Mendeleev Commun., 2007, 17, 29–31

Mendeleev
Communications

Hydrogen bonding- and stacking-induced stereospecific [2 + 2]-photocycloaddition within a pseudodimeric complex of two styryl dyes

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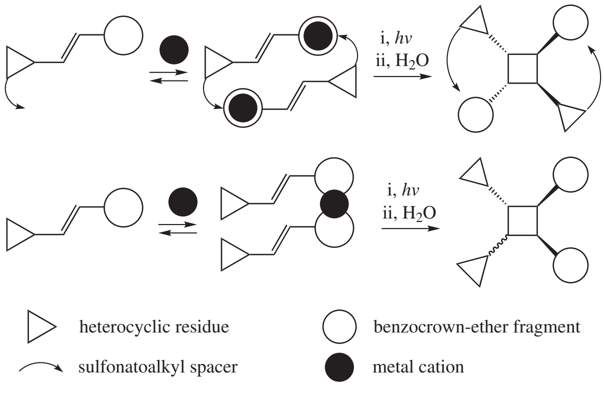
DOI: 10.1016/j.mencom.2007.01.012

A new *N*-ammoniopropyl styryl dye and 18-crown-6 ether styryl dye of the pyridine series form a head-to-tail pseudodimeric complex through host-guest hydrogen bonding; the complex undergoes stereospecific [2 + 2]-photocycloaddition due to the stacking-induced pre-organization of the ethylene bonds of dye chromophores.

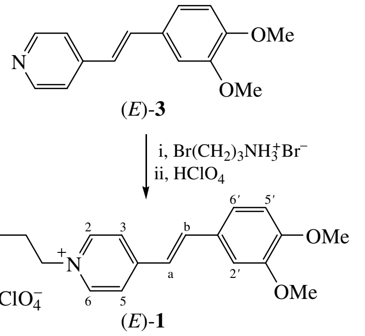
The self-assembly of organic molecules with the participation of relatively weak interactions attracts persisting interest due to unusual physico-chemical properties and/or the possibility of some chemical reactions that appear in supramolecular ensembles and are missing under other conditions.[1–3] The complexes formed by crown-containing unsaturated compounds with various metal cations represent examples of such a self-assembly in solutions (Scheme 1). For instance, stereospecific [2 + 2]-autophotocycloaddition (autoPCA) was observed in the metal complexes of styryl dyes containing a sulfonatoalkyl N-substituent owing to self-assembly of two dye molecules into a head-to-tail 2(L):2(M^{2+}) dimer.[4] Stereoselective autoPCA was also observed in sandwich head-to-head metal complexes of 15-crown-5-containing styrylbenzothiazole.[5]



Scheme 1 Examples of self-assembly-induced autoPCA reaction in metal complexes of crown-containing styryl dyes and styryl heterocycles.

The self-assembly of unsaturated compounds through hydrogen bonds between the crown-ether fragments and ammonium groups has been little studied, although our investigations have demonstrated the formation of an unusually stable charge-transfer complex between bis(crown)-containing stilbene and *N*,*N*′-di(ammoniopropyl) derivative of dipyridylethylene[6] and high selectivity of binding of diammonium ions by the crown-containing bis(styryl) dye.[7] All of these studies dealt with complexes based on diammonium compounds, which had enhanced stabilities owing to homoditopic binding of the NH_3^+ groups by two 18-crown-6 ether fragments. Of considerable interest, however, are the stability, and spectral and photochemical behaviours of supramolecular complexes in which the unsaturated components are held together due to the interaction of one crown-ether fragment with one NH_3^+ group.

This communication deals with the self-assembly, structural features and physico-chemical properties of the pseudodimeric complex formed by two pyridine styryl dyes **1** and **2**, one of which contains a terminal NH_3^+ group within the N-substituent, and the second, a 18-crown-6 ether fragment.

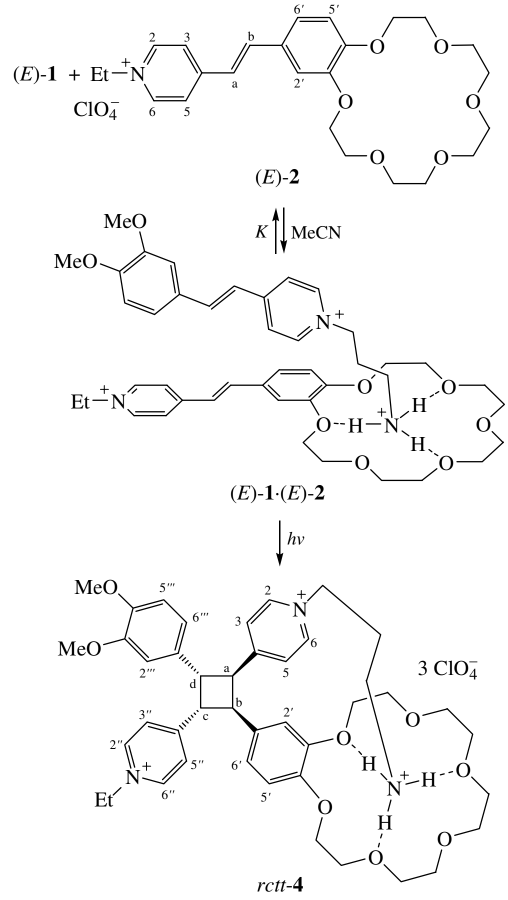


Scheme 2

Dye **1** with the *N*-ammoniopropyl substituent was synthesised by quaternization of dimethoxystyrylpyridine (*E*)-**3**[8] with bromopropylammonium bromide followed by replacement of the bromide anions by perchlorate on treatment with perchloric acid (Scheme 2).[†] Compound **1** has a *E*-configuration, as indicated by the spin–spin coupling constants of the ethylene protons $^3J_{\text{trans}}$ 16.2 Hz. The synthesis of 18-crown-6-containing styryl dye (*E*)-**2** has been described previously.[9]

Dyes **1** and **2** have similar chromophore structures; therefore, in acetonitrile, they exhibit intense long-wavelength absorption bands[‡] with peaks at 398 and 399 nm, respectively (Figure 1). Irradiation of dye solutions in acetonitrile with visible light induced only reversible *E*–*Z*-isomerization to give a photostationary mixture of *trans* and *cis* isomers in a 1.86:1 ratio for **1** (monitoring by spectrophotometry and ^{1}H NMR) or a 1.80:1 ratio for **2**.[9]

The structure of 18-crown-6 ether is known to fit best to geometric requirements of the primary ammonium group for the formation of strong host-guest complexes through three N^+–H···O hydrogen bonds. We suggested that 18-crown-6-containing compound **2** would be an efficient ligand for binding



Scheme 3

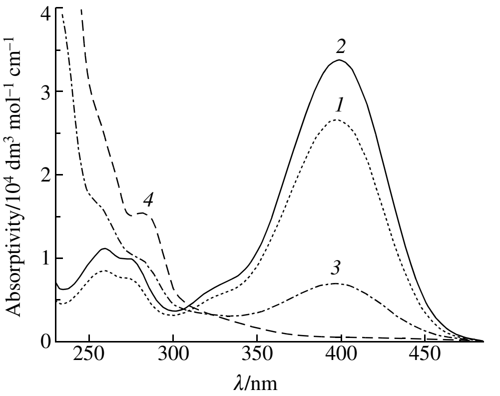


Figure 1 UV-VIS spectra of (*1*) (*E*)-**1**, (*2*) (*E*)-**2** (5×10^{-5} M, 1 cm cell) and (*4*) *rctt*-**4** (2.5×10^{-5} M, 1 cm cell) in MeCN; (*3*) the spectrum of the 1:1 mixture of (*E*)-**1** and (*E*)-**2** ($C_1 = C_2 = 5\times10^{-4}$ M, 0.1 cm cell) after photolysis with visible light for 13 h.

the ammonium group of dye **1**. Indeed, the ^{1}H NMR study of an equimolar mixture of **1** and **2** in a CD_3CN solution showed a substantial change in the positions of most proton signals of both components with respect to free **1** and **2**. The methylene protons of the crown-ether fragment of **2** shifted downfield ($\Delta\delta_H$ up to 0.11 ppm) upon mixing with **1**, as is typical of ammonium ion binding by crown compounds.[6,7] The signals of the receptor and substrate protons remote from the binding side have low sensitivity to complexation. However, in the case of an equimolar mixture of **1** and **2**, the signals of ethylene and most aromatic protons of both components markedly shifted upfield ($\Delta\delta_H$ up to 0.24 ppm) (Figure 2). This unusual spectral behaviour can be interpreted assuming that in complex **1**·**2**, the chromophore fragments of the components are mainly arranged one above another due to intermolecular stacking of conjugated systems (Scheme 3). Using ^{1}H NMR titration, the stability constant of the supramolecular complex was found[§] to be lg $K = 3.52\pm0.05$, which is a typical thermodynamic value for complexes formed by benzo-18-crown-6 ether derivatives with alkylammonium ions in MeCN.[11]

The exposure of a solution of an equimolar mixture of **1** and **2** to visible light resulted in a substantial decrease in the long-wavelength absorption intensity (for example, curve *3* in Figure 1). The ^{1}H NMR spectrum of the photolysate exhibited, apart from the signals for the minor *E*- and *Z*-isomers of the starting compounds, a set of signals, indicating the formation of a new photoproduct.[¶] The spectrum of this photoproduct isolated by crystallization is shown in Figure 1, curve *4*. Its structure was determined based on analysis of 2D COSY and NOESY spectra. A typical feature is the disappearance of signals for the ethylene protons from the aromatic region and the appearance of four new signals at 4.8–5.0 ppm, each corresponding to one proton according to the integral intensity (Figure 3). The positions and shapes of these signals (doublets of doublets) indicate the presence of asymmetric cyclobutane

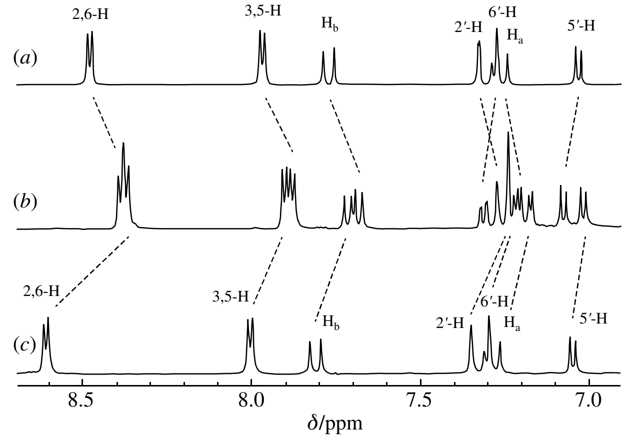


Figure 2 ^{1}H NMR spectra of (*a*) (*E*)-**2**, (*c*) (*E*)-**1**, and (*b*) a 1:1 mixture of (*E*)-**2** and (*E*)-**1** (aromatic region, CD_3CN, 30 °C).

[†] *1-(3-Ammoniopropyl)-4-[(*E*)-2-(3,4-dimethoxyphenyl)-1-ethenyl]pyridinium diperchlorate* (*E*)-**1**. A mixture of 4-[(*E*)-2-(3,4-dimethoxyphenyl)-1-ethenyl]pyridine (*E*)-**3** (0.30 g, 1.25 mmol) and 3-bromo-1-propylammonium bromide (Aldrich) (0.82 g, 3.75 mmol) was heated at 180 °C for 4 h, cooled to room temperature, treated with hot ethanol (5 ml) and then cooled to 5 °C. The precipitate formed was filtered off, washed with cold ethanol (2×3 ml) and dried in air to give yellow dibromide of the dye (0.41 g, 0.89 mmol). The dibromide was dissolved in a hot mixture of ethanol (4 ml) and a minimum quantity of water, and 70% aqueous $HClO_4$ (0.31 ml, 3.6 mmol) was added to the solution. After cooling to 5 °C, the precipitate formed was filtered off, washed with cold ethanol (2×2 ml) and dried in air to give dye (*E*)-**1** as dark yellow crystals (0.35 g, overall yield 56%); mp 224–226 °C (ethanol). ^{1}H NMR (Bruker DRX500, [$^2H_6$]DMSO, 23 °C) δ: 2.19 (m, 2H, $C\mathit{H}_2CH_2N$), 2.86 (m, 2H, $C\mathit{H}_2NH_3$), 3.84 (s, 3H, MeO), 3.86 (s, 3H, MeO), 4.55 (t, 2H, CH_2N, *J* 7.0 Hz), 7.09 (d, 1H, 5′-H, *J* 8.4 Hz), 7.31 (dd, 1H, 6′-H, *J* 8.4 Hz, *J* 1.6 Hz), 7.40 (d, 1H, 2′-H, *J* 1.6 Hz), 7.45 (d, 1H, H$_a$, *J* 16.2 Hz), 7.78 (br. s, 3H, NH_3), 8.00 (d, H, H$_b$, *J* 16.2 Hz), 8.21 (d, 2H, 3-H, 5-H, *J* 6.8 Hz), 8.89 (d, 2H, 2-H, 6-H, *J* 6.8 Hz). Found (%): C, 43.44; H, 4.91; N, 5.45. Calc. for $C_{18}H_{24}Cl_2N_2O_{10}$ (499.30) (%): C, 43.30; H, 4.85; N, 5.61.

[‡] UV-VIS spectra were recorded on a UV–3101PC spectrophotometer (Shimadzu) in a range of 200–600 nm with an increment of 0.5 nm (MeCN, room temperature).

[§] ^{1}H NMR titration was performed on a Bruker DRX500 instrument in CD_3CN, 30 °C. The concentration of (*E*)-**2** was maintained at 1×10^{-3} M, and the concentration of (*E*)-**1** was varied from 0 to 3×10^{-3} M. The stability constant was determined by analysis of changes in the positions of signals for the protons of **2** *vs.* varied concentration of **1**. The $\Delta\delta_H$ values were measured with an accuracy of 0.001 ppm. The HYPNMR program[10] was used for the calculations.

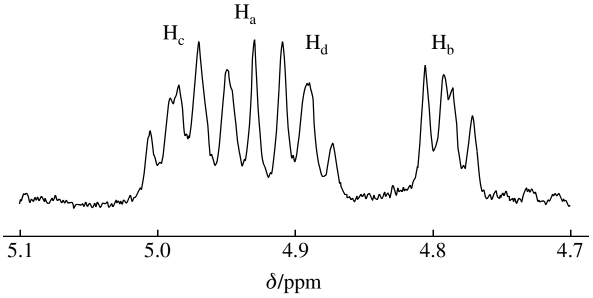


Figure 3 ^{1}H NMR spectrum of the cyclobutane protons of *rctt*-**4** ([^{2}H$_6$]DMSO, 23 °C).

derivative *rctt*-**4** (an ABCD type spin system with the coupling constants $^3J_{cis\text{-H}_a,\text{H}_b}$ 10.0 Hz, $^3J_{trans\text{-H}_b,\text{H}_c}$ 7.1 Hz, $^3J_{cis\text{-H}_c,\text{H}_d}$ 10.0 Hz, and $^3J_{trans\text{-H}_d,\text{H}_a}$ 8.1 Hz) formed from the pseudo-dimer (*E*)-**1**·(*E*)-**2** upon cycloaddition. Note that the head-to-tail preorganization of the chromophore groups owing to the complexation of NH_3^+ with the crown-ether fragment and the *syn* arrangement of the conjugated fragments in the *E*-configuration favourable for stacking lead to a single isomer of the cyclobutane derivative out of the 16 theoretically possible isomers. Thus, the combined participation of two types of weak intermolecular interactions in the stabilization of supramolecular complex **1**·**2** ensures an exceptional stereospecificity of the photoprocess.

We demonstrated the ability of the *N*-ammonioalkyl derivative of the pyridine styryl dye to form a stable pseudodimeric head-to-tail complex with 18-crown-6-containing styryl dye in which chromogenic fragments of the molecules are proximate. Due to the fixed positions of the ethylene bonds in the complex dictated by ammonium group binding to the crown ether fragment and by favourability of the *syn* orientation of the chromogens related to secondary orbital p_z interactions, the irradiation of a solution of the complex induces stereospecific [2 + 2]-photocycloaddition to give the only *rctt*-isomer of the cyclobutane derivative. Optimization of the structures of both components of the pseudodimer may provide the design of effective systems for information recording and storage at a molecular level.

This work was supported by the Russian Foundation for Basic Research and the Russian Academy of Sciences.

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Received: 25th September 2006; Com. 06/2783

¶ *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)-4-*t*-(3,4-dimethoxyphenyl)-3-*t*-(1-ethyl-4-pyridiniumyl)cyclobutyl]pyridinium triperchlorate* (*rctt*-**4**). A solution of (*E*)-**1** (4.2 mg, 8.4 μmol) and (*E*)-**2** (4.6 mg, 8.4 μmol) in acetonitrile (15 ml) placed in a thin-walled glass flask was irradiated with light from a 60 W incandescent lamp (the distance from the light source was 15 cm) and then evaporated *in vacuo*. According to ^{1}H NMR data, the residue consisted of initial **1**, **2** and photoadduct *rctt*-**4** present in a 1:1:1 ratio after 4 h irradiation and in a 1:1:20 ratio after 64 h irradiation. Compound *rctt*-**4** was separated by slow saturation of the MeCN solution with benzene through gas phase at room temperature: yellowish solid (4.8 mg, yield 55%), mp 254–258 °C (decomp.). ^{1}H NMR (Bruker DRX500, [^{2}H$_6$]DMSO, 23 °C) δ: 1.42 (t, 3H, *Me*CH$_2$, *J* 7.3 Hz), 2.10 (m, 2H, C*H*$_2$CH$_2$N), 2.28 (m, 1H, C*H*H'NH$_3$), 2.39 (m, 1H, CH*H'*NH$_3$), 3.62 (s, 4H, 2CH$_2$O), 3.65 (m, 7H, 2CH$_2$O, 3'''-MeO), 3.68 (s, 3H, 4'''-MeO), 3.71 (m, 4H, 2CH$_2$O), 3.79 (m, 4H, 2C*H*$_2$CH$_2$OAr), 3.91 (m, 2H, 3'-C*H*$_2$OAr), 4.08 (m, 2H, 4'-C*H*$_2$OAr), 4.51 (q, 2H, MeCH$_2$, *J* 7.3 Hz), 4.54 (m, 2H, CH$_2$C*H*$_2$N), 4.79 (dd, 1H, H$_b$, *J* 10.0 Hz, *J* 7.1 Hz), 4.89 (dd, 1H, H$_d$, *J* 10.0 Hz, *J* 8.1 Hz), 4.95 (dd, 1H, H$_a$, *J* 10.0 Hz, *J* 8.1 Hz), 4.99 (dd, 1H, H$_c$, *J* 10.0 Hz, *J* 7.1 Hz), 6.50 (br. s, 1H, 2'-H), 6.77 (br. s, 2H, 5'''-H, 6'''-H), 6.81 (br. s, 1H, 2'''-H), 6.94 (d, 1H, 5'-H, *J* 8.4 Hz), 7.04 (br. d, 1H, 6'-H, *J* 8.4 Hz), 7.19 (br. s, 3H, NH$_3$), 7.92 (d, 2H, 3-H, 5-H, *J* 6.5 Hz), 7.97 (d, 2H, 3''-H, 5''-H, *J* 6.6 Hz), 8.80 (d, 2H, 2-H, 6-H, *J* 6.5 Hz), 8.90 (d, 2H, 2''-H, 6''-H, *J* 6.6 Hz). Found (%): C, 49.51; H, 5.38; N, 4.06. Calc. for $C_{43}H_{58}Cl_3N_3O_{20}$ (1043.29) (%): C, 49.50; H, 5.60; N, 4.03.