Self-assembly of supramolecular complexes of cyanine dyes containing terminal ammonium groups with bis(18-crown-6)stilbene

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Mono-, tri-, and pentamethine cyanine dyes containing two terminal ammonium groups in the N-substituents and bis(18-crown-6)-stilbene in MeCN form pseudocyclic 1:1 complexes ($\log K_{1:1}$ up to 8.1) and triple-decker 1:2 complexes ($\log K_{1:2}$ up to 2.6).

Development of organic electronics and photonics requires the design of photoactive supramolecular systems possessing a specified architecture and diverse properties. In this connection, of interest are cyanine dyes, which have been comprehensively studied owing to their use in photographic materials;[1–3] they exhibit intense narrow isolated absorption bands and actively fluoresce. Recently, polymethine cyanine dyes have attracted attention as fluorescence labels,[4–7] comprising electroluminescent materials,[8,9] and components of supramolecular systems.[10–13]

Previously, we described supramolecular donor–acceptor systems formed by bis(ammonioalkyl) derivatives of viologen and its analogues and bis-crown stilbenes.[14,15]

In order to elucidate the possibility to construct donor–acceptor systems based on cyanine dyes as acceptors and the influence of their structure on the properties of supramolecular complexes, we synthesized cyanine dyes with terminal ammonium groups in the N-substituents of heterocyclic residues.[14,15] The presence of primary ammonium groups capable of hydrogen bonding enables self-assembly of the dye with crown molecules containing electron-donating oxygen heteroatoms to form supramolecular complexes. This interaction may give rise to highly stable donor–acceptor complexes in which unusual photochemical processes may occur.[14–17] Here, we present an account of construction of supramolecular systems based on cyanine dyes **1a–d**,[18,19] which contain ammonioalkyl groups, and bis(18-crown-6)stilbene **2**.[20]

The changes in the absorption and fluorescence spectra upon mixing of the components were found to be insignificant, which

indicates weak intermolecular interaction between the dye and stilbene chromophores in the complexes. ^{1}H NMR study of complexation of **1a–d** with **2** proved to be much more informative. Formation of supramolecular complexes induces considerable changes in the ^{1}H NMR spectra of both components. Mixing of **1b** and **2** in equimolar amounts results in upfield shifts of signals for all protons of conjugated moieties of **1b** and **2**, CH_2N groups of **1b**, and CH_2O groups adjacent to the benzene rings of **2** with respect to these signals in the spectra of free components (Figure S1, Online Supplementary Materials). The most pronounced upfield shift of dye **1b** was observed for the H-7′ signal ($\Delta\delta = -0.26$ ppm), while for stilbene, this was the signal of ethylene hydrogen atoms ($\Delta\delta = -0.13$ ppm). Apparently, owing to the ditopic host-guest interaction of two terminal ammonium groups of the dye and two crown-ether moieties of stilbene, the conjugated moieties of the components are spatially proximate, which results in mutual shielding of their hydrogen atoms by the conjugated moieties. Conversely, binding of ammonium groups to the crown ether moieties induces downfield shifts of most proton signals for the crown ether CH_2O groups, which is caused by the electron-withdrawing effect of the NH_3^+ groups.

When dyes **1a,c,d** are mixed with **2**, similar changes occur in the ^{1}H NMR spectra, indicating the formation of analogous supramolecular complexes. The most probable structure of the bimolecular pseudocyclic complexes **1a–d·2** that complies with this spectral behaviour is shown in Scheme 1. Complex **1b·2** was isolated and characterized as a single compound.[†]
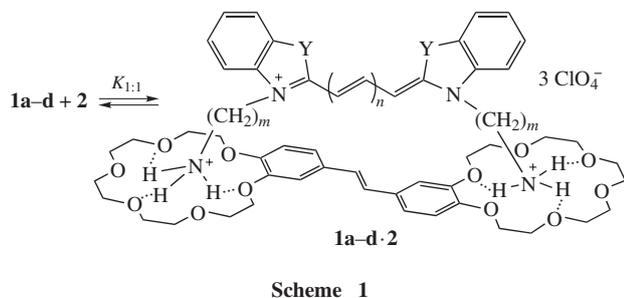
Mixing of equivalent amounts of model dye **3**[‡] devoid of ammonium groups with **2** does not induce noticeable changes in the ^{1}H NMR signals of both components. This indicates the absence of complexation between dye **3** and stilbene **2** ($\log K_{1:1} < 0.5$).
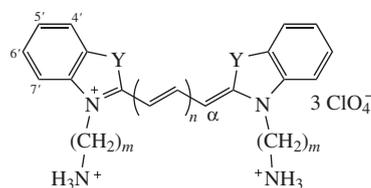

1a $n = 0$, $m = 6$, Y = S
1b $n = 1$, $m = 3$, Y = CMe_2
1c $n = 2$, $m = 3$, Y = CMe_2
1d $n = 2$, $m = 4$, Y = CMe_2

2
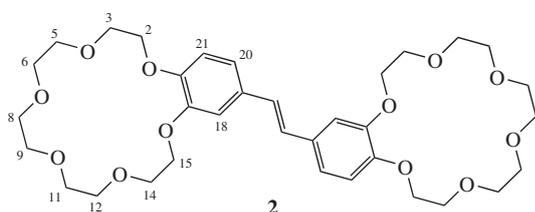
[†] A mixture of **1b** (7.8 mg, 10 μmol) and **2** (6.5 mg, 10 μmol) was dissolved with heating in a minimum MeCN. After cooling to room temperature, the precipitate that formed was filtered off and recrystallized from EtOH to give 7.3 mg (51%) of **1b·2** as a violet-red crystalline powder, mp 237–238 °C. IR (Bruker IFS-113V, KBr, ν/cm^{-1}): 3177, 2874 ($\nu_{NH_3^+}$). ^{1}H NMR (Bruker DRX500, CD$_3$CN, 30 °C) δ: 1.63 (s, 12 H, 2 CMe_2), 1.90 (m, 4 H, 2 CH_2CH$_2$NH$_3^+$), 2.99 (m, 4 H, 2CH$_2$CH_2NH$_3^+$), 3.67–3.72 (m, 24 H, 4 H-5, 4 H-6, 4 H-8, 4 H-9, 4 H-11, 4 H-12), 3.38–3.85 (m, 8 H, 4 H-3, 4 H-14), 3.99 (t, 4 H, 2 CH$_2$N$^+$, J 6.8 Hz), 4.13 (m, 4 H, 4 H-15), 4.21 (m, 4 H, 4 H-2), 6.30 (d, 2 H, 2 H-α, J 13.6 Hz), 6.81 (d, 2 H, 2 H-21, J 8.2 Hz), 6.88 (s, 2 H, CH=CH), 6.93 (d, 2 H, 2 H-20, J 8.2 Hz), 7.05 (d, 2 H, 2 H-7′, J 8.2 Hz), 7.08 (s, 2 H, 2 H-18), 7.25 (br. s, 6 H, 2 NH$_3^+$), 7.28 (m, 2 H, 2 H-5′), 7.37 (m, 2 H, 2 H-6′), 7.46 (d, 2 H, 2 H-4′, J 6.8 Hz), 8.32 (t, 1 H, *meso*-H, J 13.6 Hz). Found (%): C, 53.37; H, 6.46; N, 3.94. Calc. for $C_{65}H_{93}Cl_3N_4O_{24}\cdot H_2O$ (%): C, 53.64; H, 6.50; N, 3.97.

Scheme 1

Figure 1 Change in the chemical shifts of some proton signals of **1b** *vs.* the concentration ratio of **2** and **1b**.

Thus, the formation of complexes **1a–d·2** is caused, first of all, by interaction of the ammonium groups of the dye with the crown ether moieties of stilbene.

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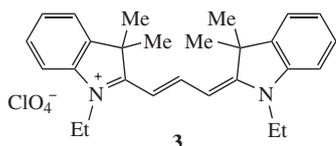
The stoichiometry and stability constants of the complexes **1a–d** with **2** were determined using ^{1}H NMR titration in CD$_3$CN.§ At any C_2/C_{1a-d} ratios, the ^{1}H NMR spectra exhibited narrow averaged proton signals for the complex and free components, which is attributable to exchange processes fast on the ^{1}H NMR time scale. The obtained plots $\Delta\delta_H$–C_2/C_{1a-d} are nearly linear in the $C_2/C_{1a-d} < 1$ region, have an inflection at $C_2/C_{1a-d} = 1$, and continue to monotonically rise as the stilbene concentration is further raised (Figure 1). This attests to very high stability of the bimolecular complexes ($K_{1:1} > 10^5$ dm^3 mol^{-1}) and also formation of trimolecular 1(**1**):2(**2**) complexes (Scheme 2). An exception is dye **1d** for which no further changes are observed in the spectra at $C_2/C_{1a-d} > 1$, *i.e.*, the possible **1d·(2)$_2$** complex has a very low stability.

The further upfield shift of the signals of dyes **1a–c** in the presence of an excess of **2** with respect to the equimolar mixture

Scheme 2

implies that the dye molecule in the complexes being formed is exposed to anisotropic effect of simultaneously two molecules of **2**. This fact suggests that in trimolecular complexes, the dye molecules **1a–c** are located between two stilbene molecules, and their ammonium groups are linked to the crown ether moieties of two molecules of **2**. Thus, these complexes have a triple-decker architecture. We have already studied structures of this type for systems based on bis(ammonioalkyl) derivatives of 4,4′-bipyridine and its analogues and stilbene **2**; for those complexes, similar changes in the ^{1}H NMR spectra were observed.[14,15,24]

The variation of the chemical shifts of the proton signals of the dyes as functions of the dye and **2** concentration ratio is well described by the model based on two equilibria:

$$\mathbf{1a\text{--}d} + \mathbf{2} \underset{}{\overset{K_{1:1}}{\rightleftharpoons}} \mathbf{1a\text{--}d\cdot 2}, \qquad (1)$$

$$\mathbf{1a\text{--}c\cdot 2} + \mathbf{2} \underset{}{\overset{K_{1:2}}{\rightleftharpoons}} \mathbf{1a\text{--}c\cdot(2)_2}, \qquad (2)$$

where $K_{1:1} = [\mathbf{1a\text{--}d\cdot 2}]/([\mathbf{1a\text{--}d}][\mathbf{2}])$ (dm^3 mol^{-1}) and $K_{1:2} = [\mathbf{1a\text{--}c\cdot(2)_2}]/([\mathbf{1a\text{--}c\cdot 2}][\mathbf{2}])$ (dm^3 mol^{-1}).

Since all of the values of $K_{1:1}$ proved to be above the upper limit of applicability of the method (log $K_{1:1} > 5$), competitive titration was carried out in the **1a–d/2/4** systems in CD$_3$CN. The diammonium compound **4** forms only the 1:1 complex with **2**:

$$\mathbf{4} + \mathbf{2} \underset{}{\overset{K_C}{\rightleftharpoons}} \mathbf{4\cdot 2}, \qquad (3)$$

where $K_C = [\mathbf{4\cdot 2}]/([\mathbf{4}][\mathbf{2}])$ (dm^3 mol^{-1}). The stability constant of complex **4·2** is known from the data of spectrophotometric titration: log $K_C = 7.58$;[25] this was used to determine the stability constants of bimolecular complexes **1a–d·2** taking account of equilibria (1) and (3). Treatment of the data of direct ^{1}H NMR titration with inclusion of two equilibria (1) and (2), using the determined values of $K_{1:1}$, afforded the stability constants of trimolecular complexes **1a–c·(2)$_2$** (Table 1).

It follows from the obtained data that the nature of the heterocyclic residue of the dye does not affect the complex formation,

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‡ Triethyl orthoformate (75 µl, 67 mg, 0.45 mmol) was added to a solution of 1-ethyl-2,3,3-trimethyl-3*H*-indolium perchlorate[21] (86 mg, 0.3 mmol) in pyridine (1 ml), and the mixture was heated with stirring at 100 °C for 2 h. The mixture was concentrated and dissolved with heating in EtOH (2 ml) with addition of 70% perchloric acid (20 µl), and the solution was cooled to –10 °C. The precipitated crystals were filtered off, washed with Et$_2$O–EtOH (2:1) and Et$_2$O, and dried in air to give 63 mg (88%) of **3** as dark-violet crystals with bronze luster, mp 227–228 °C. ^{1}H NMR (Bruker DRX500, DMSO-*d$_6$*) δ: 1.32 (t, 6H, 2*Me*CH$_2$, *J* 7.3 Hz), 1.69 (s, 12H, 2C*Me$_2$*), 4.17 (q, 4H, 2Me*CH$_2$*, *J* 7.3 Hz), 6.53 (d, 2H, 2H-α, *J* 13.5 Hz), 7.30 (m, 2H, 2H-5), 7.43–7.58 (m, 4H, 2H-6, 2H-7), 7.65 (m, 2H, H-4), 8.35 (t, 1H, *meso*-H, *J* 13.5 Hz). ^{13}C NMR (Bruker DRX500, DMSO-*d$_6$*) δ: 12.17 (2*Me*CH$_2$), 27.28 (2C*Me$_2$*), 38.46 (2CH$_2$N$^+$), 48.82 (2C*Me$_2$*), 102.27 (2C-α), 111.23 (2C-7), 122.50 (2C-4), 125.14 (2C-5)), 128.62 (2C-6), 140.66 (2C-3a), 141.37 (2C-7a), 149.90 (*meso*-C), 173.36 (2C-2). UV-VIS (MeCN, λ_{max}/nm): 279, 514 (sh), 544. Fluorescence (MeCN), λ_{ex}/nm: 550; λ^f_{max}/nm: 567. Found (%): C, 65.73; H, 6.86; N, 5.81. Calc. for C$_{27}$H$_{33}$ClN$_2$O$_4$·0.5H$_2$O (%): C, 65.64; H, 6.94; N, 5.67.

§ ^{1}H NMR titration was performed on a Bruker DRX500 instrument in CD$_3$CN at 30 °C. For titration in the **1a–d/2** system, the concentration of **1a–d** was maintained at about 1×10^{-3} mol dm^{-3}, while the concentration of **2** was varied from 0 to 3×10^{-3} mol dm^{-3}. During competitive titration in the **1a–d/2**/1,10-diammoniodecane diperchlorate (**4**) system,[22] the concentration of **1a–d** was maintained at about 1×10^{-3} mol dm^{-3}, the concentration of **2** was about 1.2×10^{-3} mol dm^{-3}, and the concentration of **4** was varied from 0 to 1×10^{-2} mol dm^{-3}. The stability constants were calculated to an accuracy of ±30% by analyzing the changes in the positions of proton signals of **1a–d** using HYPNMR software.[23] The absorption spectrum of **3** (1×10^{-5} mol dm^{-3}) was recorded on a UV–3101PC spectrophotometer (Shimadzu) in the 250–550 nm range with a 1 nm step (MeCN, a 1 cm-thick cell, room temperature).
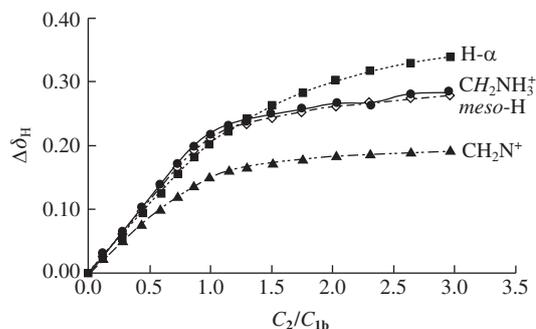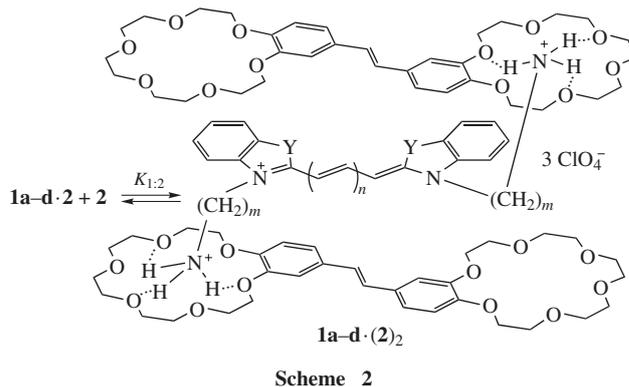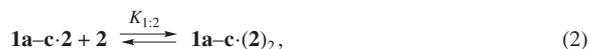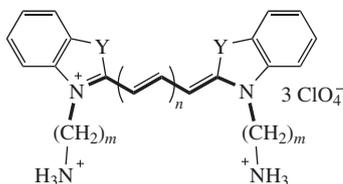
Table 1 Stability constants of complexes **1a–d·2** and **1a–c·(2)₂**.[a]

Dye	L^b	$\log K_{1:1}$	$\log K_{1:2}$
1a	17	8.1	1.7
1b	13	6.1	2.6
1c	15	6.4	2.1
1d	17	7.8	<0.5

[a] ^{1}H NMR titration in CD_3CN, 30 °C. The error of measurement of the constants is ±30%. [b] $L = 5 + 2(n + m)$ is the number of atoms in the chain (shown in boldface) connecting two NH_3^+ groups in the dye molecule.

the stability of bimolecular complexes depends on the distance L between the terminal NH_3^+ groups in the dye molecule; this distance can be conventionally defined as the number of atoms in the chain connecting the ammonium groups. The highest stability constants for bimolecular complexes are found for dyes **1a** and **1d** with $L = 17$. The driving force for the formation of trimolecular complexes is apparently the steric strain in the corresponding bimolecular complexes caused by the geometric mismatch of the distances between the binding sites of the dye and stilbene molecules in complexes **1·2**. Previously,[14,15] we established, in relation to the complexes of bis(ammonioalkyl) derivatives of 4,4′-bipyridine and its analogues with **2**, that the stabilities of bi- and trimolecular complexes based on homologous compounds change in the opposite directions: the higher the stability of 1:1 complexes, the lower the stability of the corresponding 1:2 complexes and *vice versa*. The low stability of the possible complex **1d·(2)₂** ($\log K_{1:2} < 0.5$) as compared with that of the homologous complex **1c·(2)₂** ($\log K_{1:2} = 2.1$) also supports this trend (see Table 1).

Thus, we exemplified for the first time the possibility to construct the supramolecular systems based on cyanine dyes with two ammonioalkyl N-substituents using their complexes with bis(18-crown-6)stilbene. These reactants form highly stable bimolecular and relatively unstable trimolecular complexes in which the dye ammonium groups are hydrogen-bonded to the crown ether moieties of the stilbene and their π-conjugated moieties are located one above the other. The stability of the complexes was shown to depend on the dye structure, in particular, on the geometric matching of components, which is manifested as the distance between the ammonium groups of the dye and the stilbene binding sites. The revealed trends can be used for the design of photoactive supramolecular systems.

Online Supplementary Materials
Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2014.09.016.

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