

New Journal of Chemistry Accepted Manuscript

Graphical abstract



Two different styryl dyes form pseudodimeric complexes via hydrogen bonding and stacking interactions; irradiation of these complexes gives *rctt*-cyclobutane derivatives.

New Journal of Chemistry Accepted Manuscript