Synthesis, Structure, and Properties of Supramolecular Charge-Transfer Complexes between Bis(18-crown-6)stilbene and Ammonioalkyl Derivatives of 4,4'-Bipyridine and 2,7-Diazapyrene

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Supporting Information



4,4'-Bipyridine and 2,7-diazapyrene derivatives (A) having two ammonioalkyl N-substituents were synthesized. The complex formation of these compounds with bis(18-crown-6)stilbene (D) was studied by spectrophotometry, cyclic voltammetry, ¹H NMR spectroscopy, and X-ray diffraction analysis. In MeCN, π -donor D and π -acceptors A form supramolecular 1:1 (D·A) and 2:1 (D·A·D) charge-transfer complexes. The D·A complexes have a pseudocyclic structure as a result of ditopic binding of the ammonium groups to the crown-ether fragments. The better the geometric matching between the components, the higher the stability of the D·A complexes (log K up to 9.39). A key driving force of the D·A·D complex formation is the excessive steric strain in the precursor D·A complexes. The pseudocyclic D·A complexes involving the ammoniopropyl derivative of 4,4'-bipyridine were obtained as single crystals. Crystallization of the related ammonioethyl derivative was accompanied by transition of the D·A complexes to a structure of the (D·A)_m coordination polymer type.

INTRODUCTION

Organic donor—acceptor complexes, or charge-transfer (CT) complexes, play an important role in chemical and photochemical reactions,¹ in molecular self-assembly,² and in biological systems,³ and they can be employed for organic photovoltaic devices and field-effect transistors.⁴ In recent years, considerable attention has been paid to the synthesis and studies of supramolecular donor—acceptor systems in relation to their possible use as components of molecular electronic devices for solar energy conversion and sensor and catalytic applications.⁵

Previously,⁶ we described supramolecular CT complexes between bis(18-crown-6)stilbene (*E*)-1 and dipyridylethylene derivatives (*E*)-2b,c. Complexes $[1\cdot 2b,c]$ are characterized by a

very high thermodynamic stability, which is due to the ditopic binding of ammonium groups of acceptor 2 to the crown-ether fragments of donor 1. It was shown that these complexes can act as fluorescence sensors for alkaline-earth metal ions.^{6a} Moreover, they are very convenient model systems for investigation of ultrafast electron transfer reactions.⁷

In order to study the effect of the acceptor structure on the properties of supramolecular CT complexes such as $[1 \cdot 2b,c]$, we synthesized 4,4'-bipyridine derivatives **3b**,c and 2,7-diazapyrene derivatives **4b**,c containing two ammonioalkyl N-substituents.

 Received:
 June 7, 2011

 Published:
 July 11, 2011

Scheme 1. Structure of Acceptors 3a, 4a and Synthesis of Acceptors 3b,c and 4b,c



This paper gives an account of the studies of the structural features and the physicochemical properties of the complexes formed by these compounds with bis(crown)stilbene 1 in solutions and in the crystalline state. As model compounds, we used acceptors 3a and 4a devoid of ammonium groups.

RESULTS AND DISCUSSION

Synthesis. Previously,⁸ we developed an efficient synthesis of symmetrical bis(crown)stilbenes, in particular (E)-1, consisting of the condensation of benzocrown ethers with 2-bromoacetaldehyde

diethyl acetal in acid medium and subsequent rearrangement of the resulting 1,1-diaryl-2-bromoethanes to desired stilbenes. The synthesis of (*E*)-1,2-di(4-pyridyl)ethylene derivatives $2\mathbf{a}-\mathbf{c}$ and model acceptor compounds $3\mathbf{a}$ and $4\mathbf{a}$ was described in our previous publications.^{6a,9} Compounds $3\mathbf{b},\mathbf{c}$ and $4\mathbf{b},\mathbf{c}$ were prepared by quaternization of 4,4'-bipyridine and 2,7-diazapyrene with ω -bromoalkylammonium bromides in MeCN, followed by exchange of the anions with the perchlorates on treatment with concentrated HClO₄ in ethanol (Scheme 1).

Supramolecular complexes $[1\cdot 3b,c]$ and $[1\cdot 4b,c]$ were obtained as dark-colored fine-crystalline powders by slow precipitation from acetonitrile solutions of equimolar mixtures of components. The 1:1 formal stoichiometry was confirmed for these complexes by ¹H NMR spectroscopy, elemental analysis, and X-ray diffraction. It is noteworthy that repeated crystallization of the black-blue crystalline complex $[1\cdot 3b]$ gave rise to almost colorless amorphous precipitate having the same stoichiometric composition. According to X-ray diffraction data (see below), in the crystalline complex $[1\cdot 3b]$, effective CT interaction may occur between the π -donor and π -acceptor moieties, which is responsible for deep coloring. Probably, in the amorphous modification of $[1\cdot 3b]$, the relative positions of these moieties are unfavorable for CT interactions and the complex components are thus connected only through hydrogen bonds.

CT Absorption Spectra and Complex Formation Constants. It has been demonstrated previously^{6b,9b} that the complexation of bis(crown)stilbene (*E*)-1 (π -donor) with the π acceptor molecules (*E*)-2b,c in MeCN in the concentration range up to 0.05 M for 1 and up to 1 × 10⁻³ M for the acceptor is perfectly described by the following equilibria:

$$\mathbf{D} + \mathbf{A} \stackrel{K_1}{\nleftrightarrow} \mathbf{D} \cdot \mathbf{A} \tag{1}$$

$$\mathbf{D} \cdot \mathbf{A} + \mathbf{D} \stackrel{K_2}{\longleftarrow} \mathbf{D} \cdot \mathbf{A} \cdot \mathbf{D}$$
(2)

where **D** is the donor, **A** is the acceptor, and K_1 (M⁻¹) and K_2 (M⁻¹) are the equilibrium constants. Spectrophotometric titration experiments on systems 1/3 and 1/4 (see Experimental Section) showed that this reaction model also holds true for acceptors 3 and 4 (Scheme 2).

Figures 1 and 2 show the CT absorption spectra of the $\mathbf{D} \cdot \mathbf{A}$ and $\mathbf{D} \cdot \mathbf{A} \cdot \mathbf{D}$ complexes involving acceptors $3\mathbf{b},\mathbf{c}$ and $4\mathbf{b},\mathbf{c}$, respectively. The formation constants K_1 and K_2 and the main characteristics of the low-energy CT absorption band for the biand termolecular complexes are listed in Table 1.

In the region $\lambda > 400$ nm, where neither 1 nor 3b,c absorb the light, complexes $[1 \cdot 3b,c]$ demonstrate a broad low-intensity absorption band, which is indicative of through-space CT interaction between the donor and the acceptor. In the case of $[1 \cdot 4b, c]$, the CT absorption reveals itself as a long-wavelength shoulder of the intense band associated with the local S_0-S_1 electronic transition of the acceptor moiety (the absorption spectra of diazapyrene derivatives 4b,c are presented in Figure S28, Supporting Information).

The termolecular complexes $[1 \cdot 3b, c \cdot 1]$ and $[1 \cdot 4b, c \cdot 1]$ exhibit more intense CT absorption bands peaked at longer wavelengths as compared with the corresponding bimolecular complexes. With acceptors (*E*)-2b,c, transition from **D** \cdot **A** to **D** \cdot **A** \cdot **D** also leads to a red shift of the CT absorption band, ^{9b} i.e., to a decrease in the energy of CT electronic transition (ΔE_{CT}). At least two factors can be responsible for this feature. First,







Figure 1. CT absorption spectra of (a) $[1\cdot 3b]$, (b) $[1\cdot 3b\cdot 1]$, (c) $[1\cdot 3c]$, and (d) $[1\cdot 3c\cdot 1]$ in MeCN.

 $\Delta E_{\rm CT}$ of symmetrical **D**·**A**·**D** complexes can be affected by coupling of two equivalent CT excited states.¹⁰ Second, the termolecular complexes have less sterically strained structures than the pseudocyclic **D**·**A** systems, resulting in shorter do-nor-acceptor separation distance and, consequently, stronger CT interaction between the donor and the acceptor.

In the case of **3b**, the transition from $\mathbf{D} \cdot \mathbf{A}$ to $\mathbf{D} \cdot \mathbf{A} \cdot \mathbf{D}$ is accompanied by the most significant change of CT absorption: the low-energy CT band shifts bathochromically by 66 nm, and its intensity increases by a factor of 4.5. We suppose that the bipyridinium fragment in $[1 \cdot 3b]$ has a nonplanar geometry, typical of viologen derivatives. In $[1 \cdot 3b \cdot 1]$, this fragment is likely to adopt a more planar conformation due to stacking with the two stilbene fragments, which provides relatively large gain in the CT interaction.



Figure 2. CT absorption spectra of (a) $[1\cdot4b]$, (b) $[1\cdot4b\cdot1]$, (c) $[1\cdot4c]$, and (d) $[1\cdot4c\cdot1]$ in MeCN.

Table 1. Formation Equilibrium Constants and Characteristics of the Low-Energy CT Absorption Band for the Bi- and Termolecular Complexes between (E)-1 and Compounds 2–4

		D·A			D·A·D			
acceptor (A)	$\log_{K_1^a}$	λ _{max} , nm	\mathcal{E}_{max} $M^{-1} \cdot cm^{-1}$	log K2 ^a	λ _{max} , nm	ϵ_{max} $M^{-1} \cdot cm^{-1}$		
$2\mathbf{b}^b$	9.42	535	340	2.73	555	900		
$2c^b$	9.08	502	390	3.20	519	1020		
3b	7.36	522	160	2.73	588	730		
3c	9.15	493	200	1.73	530	490		
4b	7.72	С	С	3.30	535	1290		
4c	9.39	С	С	2.33	503	1170		
^a MeCN,	23 ± 1	°C. K_1	$= [\mathbf{D} \cdot \mathbf{A}]/($	$[D] \times$	[A])	$(M^{-1}), K_2 =$		

 $[\mathbf{D}\cdot\mathbf{A}\cdot\mathbf{D}]/([\mathbf{D}\cdot\mathbf{A}] \times [\mathbf{D}])$ (M⁻¹). The formation constants are measured to within ±20%. ^b From ref 9b. ^c Shoulder (see Figure 2).

The change from the ammoniopropyl to ammonioethyl tails in acceptors 2-4 results in a decrease in $\Delta E_{\rm CT}$ for both bi- and termolecular complexes. This feature can be explained by a shorter donor-acceptor separation distance in the complexes having shorter ammonioalkyl spacers.

For common organic donor-acceptor complexes, $\Delta E_{\rm CT}$ normally decreases with a decrease in the reduction potential of the acceptor. In the case of supramolecular **D**•**A** complexes, we observe some deviations from this correlation. For example, viologen derivative 3**c** is a stronger electron acceptor than 2**c** (see below); nevertheless, complex [1·3**c**] shows a higher $\Delta E_{\rm CT}$ than [1·2**c**]. This fact suggests that complexes [1·3**c**] and [1·2**c**] significantly differ from each other in the reorganization energy associated with the photoinduced charge transfer reaction.⁷

Figure 3 shows the log K_1 and log K_2 values for the bi- and termolecular CT complexes as functions of the distance between the ammonium nitrogen atoms in the acceptor molecule (R_{am}) . The R_{am} values were determined by quantum-chemical calculation of the geometry of 2-4 in MeCN. Acceptors 2-4 are divided into two groups. Group I comprises compounds in which the π -acceptor fragment has a planar geometry (2b,c and 4b,c). Group II includes compounds with a nonplanar π -acceptor fragment (3b,c).

The dependences presented in Figure 3 have two specific features. First, in the region of $R_{am} = 16.0-16.5$ Å, the log K_1



Figure 3. Formation equilibrium constants for the CT complexes $\mathbf{D} \cdot \mathbf{A}$ and $\mathbf{D} \cdot \mathbf{A} \cdot \mathbf{D}$ vs the distance between the ammonium nitrogen atoms in the acceptor molecule, R_{am} .

values for acceptors of both groups reach a maximum and the log K_2 values reach a minimum. Second, the plots of log K_1 vs R_{am} and log K_2 vs R_{am} for acceptors of group I lie above the corresponding plots for viologens **3b**,**c**. These two specific features can be interpreted using the general views on the driving force of formation of complexes **D** · **A** and **D** · **A** · **D**.^{9b}

Undoubtedly, the main driving force of the formation of pseudocyclic bimolecular complexes is two-center hydrogen bonding. This bonding is most effective when there is exact geometric correspondence between the reactants. Any change in the geometry of one reactant (e.g., the change in the length of ammonioalkyl tails in 2-4) would result in excess steric strain in the pseudocyclic complex $\mathbf{D}\cdot\mathbf{A}$. For systems 1/2-4, the best geometric correspondence for the two-center hydrogen bonding is attained apparently for $R_{\rm am} = 16.0-16.5$ Å, where log K_1 for acceptors of both groups are maximum.

A certain contribution to the free energy of formation of complexes $\mathbf{D} \cdot \mathbf{A}$ can be made by stacking interactions between the unsaturated fragments of \mathbf{D} and \mathbf{A} . The acceptors having a planar unsaturated fragment (group I) are more prone to stacking interactions; therefore, the plot of log K_1 vs R_{am} for these acceptors runs above the corresponding plot for viologens **3b**,**c**.

A key driving force of the reaction $\mathbf{D} \cdot \mathbf{A} + \mathbf{D} \rightarrow \mathbf{D} \cdot \mathbf{A} \cdot \mathbf{D}$ is the excessive steric strain in the pseudocyclic $\mathbf{D} \cdot \mathbf{A}$ structures, which is released upon transition to the $\mathbf{D} \cdot \mathbf{A} \cdot \mathbf{D}$ complexes. This conclusion is consistent with the fact that the positions of the minima in the log K_2 vs R_{am} plots coincide with the maxima in the log K_1 vs R_{am} plots (the maxima correspond to the $\mathbf{D} \cdot \mathbf{A}$ complexes having the lowest steric strain).

The three-decker structure of $\mathbf{D} \cdot \mathbf{A} \cdot \mathbf{D}$ complexes suggests stronger stacking interactions than those possible in pseudocyclic $\mathbf{D} \cdot \mathbf{A}$ precursors. This is another factor that can promote the



Figure 4. Fluorescence spectra in acetonitrile containing CT complex $[1 \cdot 4c]$ at a concentration of 1.0×10^{-5} M and Ca(ClO₄)₂ at different concentrations, C_{MJ} ranging from 0 to ca. 7×10^{-5} M; excitation at 402 nm. The spectra are assigned to the uncomplexed diazapyrene derivative 4c.

reaction $\mathbf{D} \cdot \mathbf{A} + \mathbf{D} \rightarrow \mathbf{D} \cdot \mathbf{A} \cdot \mathbf{D}$. In the case of group I acceptors, this factor does make a significant contribution to the free energy of this reaction; this conclusion follows from a comparison of the two plots of log K_2 vs R_{am} .

Fluorescence Studies. CT complex $[1 \cdot 4c]$ was tested for use as a fluorescent sensor for alkaline-earth metal ions. Figure 4 shows the fluorescence spectra in acetonitrile containing $[1 \cdot 4c]$ at a concentration, $C_{D \cdot A}$, of 1.0×10^{-5} M and $Ca(ClO_4)_2$ at different concentrations, C_{M} ranging from 0 to ca. 7×10^{-5} M (excitation at 402 nm).

Complex $[1 \cdot 4c]$ is intrinsically nonfluorescent, but its solution shows a very weak fluorescence coming from the uncomplexed 4c molecules, the percentage of which at $C_{D \cdot A} = 1.0 \times 10^{-5}$ M is <1%. On addition of Ca(ClO₄)₂, the percentage of uncomplexed 4c molecules increases due to the binding of Ca²⁺ ions to the crown-ether fragments of stilbene 1 (Scheme 3), which results in an increase in the fluorescence intensity (the fluorescence quantum yield of 4c in MeCN was estimated to be 0.31).

Figure 5 shows the dependencies of fluorescence yield (Φ_f) on the concentration of metal perchlorate for acetonitrile solutions of $[1 \cdot 4c]/Mg(ClO_4)_2$, $[1 \cdot 4c]/Ca(ClO_4)_2$, and $[1 \cdot 4c]/Ba-(ClO_4)_2$ ($C_{D \cdot A} = 1.0 \times 10^{-5}$ M, excitation at 402 nm). These data demonstrate a high selectivity of the fluorescence response of complex $[1 \cdot 4c]$ toward Ca²⁺ and Ba²⁺ versus Mg²⁺.

The molar absorptivities of complex [$1 \cdot 4c$] and compound 4c at 402 nm are equal (see Figure S37, Supporting Information); therefore, the fluorescence yield Φ_f is directly proportional to the concentration of uncomplexed 4c molecules (note that bis-(crown)stilbene 1 and its complexes with alkaline-earth metal ions do not absorb the light with $\lambda > 400$ nm). The dependencies of Φ_f on $C_M/C_{D\cdot A}$ measured for Ca(ClO₄)₂ and Ba(ClO₄)₂ were interpreted in terms of the complexation model comprising the equilibria of eqs 1 and 3:

$$\mathbf{D} + 2\mathbf{M}^{2+} \stackrel{K_{\mathrm{M}}}{\longleftrightarrow} \mathbf{D} \cdot (\mathbf{M}^{2+})_2 \tag{3}$$

where M is the metal cation and $K_{\rm M}$ is the complex stability constant. The best fits to this model (Figure 5) were found when log $K_{\rm M}$ = 15.5 for Ca²⁺ and 16.5 for Ba²⁺.

Scheme 3. Reaction of Ca^{2+} with Complex $[1 \cdot 4c]$



Figure 5. Fluorescence yield, $\Phi_{\rm fr}$ as a function of the concentration of metal perchlorate for acetonitrile solutions of $[1\cdot4c]/Mg(ClO_4)_{2r}$, $[1\cdot4c]/Ca(ClO_4)_{2r}$, and $[1\cdot4c]/Ba(ClO_4)_2$ ($C_{\rm D\cdot A} = 1.0 \times 10^{-5}$ M, excitation at 402 nm). The solid curves are the best fits to the complexation model comprising the equilibria of eqs 1 and 3.

Redox Properties. The electrochemical properties of the supramolecular CT complexes $[1 \cdot 3b, c]$ and $[1 \cdot 4b, c]$ were studied using cyclic voltammetry at a glassy carbon electrode in acetonitrile containing Bu₄NClO₄ (0.1 M). Selected cyclic voltammograms are shown in Figure S39 (Supporting Information). The peak potentials of the first redox transitions, vs Ag|AgCl|KCl (aq., sat.), for complexes $[1 \cdot 2b, c]$, $[1 \cdot 3b, c]$, and $[1 \cdot 4b, c]$ as well as for the uncomplexed compounds 1, 2b, c, 3b, c, and 4b, c are presented in Table 2. The electrochemical data for systems 1/2b, c are taken from ref 11.

The formation of pseudocyclic $\mathbf{D} \cdot \mathbf{A}$ complexes is accompanied in all cases by a considerable anodic shift of the first oxidation potential of donor 1, and the first redox transition becomes irreversible. The anodic shift ΔE_p^{ox} varies from 130 to

240 mV depending on the acceptor structure. The more difficult oxidation of complexed 1 compared with free 1 is caused by two factors. First, the two-center interaction of the ammonium groups of the acceptor with the heteroatoms of the crown-ether fragments of 1 through hydrogen bonding reduces the electron density on the π -electron-donor fragment of 1. In sterically strained $[1\cdot 3b]$ and $[1\cdot 4b]$, this interaction is least effective; hence, $[1\cdot 3b]$ and $[1\cdot 4b]$ have the lowest ΔE_p^{ox} values. Second, the oxidized form of 1, i.e., the radical cation $1^{\bullet+}$, in the complex with the tetracationic acceptor is destabilized due to Coulomb repulsion.

The first reduction potentials of the complexes $\mathbf{D} \cdot \mathbf{A}$ are shifted to less negative values relative to the reduction potential of the free acceptor. The magnitude of this shift, $\Delta E_{\rm p}^{\rm red}$, varies in the range of 10–100 mV depending on the acceptor structure. In all cases except for 4b, the redox transition remains reversible. A positive value of $\Delta E_{\rm p}^{\rm red}$ implies that the reduced form of the acceptor is more stable when complexed with 1 than in the free state. Note that for complexes $\mathbf{D} \cdot \mathbf{A}$, the positive shift of the reduction potential of the acceptor is consistent with the decrease in the energy of the local S_0-S_1 electronic transition of the acceptor (see Figures S31 and S32 for 4b,c (Supporting Information)).

Electrochemical data for various supramolecular viologen complexes have been reported, in particular, "host–guest" complexes with cyclodextrins,¹² calixarenes,¹³ cucurbiturils,¹⁴ aromatic molecular pincers,¹⁵ and pseudorotaxane donor–acceptor complexes.¹⁶ In most cases, the complexation induced a negative shift of the first reduction potential of viologen. The exceptions are the inclusion complexes with β - and γ -cyclodextrins and cucurbit[8]uril, for which an opposite effect is observed. The positive shift of the reduction potential in the methylviologen/ β -cyclodextrin system^{12a} is because of the fact that β -cyclodextrin does not bind methylviologen but can encapsulate its reduced form. In the case of complexes formed by viologens with γ -cyclodextrin^{12a} and cucurbit[8]uril,^{14b} the positive shift of the reduction potential is caused by stabilization of the viologen radical cation dimer in the host cavity.

It is evident that these mechanisms are inappropriate for interpreting the positive $\Delta E_{\rm p}^{\rm red}$ values observed for pseudocyclic complexes $[1\cdot 2{\rm b,c}]$, $[1\cdot 3{\rm b,c}]$, and $[1\cdot 4{\rm b,c}]$. Presumably, easier reduction of the complexed acceptor as compared with its free molecule is attributable, first, to considerable changes in the solvation shell of the charged acceptor molecule upon the formation of the pseudocyclic complex, and second, to specific interaction of the reduced form of the acceptor with the stilbene fragment of 1.

¹H NMR Spectroscopy Studies. The addition of equimolar amounts of compounds 3b,c or 4b,c to MeCN- d_3 solutions of (*E*)-1 induced considerable shifts of most proton signals, $\Delta \delta_{\rm H}$, in the ¹H NMR spectra (e.g., Figure 6a-c), indicating the formation of pseudocyclic D·A complexes in which the components are arranged one above another (Scheme 2). The $\Delta \delta_{\rm H}$ values measured for these equimolar mixtures are shown in Figure 7. The downfield shifts of most CH₂O signals ($\Delta \delta_{\rm H}$ of up to 0.24 ppm) are attributable to the electron-withdrawing effect of the ammonium ions bound to the crown-ether fragments of 1. Most of the proton signals corresponding to the central fragments of the donor and the acceptor show upfield shifts due to the mutual shielding effect ($\Delta \delta_{\rm H}$ of up to -1.17 ppm).

As the content of **1** in solution increases, the proton signals of the acceptor continue to regularly shift upfield (see Figure 6c,d).

compound	$E_{\rm p}^{\rm ox}/E_{\rm p}^{\rm red}/{\rm V}$	complex	$E_{\rm p}^{\rm ox}/{\rm V}$	$E_{\rm p}^{\rm red}/{ m V}$	$\Delta E_{ m p}{}^{ m ox}/{ m mV}^b$	$\Delta E_{ m p}^{ m red}/{ m mV}^b$	
1 ^{<i>c</i>}	1.0 rev/-2.48						
$2b^c$	-/-0.50 rev	$[1 \cdot 2b]^c$	1.24	-0.43 rev	240	70	
$2c^{c}$	−/−0.50 rev	$[1 \cdot \mathbf{2c}]^c$	1.24	-0.43 rev	240	70	
3b	−/−0.40 rev	[1·3b]	1.13	-0.33 rev	130	70	
3c	−/−0.41 rev	[1·3c]	1.19	-0.38 rev	190	30	
4b	−/−0.42 rev	[1·4b]	1.15	-0.32	150	100	
4c	−/−0.43 rev	[1·4c]	1.20	-0.42 rev	200	10	
⁴ M-CNI suggesting all studiets Dr. NCIO (0.1 M) all and all studies all and A-CI/VCI (second based on the studies of the stu							

Table 2. Peak Potentials of the First Redox Transitions for π -Electron Donor (E)-1, π -Electron Acceptors 2–4, and Supramolecular D·A Complexes^a

^{*a*} MeCN, supporting electrolyte Bu₄NClO₄ (0.1 M), glassy carbon electrode vs Ag|AgCl|KCl (aq., sat.), rev denotes reversible (the forward to reverse peak potential difference is about 60 mV). ^{*b*} $\Delta E_p^{\text{ox}} = E_p^{\text{ox}}(\text{complex}) - E_p^{\text{ox}}(\text{free donor})$. $\Delta E_p^{\text{red}} = E_p^{\text{red}}(\text{complex}) - E_p^{\text{red}}(\text{free acceptor})$. ^{*c*} From ref 11.



Figure 6. ¹H NMR spectra (aromatic proton region) of (*a*) 3c (1 × 10^{-3} M), (*b*) (*E*)-1 (1 × 10^{-3} M), and their mixtures in molar ratios (*c*) 1:1 and (*d*) 1:6 (500.13 MHz, MeCN- d_{32} 25 °C).

This implies transition from the bimolecular $\mathbf{D} \cdot \mathbf{A}$ complex to termolecular $\mathbf{D} \cdot \mathbf{A} \cdot \mathbf{D}$ complex, in which the acceptor molecule is sandwiched between two bis(crown)stilbene molecules (Scheme 2), and, hence, the acceptor hydrogen atoms become even more shielded.

Detailed analysis of the $\Delta \delta_{\rm H}$ values presented in Figure 7 shows that the unsaturated fragments of the donor and acceptor molecules in the **D**·**A** complexes are not located exactly one above another but are preferably projected X-wise. It is this arrangement of the unsaturated fragments that occurs for complexes $[1\cdot 3c]$ in the crystal (see below). Figure 8 shows schematically the intermolecular NOE interactions found for systems $[1\cdot 3b,c]$. All of the detected intermolecular NOE cross peaks are weak as compared with intramolecular NOE signals; therefore, the distances between the interacting protons can be roughly estimated as ranging from 3.0 to 3.5 Å. The number of intermolecular NOE interactions increases with a decrease in the linear dimensions of the diammonium compound, evidently, due to a decrease in the donor—acceptor separation distance.

The complex formation constants for systems 1/2(3,4)a-cwere estimated using ¹H NMR titration (see Experimental Section). For model acceptors **3a** and **4a**, the experimental dependences of $\Delta \delta_{\rm H}$ on the amount of **1** added were interpreted in terms of 1:1 complex formation. For diammonium compounds 2(3,4)b,c, the ¹H NMR titration data were described well by the complexation model comprising the equilibria of eqs 1 and 2. The measured log K_1 and log K_2 values are presented in Table 3.

Good agreement between the log K_2 values determined by NMR spectroscopy and spectrophotometry (compare the data in Tables 3 and 1) confirms the applicability of the approaches used. For the supramolecular **D**•**A** complexes, the log K_1 values derived from ¹H NMR experiments are lower by 0.1–0.6 than those measured by spectrophotometry. This is attributable to a higher content of water impurity in MeCN- d_3 . The presence of water can lead to a decrease in the equilibrium constant K_1 of eq 1 due to preferable hydration of uncomplexed ammonium ions (this factor has less influence on the equilibrium of eq 2).

For the model acceptors, the complex stability constants K_1 are relatively low (log $K_1 < 1.7$) and increase in the series 3a < 2a < 4a, which evidently reflects the enhancement of the stacking interactions in the complexes following increase in the conjugation system of the acceptor. The huge differences in the K_1 values between the model acceptors and the corresponding diammonium compounds (2-4)b,c clearly attest that the two-center hydrogen bonding in the supramolecular $D \cdot A$ complexes makes a much greater contribution to the free energy of complex formation than the stacking interactions between the unsaturated fragments of the components.

X-ray Diffraction Studies. Compounds 3c and 4a and complexes $[1 \cdot 3b]$ and $[1 \cdot 3c]$ were grown as single crystals suitable for X-ray diffraction analysis. The structures of the key crystal components are shown in Figure 9.

In the structure of $3c \cdot 2H_2O$, the viologen tetracation is located at the symmetry center of the crystal, which coincides with the midpoint of the C(6)–C(6A) bond connecting two pyridine residues. Because of this position, the bipyridinium fragment occurs in an ideally planar conformation. Note that X-ray diffraction study of the model viologen 3a has shown^{9a} that its pyridinium rings are twisted by 15.8°; this is more typical of 4,4'-bipyridine derivatives due to the steric interaction of the *ortho*-hydrogen atoms.

The distance between the N(1) and N(1A) atoms of ammonium groups in 3c is 16.13 Å, which practically coincides with the calculated data. The N(1) H_3^+ group forms a network of



Figure 7. Changes in the proton chemical shifts, $\Delta \delta_{\rm H} = \delta_{\rm H}(\text{complex}) - \delta_{\rm H}(\text{free compound})$, upon complexation of (*E*)-1 with 3b,c, 4b,c (500.13 MHz, MeCN- d_3 , 25 °C) (red = deshielding, blue = shielding).



Figure 8. Intermolecular NOE interactions detected for complexes $[1\cdot 3b]$ and $[1\cdot 3c]$.

Table 3. Formation Equilibrium Constants for the Bi- and Termolecular Complexes between (E)-1 and Compounds 2–4, as Derived from ¹H NMR Titration Experiments^{*a*}

acceptor	$\log K_1$	$\log K_2$
2a	1.14^{b}	
2b	9.0	2.78^{b}
2c	8.9	3.27^{b}
3a	0.86	
3b	6.8	2.72
3c	8.9	1.79
4a	1.65	
4b	7.1	3.22
4c	9.3	2.34
^{<i>a</i>} MeCN- d_3 , 25 \pm 1 °C.	$K_1 = [\mathbf{D} \cdot \mathbf{A}]/([\mathbf{D}])$	< [A]) (M ⁻¹), K ₂ =
$[\mathbf{D}, \mathbf{A}, \mathbf{D}] / ([\mathbf{D}, \mathbf{A}]) \times [1]$	\mathbf{D}]) (\mathbf{M}^{-1}) The form	mation constants are

 $[\mathbf{D}\cdot\mathbf{A}\cdot\mathbf{D}]/([\mathbf{D}\cdot\mathbf{A}] \times [\mathbf{D}])$ (M⁻¹). The formation constants are measured to within ±20%. ^b From ref 9b.

hydrogen bonds with the oxygen atoms of two independent perchlorate anions and with the O(1W) water molecule.

In the structure of model compound 4a, the diazapyrene dication is located at the symmetry center of the crystal, which determines the perfectly planar conformation of its conjugated

fragment. Note that the planarity of the diazapyrene fragment is rather predetermined by its rigid structure, although upon stacking, this fragment can be noticeably crooked, as shown in our study^{9a} of the crystal structure of the benzene solvate of **4a**.

It has been shown previously^{9b} that crystalline free stilbene (E)-1 is the *s-anti,s-anti-*conformer. In solutions, (E)-1 exists as an equilibrated mixture of *s-anti,s-anti-* and *s-syn,s-syn-*conformers (Scheme 4); according to ¹H NMR data, more compact *s-syn,s-syn-*conformer predominates.⁸ In crystalline complexes $[1\cdot3b]$ and $[1\cdot3c]$, stilbene 1 is revealed as an *s-syn,s-syn-*conformer (Figure 9c,d).

The structure $[1\cdot 3c]\cdot 0.25$ MeCN $\cdot 0.44$ H₂O contains two independent pseudocyclic complexes $[1\cdot 3c]$, differing by the conformations of the donor and acceptor components. In one complex, two $(CH_2)_3NH_3^+$ groups occur in different conformations (*trans,trans* and *trans,gauche*). In the other independent complex, both $(CH_2)_3NH_3^+$ groups have a fully transoid conformation. In pseudocyclic complexes, the ammonium groups are located on one side of the mean plane of the bipyridinium fragment; therefore, the distances between the ammonium nitrogen atoms, $N(1)\cdots N(4)$ (14.71 Å) and $N(1')\cdots N(4')$ (14.23 Å), are smaller than this parameter in $3c \cdot 2H_2O$. Each ammonium group forms directed hydrogen bonds with three oxygen atoms of the 18-membered macrocycle; the $N \cdots O$ -(macrocycle) distances are in the range of 2.801(6)-2.940(6) Å.

Note that the bipyridinium fragments in both independent complexes $[1 \cdot 3c]$ are nonplanar: the dihedral angles between the pyridinium rings, N(2)C₅/N(3)C₅ and N(2')C₅/N(3')C₅, are 34.2 and 35.9°, respectively. The stilbene fragments in these complexes also have nonplanar conformations: the dihedral angles between the benzene rings, C(11), ..., C(16)/C(28), ..., C(33) and C(11'), ..., C(16')/C(28'), ..., C(33'), are 24.8 and 31.1°, respectively. These facts imply relatively weak stacking interactions in crystalline complexes $[1 \cdot 3c]$.

In $[1 \cdot 3b] \cdot C_4H_8O_2 \cdot 3H_2O$, both the stilbene fragment of 1 and the bipyridinium fragment of 3b have a perfectly planar structure because the midpoints of the C(17)=C(17A) and C(5')-C(5'A) bonds coincide with the symmetry centers of the crystal. However, in this case, a different crystal packing motif is observed. The centrosymmetric structure of tetracation 3b implies that the ammonioethyl N-substituents are located on



Figure 9. Structures of the main components of the crystals (*a*) 4a, (*b*) $3c \cdot 2H_2O$, (*c*) $[1 \cdot 3b] \cdot C_4H_8O_2 \cdot 3H_2O$, and (*d*) $[1 \cdot 3c] \cdot 0.25$ MeCN $\cdot 0.44H_2O$ (two independent complexes). Thermal anisotropic ellipsoids are drawn at the (*a*, *b*) 50, (*c*) 40, and (*d*) 30% probability level. The additional letters "A" and "B" indicate that atoms belong to symmetrically related positions. Hydrogen bonds are drawn with dash lines.

Scheme 4. Conformers of (E)-1



different sides of the plane of bipyridinium fragment (the distance between the N(1) and N(1A) atoms is 11.68 Å). This gives rise to infinite skewed $(\mathbf{D} \cdot \mathbf{A})_m$ type stacks consisting of alternating donor and acceptor molecules hydrogen-bonded to one another (Figure 10). The ammonium groups of **3b** mainly form bifurcate hydrogen bonds with the oxygen atoms of

18-membered macrocycles. Here the $N \cdot \cdot \cdot O(\text{macrocycle})$ distances are in the range of 2.839(9) - 2.969(9) Å. Thus, owing to the formation of the coordination polymer, the relatively short viologen **3b** molecule and the bis(18-crown-6)stilbene molecule can avoid considerable twisting of their central fragments, which would inevitably arise upon the formation of pseudocyclic complexes as is the case for complex [$1 \cdot 3c$]. In structure [$1 \cdot 3b$], the dihedral angle between the mean planes of the stilbene and bipyridinium fragments adjoining each other in the stack is only 4.5° and the interplanar spacing is 3.4 Å. This structure allows relatively strong stacking interactions in the crystalline state without considerable steric strain.

CONCLUSIONS

4,4'-Bipyridine 3b,c and 2,7-diazapyrene 4b,c derivatives (acceptors, A) containing two ammonioalkyl N-substituents interact with bis(18-crown-6)stilbene 1 (donor, D) to form supramolecular 1:1 (D·A) and 2:1 (D·A·D) CT complexes. CT complex [1·4c] in nonaqueous media performs as a fluorescent sensor with a very selective response toward Ca²⁺ and Ba²⁺ versus Mg²⁺. The key driving force of the formation of pseudocyclic D·A complexes is the macrocycle–ammonium cation ditopic binding; therefore, the better the geometric matching between the components for the ditopic binding, the



Figure 10. Stacking of $(\mathbf{D} \cdot \mathbf{A})_m$ type in structure $[\mathbf{1} \cdot \mathbf{3b}] \cdot C_4 H_8 O_2 \cdot 3 H_2 O$. Most of the hydrogen atoms, perchlorate anions, and solvate molecules are omitted for clarity. Hydrogen bonds are drawn with dash lines.

higher the stability of the $\mathbf{D} \cdot \mathbf{A}$ complexes. A key driving force of the $\mathbf{D} \cdot \mathbf{A} + \mathbf{D} \rightarrow \mathbf{D} \cdot \mathbf{A} \cdot \mathbf{D}$ reaction resulting in unusual threedecker CT complexes is the steric strain in the pseudocyclic $\mathbf{D} \cdot \mathbf{A}$ complexes. Yet another factor promoting this reaction is the ability of the π -acceptor and π -donor fragments to undergo stacking interactions. The transition from $\mathbf{D} \cdot \mathbf{A}$ to $\mathbf{D} \cdot \mathbf{A} \cdot \mathbf{D}$ can be accompanied by considerable enhancement of stacking interactions as the steric strain is rather low in the three-decker $\mathbf{D} \cdot \mathbf{A} \cdot \mathbf{D}$ structures. Analogous causes induce the transition of the $\mathbf{D} \cdot \mathbf{A}$ complexes to structures like the $(\mathbf{D} \cdot \mathbf{A})_m$ coordination polymer upon crystallization. The found features of the construction of stacked $\mathbf{D} \cdot \mathbf{A}$ complexes can be used to design light-sensitive architectures in bottom-up nanotechnology.

EXPERIMENTAL SECTION

General Methods. The ¹H and ¹³C NMR spectra were recorded in MeCN- d_3 and DMSO- d_6 using the solvent as the internal reference ($\delta_{\rm H}$ 1.96 and 2.50, respectively; $\delta_{\rm C}$ 39.4 for DMSO- d_6). 2D NOESY and HSQC spectra were used to assign the proton and carbon signals; the mixing time in the NOESY experiment was 300 μ s.

Synthesis and characterization of bis(crown)stilbene (*E*)-1 and acceptor compounds 2a,c were described earlier.^{6a,8}

4,4'-(E)-Ethene-1,2-diylbis[1-(2-ammonioethyl)pyridinium] Tetraperchlorate (**2b**). Compound **2b** was synthesized by a known method:^{9b} mp 281–283 °C (decomp.); ¹H NMR (500.13 MHz, MeCNd₃-CDCl₃ (24:1, v/v), 25 °C) δ 3.60 (t, *J* = 6.6 Hz, 4H, 2 CH₂NH₃), 4.84 (t, *J* = 6.6 Hz, 4H, 2 CH₂N), 7.94 (s, 2H, CH=CH), 8.31 (d, *J* = 6.9 Hz, 4H, 2 3-H, 2 5-H), 8.80 (d, *J* = 6.9 Hz, 4H, 2 2-H, 2 6-H) ppm; ¹³C NMR (125.76 MHz, DMSO-d₆, 26 °C) δ 38.9 (2 CH₂NH₃), 57.7 (2 CH₂N), 125.5 (2 3-C, 2 5-C), 134.2 (CH=CH), 145.8 (2 2-C, 2 6-C), 150.9 (2 4-C) ppm.

1,1'-Diethyl-4,4'-bipyridinium Diperchlorate (**3a**). Compound **3a** was synthesized by a known method: ^{9a} mp 270–272 °C (decomp.); ¹H NMR (500.13 MHz, MeCN- d_3 , 25 °C) δ 1.68 (t, *J* = 7.3 Hz, 6H, 2 Me), 4.70 (q, *J* = 7.3 Hz, 4H, 2 CH₂), 8.40 (m, 4H, 2 3-H, 2 5-H), 8.94 (d, *J* = 6.8 Hz, 4H, 2 2-H, 2 6-H) ppm; ¹³C NMR (125.76 MHz, DMSO- d_6 , 25 °C) δ 16.2 (2 Me), 56.5 (2 CH₂N), 126.5 (2 3-C, 2 5-C), 145.5 (2 2-C, 2 6-C), 148.5 (2 4-C) ppm.

2,7-Diethylbenzo[Imn]-3,8-phenanthrolinediium Diperchlorate (**4a**). Compound **4a** was synthesized by a known method:^{9a} mp 322 °C (decomp.); ¹H NMR (500.13 MHz, MeCN- d_3 , 25 °C) δ 1.90 (t, J = 7.3 Hz, 6H, 2 Me), 5.16 (q, J = 7.3 Hz, 4H, 2 CH₂), 8.85 (s, 4H, 4-H, 5-H, 9-H, 10-H), 9.92 (s, 4H, 2 1-H, 3-H, 6-H, 8-H) ppm; ¹³C NMR (125.76 MHz, DMSO- d_6 , 26 °C) δ 16.5 (2 Me), 58.5 (2 CH₂N), 126.0 (10b-C, 10c-C), 128.7 (3a-C, 5a-C, 8a-C, 10a-C), 129.7 (4-C, 5-C, 9-C, 10-C), 141.6 (1-C, 3-C, 6-C, 8-C) ppm.

Synthesis of N,N'-Di(ammonioalkyl) Derivatives 3b,c and 4b,c (General Method). A mixture of 4,4'-bipyridine or 2,7diazapyrene¹⁷ (1 mmol) and 2-bromoethylammonium bromide or 3-bromopropylammonium bromide (6 mmol) in dry MeCN (20 mL) was refluxed with stirring for 140 h. The reaction mixture was cooled to room temperature, and a precipitate that formed was filtered, washed with abs. EtOH (4 \times 20 mL) and chloroform (2 \times 10 mL), and dissolved in water (20 mL). The aqueous solution was filtered and evaporated in vacuo to give the tetrabromide salt of corresponding $N_{,N'}$ di(ammonioalkyl) derivative as a yellow solid. The tetrabromide salt was dissolved upon heating in a mixture of EtOH (5 mL) and minimum quantity of water (several drops), and 70% aq. HClO₄ (0.6 mL, 7 mmol) and EtOH (5 mL) were added to the solution. The resulting solution was cooled to 5 °C, and a precipitate that formed was filtered, washed with EtOH (2 \times 5 mL), and dried in air. This treatment was repeated using 70% aq. HClO₄ (0.3 mL, 3.5 mmol) to give the corresponding tetraperchlorate salt.

1,1'-Bis(2-ammonioethyl)-4,4'-bipyridinium Tetraperchlorate (**3b**). A white powder (0.18 g, 26% yield): mp 272–276 °C (decomp.); ¹H NMR (500.13 MHz, MeCN- d_3 , 25 °C) δ 3.67 (t, *J* = 6.4 Hz, 4H, 2 CH₂NH₃), 4.94 (t, *J* = 6.4 Hz, 4H, 2 CH₂N), 8.53 (d, *J* = 6.8 Hz, 4H, 2 3-H, 2 5-H), 8.99 (d, *J* = 6.8 Hz, 4H, 2 2-H, 2 6-H) ppm; ¹³C NMR (125.76 MHz, DMSO- d_6 , 25 °C) δ 38.9 (2 CH₂NH₃), 58.1 (2 CH₂N), 126.4 (2 3-C, 2 5-C), 146.8 (2 2-C, 2 6-C), 148.8 (2 4-C) ppm; IR (Nujol) 3246, 3200 (N⁺-H) cm⁻¹. Anal. Calcd. for C₁₄H₂₂Cl₄N₄O₁₆· 2H₂O: C 24.72, H 3.85, N 8.24. Found: C 24.61, H 3.40, N 8.26.

1,1'-Bis(3-ammoniopropyl)-4,4'-bipyridinium Tetraperchlorate (**3c**). A white powder (0.48 g, 71% yield): mp 278–283 °C (decomp.); ¹H NMR (500.13 MHz, MeCN-d₃, 25 °C) δ 2.41 (m, 4H, 2 CH₂CH₂N), 3.13 (m, 4H, 2 CH₂NH₃), 4.72 (t, *J* = 7.7 Hz, 4H, 2 CH₂N), 8.47 (d, *J* = 6.7 Hz, 4H, 2 3-H, 2 5-H), 8.97 (d, *J* = 6.7 Hz, 4H, 2 2-H, 2 6-H) ppm; ¹³C NMR (125.76 MHz, DMSO-d₆, 25 °C) δ 28.6 (2 CH₂CH₂N), 35.7 (2 CH₂NH₃), 58.0 (2 CH₂N), 126.6 (2 3-C, 2 5-C), 145.9 (2 2-C, 2 6-C), 148.8 (2 4-C) ppm; IR (Nujol) 3253, 3177 (N⁺-H) cm⁻¹. Anal. Calcd. for C₁₆H₂₆Cl₄N₄O₁₆•0.5H₂O: C 28.21, H 4.00, N 8.23. Found: C 28.25, H 3.96, N 8.18.

2,7-Bis(2-ammonioethyl)benzo[Imn][3,8]phenanthrolinediium Tetraperchlorate (**4b**). A yellow powder (0.22 g, 32% yield): mp 335–338 °C (decomp.); ¹H NMR (500.13 MHz, MeCN- d_3 , 30 °C) δ 3.91 (t, *J* = 6.2 Hz, 4H, 2 CH₂NH₃), 5.41 (t, *J* = 6.2 Hz, 4H, 2 CH₂N), 8.95 (s, 4H, 4-H, 5-H, 9-H, 10-H), 9.98 (s, 4H, 1-H, 3-H, 6-H, 8-H) pm; ¹³C NMR (125.76 MHz, DMSO- d_6 , 25 °C) δ 39.4 (2 CH₂NH₃), 60.0 (2 CH₂N), 126.0 (10b-C, 10c-C), 128.8 (3a-C, 5a-C, 8a-C, 10a-C), 130.1 (4-C, 5-C, 9-C, 10-C), 142.8 (1-C, 3-C, 6-C, 8-C) ppm; IR (Nujol) 3172 (N⁺-H) cm⁻¹. Anal. Calcd. for C₁₈H₂₂Cl₄N₄O₁₆: C 31.23, H 3.20, N 8.09. Found: C 31.17, H 3.21, N 8.11.

2,7-Bis(3-ammoniopropyl)benzo[lmn][3,8]phenanthrolinediium Tetraperchlorate (**4c**). A yellow powder (0.42 g, 58% yield): mp >340 °C (decomp.); ¹H NMR (500.13 MHz, MeCN- d_3 , 30 °C) δ 2.66 (m, 4H, 2 CH₂CH₂N), 3.25 (br.m, 4H, 2 CH₂NH₃), 5.19 (t, *J* = 7.6 Hz, 4H, 2 CH₂N), 8.91 (s, 4H, 4-H, 5-H, 9-H, 10-H), 9.96 (s, 4H, 1-H, 3-H, 6-H, 8-H) ppm; ¹³C NMR (125.76 MHz, DMSO- d_6 , 25 °C) δ 28.9 (2 CH₂CH₂N), 35.8 (2 CH₂NH₃), 60.0 (2 CH₂N), 126.0 (10b-C, 10c-C), 128.9 (3a-C, 5a-C, 8a-C, 10a-C), 129.9 (4-C, 5-C, 9-C, 10-C), 142.0 (1-C, 3-C, 6-C, 8-C) ppm; IR (Nujol) 3192 (N⁺-H) cm⁻¹. Anal. Calcd. for C₂₀H₂₆Cl₄N₄O₁₆: C 33.35, H 3.64, N 7.78. Found: C 33.39, H 3.58, N 7.74.

Synthesis of D·A Complexes between Stilbene 1 and Diammonium Compounds 3(4)b,c (General Method). Stilbene (*E*)-1 (13 mg, 20 μ mol) and a diammonium compound 3(4)b,c (20 μ mol) were dissolved in MeCN (5 mL). The solution was slowly saturated with a mixture of benzene and dioxane (~2:1, v/v) by a vapor diffusion method at ambient temperature until complete precipitation was attained (visual monitoring, 1–2 weeks). The crystalline precipitate was decanted and recrystallized in the same conditions to give supramolecular D·A complex as a fine-grained powder (amorphous powder in the case of [1·3b]). The complex stoichiometry was confirmed by ¹H NMR (in MeCN-d₃ and DMSO-d₆) and elemental analysis data.

Complex [**1**•**3b**] (First Modification). Blue-black crystals (22.3 mg, 85% yield): mp 272–279 °C (decomp.); ¹H NMR (500.13 MHz, MeCN- d_3 , 25 °C) δ 3.47 (br.s, 4H, 2 CH₂NH₃), 3.74–3.80 (m, 12H, 6 CH₂O), 3.80–3.86 (m, 12H, 6 CH₂O), 3.91 (br.m, 4H, 2 3'-CH₂CH₂OAr), 3.98 (br. m, 4H, 2 4'-CH₂CAr₂OAr), 4.12 (br.m, 4H, 2 3'-CH₂OAr), 4.36 (br.m, 4H, 2 4'-CH₂OAr), 4.62 (t, *J* = 6.5 Hz, 4H, 2 CH₂N), 6.93 (s, 2H, CH=CH), 6.95 (br.s, 2H, 2 2'-H), 7.13 (d, *J* = 8.3 Hz, 2H, 2 5'-H), 7.23 (br.d, *J* = 8.3 Hz, 2H, 2 6'-H), 7.68 (br.s, 6H, 2 NH₃), 8.25 (d, *J* = 6.3 Hz, 4H, 2 3-H, 2 5-H), 8.37 (br.s, 4H, 2 2-H, 2 6-H) ppm; IR (Nujol) 3165 (N⁺-H) cm⁻¹. Anal. Calcd. for C₃₄H₄₈O₁₂·C₁₄H₂₂Cl₄N₄O₁₆·H₂O: C 43.98, H 5.54, N 4.27. Found: C 43.87, H 5.45, N 4.07.

Complex **[1·3b]** (Second Modification). Obtained by recrystallization of the first modification $[1\cdot 3b]$, a light beige powder (20.2 mg, 92% yield): mp 267–268 °C (decomp.); ¹H NMR (500.13 MHz, MeCN- d_3 , 25 °C) δ 3.44 (t, J = 6.4 Hz, 4H, 2 CH₂NH₃), 3.73–3.80 (m, 12H, 6 CH₂O), 3.80–3.87 (m, 12H, 6 CH₂O), 3.91 (m, 4H, 2 3'-CH₂CH₂OAr), 3.98 (m, 4H, 2 4'-CH₂CH₂OAr), 4.11 (m, 4H, 2 3'-CH₂OAr), 4.36 (m, 4H, 2 4'-CH₂OAr), 4.63 (t, J = 6.4 Hz, 4H, 2 CH₂N), 6.94 (br.s, 4H, CH=CH, 2 2'-H), 7.13 (d, J = 8.0 Hz, 2H, 2 5'-H), 7.25 (br.d, J = 8.0 Hz, 2H, 2 6'-H), 7.66 (br.s, 6H, 2 NH₃), 8.24 (br.s, 4H, 2 3-H, 2 5-H), 8.34 (br.s, 4H, 2 2-H, 2 6-H) ppm; IR (Nujol) 3156 (N⁺-H) cm⁻¹. Anal. Calcd. for C₃₄H₄₈O₁₂·C₁₄H₂₂Cl₄N₄O₁₆: C 44.59, H 5.46, N 4.33. Found: C 44.60, H 5.45, N 4.41.

Complex [**1·3c**]. Brown crystals (24.3 mg, 91% yield): mp 200–205 °C; ¹H NMR (500.13 MHz, MeCN- d_3 , 25 °C) δ 1.75 (br.s, 4H, 2 CH₂CH₂N), 2.95 (br.s, 4H, 2 CH₂NH₃), 3.66–3.86 (m, 24H, 12 CH₂O), 3.94 (br.s, 8H, 4 CH₂CH₂OAr), 4.16 (br.s, 4H, 2 3'-CH₂OAr), 4.34 (br.s, 4H, 2 4'-CH₂OAr), 4.47 (t, *J* = 7.8 Hz, 4H, 2 CH₂N), 6.84 (br. s, 2H, CH=CH), 6.90 (br.s, 2H, 2 2'-H), 7.08 (br.m, 2H, 2 5'-H), 7.15 (br.s, 2H, 2 6'-H), 7.51 (br.s, 6H, 2 NH₃), 8.27 (d, *J* = 6.5 Hz, 4H, 2 3-H, 2 5-H), 8.46 (d, *J* = 6.5 Hz, 4H, 2 2-H, 2 6-H) ppm; IR (Nujol) 3178 (N⁺-H) cm⁻¹. Anal. Calcd. for C₃₄H₄₈O₁₂ · C₁₆H₂₆Cl₄N₄O₁₆ · H₂O: C 44.85, H 5.72, N 4.18. Found: C 44.84, H 5.82, N 4.18.

Complex [**1**•**4b**]. Blue-black crystals (21.4 mg, 80% yield): mp >300 °C (decomp.); ¹H NMR (500.13 MHz, MeCN- d_{33} , 50 °C) δ 3.80−3.94 (m, 36H, 2 CH₂NH₃, 16 CH₂O), 4.03 (br.m, 4H, 2 3'-CH₂OAr), 4.38 (br.s, 4H, 2 4'-CH₂OAr), 5.15 (br.t, *J* = 6.0 Hz, 4H, 2 CH₂N), 6.21 (s, 2H, CH=CH), 6.29 (br.s, 2H, 2 2'-H), 6.98 (br.s, 2H, 2 6'-H), 7.03 (br.s, 2H, 2 5'-H), 7.78 (br.s, 6H, 2 NH₃), 8.69 (s, 4H, 4-H, 5-H, 9-H, 10-H), 9.54 (br. s, 4H, 1-H, 3-H, 6-H, 8-H) ppm; IR (Nujol) 3177 (N⁺−H) cm⁻¹. Anal. Calcd. for C₃₄H₄₈O₁₂·C₁₈H₂₂Cl₄N₄O₁₆: C 46.58, H 5.26, N 4.18. Found: C 46.36, H 5.26, N 4.17.

Complex [**1**•**4***c*]. Blue-black crystals (23.0 mg, 84% yield): mp >300 °C (decomp.); ¹H NMR (500.13 MHz, MeCN-*d*₃, 25 °C) δ 2.01 (br.s, 4H, 2 CH₂CH₂N), 3.13 (br.m, 4H, 2 CH₂NH₃), 3.73–3.94 (m, 28H, 14 CH₂O), 3.98 (br.s, 8H, 2 4'-CH₂CH₂OAr, 2 3'-CH₂OAr), 4.40 (br.s, 4H, 2 4'-CH₂OAr), 4.91 (t, *J* = 7.5 Hz, 4H, 2 CH₂N), 5.84 (br. s, 2H, CH=CH), 6.35 (s, 2H, 2 2'-H), 6.62 (br.s, 2H, 2 6'-H), 7.07 (br.s, 2H, 2 5'-H), 7.58 (br.s, 6H, 2 NH₃), 8.78 (s, 4H, 4-H, 5-H, 9-H, 10-H), 9.54 (br.s, 4H, 1-H, 3-H, 6-H, 8-H) ppm; IR (Nujol) 3175 (N⁺-H) cm⁻¹. Anal. Calcd. for C₃₄H₄₈O₁₂·C₂₀H₂₆Cl₄N₄O₁₆: C 47.38, H 5.45, N 4.09. Found: C 47.29, H 5.57, N 4.05.

Spectrophotometry. The CT absorption spectra of pure $\mathbf{D} \cdot \mathbf{A}$ and $\mathbf{D} \cdot \mathbf{A} \cdot \mathbf{D}$ complexes in MeCN (extra pure grade, water content <0.03%), as well as the complex formation constants K_1 and K_2 , were derived from global analysis of spectrophotometric titration data, as described previously for the 1/2c system.^{6b} Spectrophotometric titrations were conducted in 1 or 5 cm quartz cells with ground-in stoppers. All manipulations with solutions were performed in a darkroom under red light because bis(crown)stilbene 1 underwent photoisomerization under daylight.

A competitive titration method was applied to assess the formation constants K_1 for the $\mathbf{D} \cdot \mathbf{A}$ complexes. The competing reactants were 1,8-diammoniooctane diperchlorate¹⁸ (with 3b and 4b) and 1,10-diammoniodecane diperchlorate¹⁹ (with 3c and 4c). The complex formation constants for the diammonioalkane salts with 1 in MeCN are known from ref 6b. The concentration of the competing reactant was maintained at 1×10^{-3} M. With 3b,c, the concentrations of 1 were maintained at 4×10^{-5} M, and the concentration of 3b,c was varied from 0 to 4×10^{-4} M. With 4b,c, the concentration of 1 was varied from 0 to 4×10^{-4} M, and the concentration of 4b,c was maintained at 4×10^{-5} M. The competitive titration data are shown in Figures S29–S32 (Supporting Information).

The formation constants K_2 for the **D** · **A** · **D** complexes were derived from direct titration experiments: the concentration of acceptor was maintained at 5×10^{-4} M (**3b**,**c**) or at 2×10^{-4} M (**4b**,**c**), and the concentration of **1** was varied from 0 to 0.05 M. The direct titration data are shown in Figures S33–S36 (Supporting Information).

Fluorescence Studies. Experiments were conducted in MeCN at ambient temperature in 1 cm quartz cells; the atmospheric oxygen contained in solutions was not removed. Fluorescence spectra were corrected, taking into account the spectral sensitivity of the photomultiplier tube. The fluorescence quantum yield of 4c in MeCN (excitation at 340 nm) was determined using anthracene in ethanol as the standard.²⁰ Fluorometric titrations of $[1\cdot4c]$ with metal perchlorates were performed using a stock solution of complex $[1\cdot4c]$, as prepared by dissolving a crystalline sample.

Cyclic Voltammetry. Cyclic voltammetry experiments were carried out using a three-electrode system. A glassy carbon disk (d = 1.8 mm) was used as the working electrode. The reference electrode was Ag|AgCl|KCl (aq., sat.). A platinum plate ($S = 0.5 \text{ cm}^2$) served as the auxiliary electrode. Cyclic voltammograms were measured in MeCN solutions in the presence of Bu₄NClO₄ (0.1 M) at 22 °C. All solutions were deaerated by argon purging. The potential scanning rate was 200 mV/s. Ferrocene (1 mM) was used as the internal reference. The concentrations of reactants were 1 mM.

¹**H NMR Titration.** Experiments were conducted in MeCN- d_3 (water content <0.05%) at 25 ± 1 °C. The formation constants K_1

for the $[1\cdot3(4)a]$ complexes and K_2 for the $[1\cdot3(4)b,c\cdot1]$ complexes were derived from direct titration experiments; the concentration of acceptor (C_A) was maintained at 1×10^{-3} M and the concentration of 1 (C_D) was varied from 0 to $(6-20) \times 10^{-3}$ M (3b,c, 4b,c) or to 0.04 M (3a, 4a). For systems 1/2(3,4)b,c, the dependencies of $\Delta\delta_H$ on C_D/C_A measured at $C_D > C_A$ were described well by the simplified complexation model taking into account only eq 2, which allowed us to assess the formation constants K_2 for termolecular complexes $[1\cdot3(4)b,c\cdot1]$. The use of this model is justified by the fact that when $C_D > C_A$, the partial concentrations of uncomplexed acceptors 3(4)b,c are negligibly low due to very high values of the formation constants K_1 for the bimolecular complexes $[1\cdot3(4)b,c]$.

Competitive ¹H NMR titration was applied to measure the formation constants K_1 for the $[1 \cdot 2(3,4)b,c]$ complexes. The concentrations of 2(3,4)b,c and 1 were maintained at 1×10^{-3} and 1.2×10^{-3} M, respectively, and the concentration of the competing reagent, 1,10-diammoniodecane diperchlorate, was varied from 0 to $(1.0-1.3) \times 10^{-2}$ M.

The complex formation constants were calculated using the HYPNMR program. $^{\rm 21}$

X-ray Crystal Structure Determinations, Crystal Data. *Data for* $3c \cdot 2H_2O$. C₁₆H₃₀Cl₄N₄O₁₈, monoclinic, $P2_1/n$, a = 12.3277(5), b = 8.9364(4), c = 13.1357(6) Å, $\beta = 104.0710(10)^\circ$, V = 1403.68(11) Å³, Z = 2, $\mu = 0.510$ mm⁻¹, $F_{000} = 732$. T = 120.0(2) K, θ range 2.03–29.00°. Index ranges *h*, *k*, *l* (indep set): -16 to 16, -12 to 11, -17 to 17. Reflections measd: 14828, indep: 3736 [$R_{int} = 0.0162$], obsvd [$I > 2\sigma(I)$]: 3385. Final *R* indices [$I > 2\sigma(I)$]: $R_1 = 0.0305$, $wR_2 = 0.0849$, GOF = 1.079.

Data for **4a**. $C_{18}H_{18}Cl_2N_2O_{8}$, monoclinic, $P2_1/c$, a = 5.8449(13), b = 13.893(3), c = 11.655(3) Å, $\beta = 94.210(4)^\circ$, V = 943.8(4) Å³, Z = 2, $\mu = 0.397$ mm⁻¹, $F_{000} = 476$. T = 170(2) K, θ range 2.28–29.00°. Index ranges *h*, *k*, *l* (indep set): -7 to 7, -18 to 18, -15 to 15. Reflections measd: 7651, indep: 2441 [$R_{int} = 0.0429$], obsvd [$I > 2\sigma(I)$]: 1766. Final *R* indices [$I > 2\sigma(I)$]: $R_1 = 0.0575$, $wR_2 = 0.1813$, GOF = 1.097.

Data for $[\mathbf{1} \cdot \mathbf{3b}] \cdot C_4 H_8 O_2 \cdot 3H_2 O$. $C_{52} H_{84} Cl_4 N_4 O_{33}$, triclinic, $P\overline{I}$, a = 8.7194(7), b = 11.7380(10), c = 17.3124(15) Å, $\alpha = 79.194(4)$, $\beta = 80.249(3)$, $\gamma = 77.874(3)^\circ$, V = 1686.0(2) Å³, Z = 1, $\mu = 0.268$ mm⁻¹, $F_{000} = 756$. T = 120.0(2) K, θ range 2.41–25.00°. Index ranges *h*, *k*, *l* (indep set): -10 to 10, -13 to 8, -19 to 20. Reflections measd: 7340, indep: 5564 [$R_{int} = 0.0457$], obsvd [$I > 2\sigma(I)$]: 3170. Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.1138$, $wR_2 = 0.2706$, GOF = 1.026.

Data for $[1.3c] \cdot 0.25MeCN \cdot 0.44H_2O$. $C_{50.5}H_{75.63}Cl_4N_{4.25}O_{28.44}$, monoclinic, $P2_1/n$, a = 20.790(3), b = 27.460(4), c = 21.875(3) Å, $\beta = 90.096(4)^\circ$, V = 12488(3) Å³, Z = 8, $\mu = 0.279$ mm⁻¹, $F_{000} = 5631$. T = 120.0(2) K, θ range $0.74 - 27.54^\circ$. Index ranges h, k, l (indep set): -27 to 27, -35 to 35, -28 to 18. Reflections measd: 87572, indep: 28695 [$R_{int} = 0.0798$], obsvd [$I > 2\sigma(I)$]: 14199. Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0715$, $wR_2 = 0.1694$, GOF = 0.875.

The single crystals of all compounds were coated with perfluorinated oil and mounted on a diffractometer [graphite monochromatized Mo-K_{α} radiation (λ = 0.71073 Å), ω scan mode] under a stream of cold nitrogen. The sets of experimental reflections were measured and the structures were solved by direct methods and refined by full matrix least-squares methods against F^2 with anisotropic thermal parameters for all non-hydrogen atoms (except for atoms of the strongly disordered anion Cl(2)O₄⁻ and solvation dioxane and water molecules in structure $[1 \cdot 3b] \cdot C_4 H_8 O_2 \cdot 3H_2 O_1$, which were refined isotropically). In some cases, absorption correction was applied using the SADABS method. The hydrogen atoms were fixed at calculated positions at carbon atoms and then refined with the isotropic approximation for $3c \cdot 2H_2O$ and 4aor by using a riding model for the other structures. The hydrogen atoms of NH3⁺ groups were calculated geometrically and then refined isotropically (with mild restraints for N-H bond distances). The hydrogen atoms of the solvation water molecule in structure $3c \cdot 2H_2O$ were located from the difference Fourier map and refined isotropically. In

other structures, hydrogen atoms of the solvation water molecules were not located. All the calculations were performed using the SHELXTL-Plus software.²²

CCDC 831395 ($3c \cdot 2H_2O$), 831396 (4a), 831394 ($[1 \cdot 3c] \cdot 0.25MeCN \cdot 0.44H_2O$), and 831393 ($[1 \cdot 3b] \cdot C_4H_8O_2 \cdot 3H_2O$) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Quantum-Chemical Calculations. Geometries of the acceptor molecules 2-4 in MeCN were calculated by RI-DFT method using the PBE functional²³ and the def2-TZVP(-f) basis set.²⁴ The geometries were fully optimized using the ORCA program.²⁵ The solvent was simulated using the COSMO method as implemented in ORCA.²⁶

ASSOCIATED CONTENT

Supporting Information. ¹H and ¹³C NMR, HSQC, NOESY spectra, absorption and fluorescence spectra, cyclic voltammograms, X-ray crystallographic data, and molecular modeling details. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

Financial support from the Russian Foundation for Basic Research, the Russian Academy of Sciences, and the Royal Society of Chemistry is gratefully acknowledged.

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