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# Structure of Charge-Transfer Complexes Formed by Biscrown Stilbene and Dipyridylethylene Derivatives As Probed by Surface-Enhanced Raman Scattering Spectroscopy

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Charge-transfer (CT) complexes between bis(18-crown-6) stilbene (**1**) and bisammonium derivative of dipyridylethylene (**2**) were studied by surface-enhanced Raman scattering spectroscopy. It was revealed that a molar excess of **2** favored the 1:1 CT complex ([**1·2**]) formation, whereas an excess of **1** stabilized the sandwichlike [**1·2·1**] CT complex. The considerably less stable 1:1 CT complex was also detected for **1** and 1-ammoniopropyl-4-methylpyridine. On the basis of the spectral analysis, the following was concluded: in the ground state these CT complexes can be considered as usual molecular complexes, the shift of electronic density from the donor to the acceptor occurred upon interaction of the molecular complex with a photon, and a large shift of the electronic density from donor to acceptor was a property of the excited state. Using model compounds, it was shown that interactions of the ammonium groups with the crown ether moieties played a critical role in the CT complex formation by stabilizing the molecular complex. Concerning the [**1·2·1**] complex, it was concluded that each ammonium group was coordinated with a single but not with both adjacent crown ether cycles. The mere interaction between the $\pi$-electronic systems of stilbene and dipyridylethylene was not sufficient to form a tight complex required for CT. The ethylene group was not essential for CT, and the donor−acceptor pair was produced solely by the trisubstituted benzene and pyridine rings. Both [**1·2**] and [**1·2·1**] contained two equivalent donor−acceptor pairs, but a pair alone was supposed to participate in CT.

## 1. Introduction

Intermolecular charge transfer (CT) is a remarkable physical phenomenon, which is detected as the appearance of a new absorption band, when some molecules form a very tight complex and work as an electron donor and an electron acceptor within this complex.[1] Structural features of such complexes and CT mechanisms are a subject of detailed investigation, since many intriguing and vitally important chemical, biological, and physical processes occur because of the CT complex formation.[1,2] Accordingly, the advanced molecular systems being able to form the CT complexes are under development as prospective molecular devices, that is, organic conductors and photoconductors, and as second-order nonlinear optical materials.[3] Recently,[4] the highly specific interaction between the organic cation and the crown ether ring was employed to assemble the CT complex between biscrown stilbene (**1**) and bisammonium derivative of dipyridylethylene (**2**, Figure 1). The very high thermodynamic stability of this complex was revealed with spectrophotometric titration.[5] The CT complex has the strong absorption band at ca. 500 nm and works as the optical sensor for metal cations. Concurrent binding of the metal cations with the crown ether moieties induces dissociation of the CT complex and decoloration of solution.[4] The CT complexes of 1:1 and 2:1 composition, [**1·2**] and [**1·2·1**], were discriminated with the absorption spectroscopy. It was supposed that [**1·2·1**] had a sandwich-type layered structure with the acceptor **2** bound between two molecules of the donor **1** (Figure 2).

In the present work, investigation of these CT complexes was continued with the surface-enhanced Raman scattering (SERS) spectroscopy. Using vibrational resolution, it was attempted to clarify the mechanism of CT and structural features of the complexes between **1** and **2**. The formation of the [**1·2**] and [**1·2·1**] CT complexes was confirmed. A role of the ground and excited states in CT was estimated. Using model compounds **3**−**5** (Figure 1), the structural requirements for the CT complex formation were characterized. The CT complex between **1** and **5** was detected.

## 2. Experimental Section

The compounds 18-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclo-o ctadecin-18-yl)-1-ethenyl]-2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzo hexaoxacyclo- octadecine or bis(18-crown-6)stilbene (**1**), 1-(3-ammoniopropyl)-4-{(*E*)-2-[1-(3-ammoniopropyl)-4-pyridiniumyl]-1-ethenyl} pyridinium tetraperchlorate (**2**), 4-[(*E*)-2-(3,4-dimethoxyphenyl)-1-ethenyl]-1,2-dimethoxybenzene or 3,4,3′4′-tetramethoxystilbene (**3**) and 1-ethyl-4-[(*E*)-2-(1-ethyl-4-pyridiniumyl)-1-ethenyl]-pyridinium diperchlorate (**4**) were synthesized as described

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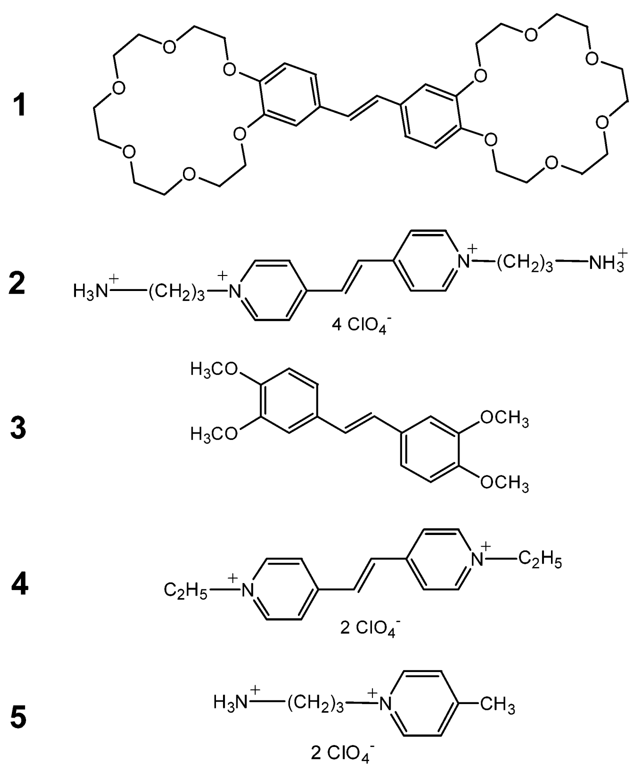

**Figure 1.** Structures of the studied compounds.

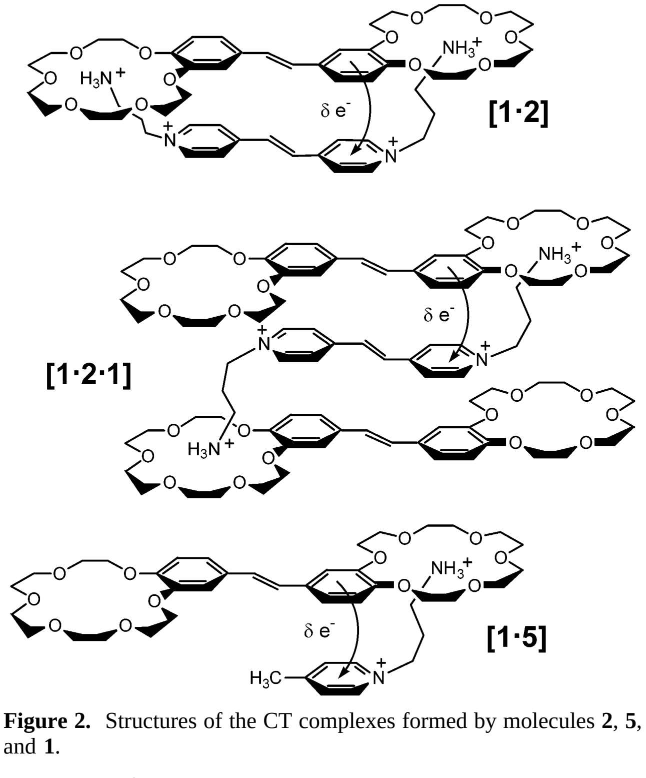

**Figure 2.** Structures of the CT complexes formed by molecules **2**, **5**, and **1**.

previously.[4,6] The synthesis of 1-(3-ammoniopropyl)-4-methylpyridinium diperchlorate (**5**) will be published elsewhere.

SERS and Raman spectra were excited with an $Ar^+$ laser (Spectra-Physics, Model 164-03, 514.5 nm) at a power of 50 mW and 150 mW, respectively, and recorded with a single-channel Ramanor HG-2S spectrometer (Jobin Yvon, France). Panoramic SERS spectra were recorded without accumulation in the 200−1800 $cm^{-1}$ range at 1 $cm^{-1}$ increment with an integration time of 1 s. The 900−1800 $cm^{-1}$ spectral region was recorded during the titration. Three to five scans were averaged when Raman spectra were accumulated. SERS spectra were obtained for the molecules adsorbed on an electrochemically roughened silver electrode, which was prepared as follows. The electrode surface was polished mechanically till a mirrorlike state. After this, the electrode was washed with ethanol and triply distilled water, boiled in 0.1 M NaOH for 3 min, rinsed several times with triply distilled water, and placed as a work electrode in a standard electrochemical cell filled with the 0.3 M KCl aqueous electrolyte solution. The second silver electrode and the platinum electrode were used as reference and auxiliary electrodes, respectively. An oxidation−reduction cycle was performed with a potentiostat-galvanostat IPC-4 (Institute of Physical Chemistry, Moscow, Russia) following the procedure optimized for a maximal enhancement of Raman signal: the electrode was maintained at the potential of −650 mV for 5 min, at 0 V for 60 s, at +250 mV for 15 s, at 0 V for 15 s, and finally at −650 mV for 60 s. Roughened in this way the electrode was washed with triply distilled water, dried, and washed again with acetonitrile to remove electrolyte and water traces. For SERS measurements, the roughened electrode was immersed in the cell with the analyte solution. SERS spectra were recorded at an undefined electrode potential. All experiments were performed in the acetonitrile solution at a room temperature. Acetonitrile (HPLC grade) was doubly distilled from $P_2O_5$ and $CaH_2$ to remove water traces.

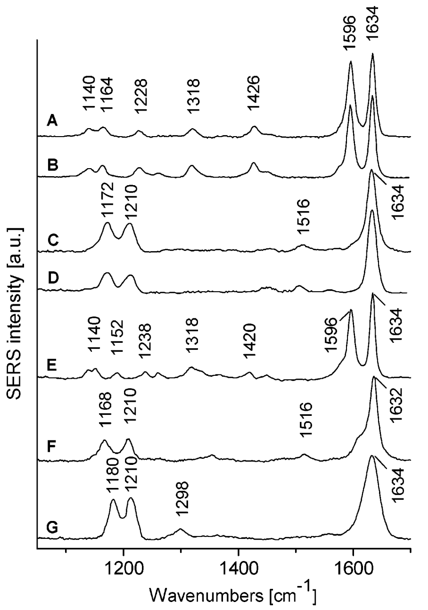

**Figure 3.** SERS (**A**, **C**, **F**, **G**) and Raman (**B**, **D**) spectra of compounds **1** (**A**, **B**), **2** (**C**, **D**), **3** (**E**), **4** (**F**), and **5** (**G**) in acetonitrile. Spectra were normalized to the maximum. Contribution of solvent was subtracted.

## 3. Results

**3.1. SERS and Raman Spectra of the Studied Compounds.** The SERS spectra of **1**−**5** and the Raman spectra of **1** and **2** in acetonitrile are shown in Figure 3. A detection limit of SERS spectrum recording was ca. 0.5 mM that was typical of the SERS spectroscopy of noncolored species in the arrangement, when the signal was collected from the point area (ca. 50 $\mu$m in diameter) of the silver electrode. The roughened silver electrode, which was used as a SERS-active substrate, quenched the fluorescence and provided the tremendous enhancement of the Raman signal for adsorbed molecules. The conventional Raman spectra were recorded at the concentration (1 mM) being close to the solubility limit for **1** and **2.** The low signal-to-noise ratio in the Raman spectra was considerably improved because of

**TABLE 1: SERS and Raman Frequencies ($cm^{-1}$) and Assignments for Compounds 1−5**

| 1 | | 3 | assignments[a] | 2 | | 4 | 5 | assignments[b] |
|---|---|---|---|---|---|---|---|---|
| SERS | Raman | | | SERS | Raman | | | |
| 1140 w | 1140 w | 1140 w[c] | 13[d] (a′)[e] ring str + def[f] | | | | | |
| 1164 w | 1164 w | 1152 w | 18a (a′) in-plane CH def | | | | | |
| | | | | 1172 s | 1172 s | 1168 s | 1180 s | 18b ($b_2$) in-plane CH def |
| | | | | 1210 s | 1212 s | 1210 s | 1210 s | 9a ($a_1$) in-plane CH def |
| 1228 w | 1228 w | 1238 w | 7a (a′) CH str | | | | | |
| | | | | | | | 1298 w | 3 ($b_2$) in-plane C-H def |
| 1318 w | 1318 w | 1318 w | | | | | | |
| 1426 w | 1426 w | 1420 w | 19a (a′) ring str + def | | | | | |
| | | | | 1516 w | 1514 w | 1516 w | | 19b ($b_2$) ring str |
| 1596 vs | 1596 vs | 1596 vs | 8a (a′)ring str | | | | | |
| 1634 vs | 1634 vs | 1634 vs | 8b (a′) ring str | 1634 vs | 1634 vs | 1632 vs | 1634 vs | 8a ($a_1$) ring str |

[a] Assignments were made from the Raman spectra and normal-mode analysis of 3-(3′,4′-dimethoxyphenyl)propanoic acid,3′,4′-dimethoxyphenethylamine and 3′,4′-dimethoxyacetophenone.[8] [b] Assignments were made from the Raman spectra and normal-mode analysis of $C_5H_5NH^+X^-$ (X = Cl, Br, I) and 1-methylpyridine-hydrochloride.[7] [c] Relative intensity of bands: w, weak; s, strong; vs, very strong. [d] Wilson notation of vibrational modes of benzene. [e] Symmetry group. [f] Approximate description of vibration: def, deformation; str, stretch.

high power of laser excitation, double pass of the laser beam through the 3 mm quartz cell, and multiple scans. A close similarity between the SERS and corresponding Raman spectra proves that adsorption at the silver surface does not disturb the vibronic state of the studied molecules as compared with a bulk phase.

Both SERS and Raman spectra of the studied molecules are characterized by a rather penurious set of bands. No bands are enhanced in the low-frequency region (150−1100 $cm^{-1}$). A set of weak and medium intensity bands is observed in the 1100−1500 $cm^{-1}$ region, and one or two most strong bands are present in the 1580−1640 $cm^{-1}$ region. The simple comparison of the spectra allows their classification in two distinct groups. The first group unites analogous spectra of the pyridine and dipyridyl derivatives **2**, **4**, and **5** that have a strong band in the 1580−1640 $cm^{-1}$ region and two medium-intensity bands in the 1150−1220 $cm^{-1}$ region. The second group contains similar spectra of the stilbene derivatives **1** and **3**, which are characterized by two strong bands in the 1580−1640 $cm^{-1}$ region.

Since the SERS spectra of **2**, **4**, and **5** are similar in appearance (Figure 3) despite the different substituents in positions 1 and 4 of the pyridine ring (Figure 1), the vibrations enhanced are directly related to the pyridine ring but not to the substituents. Confirming this conclusion, the SERS spectra of **2**, **4**, and **5** have the characteristic features common with the conventional Raman spectra of substituted pyridinium ions. Thus, $C_5H_5NH^+X^-$ (X = Cl, Br, I) in solid state and 1-methylpyridyl in aqueous solution have the very strong Raman band at 1630−1640 and 1637 $cm^{-1}$, respectively.[7] This band corresponds unambiguously to the 1634 $cm^{-1}$ band in the spectra of **2**, **4**, and **5** (Table 1). The medium-intensity bands in the 1150−1220 $cm^{-1}$ region also can be assigned to the vibrations of the pyridine ring (Table 1). The intensity of other Raman bands of pyridine derivatives is low as in the case of **2**, **4,** and **5**. The only difference is the band at ca. 1030 $cm^{-1}$, the symmetric ring breathing mode ($\nu_1$, the $a_1$ symmetry group), which is strong in the Raman spectra of some pyridine derivatives[7] but is missing from the SERS spectra of **2**, **4**, and **5** and the Raman spectrum of **2**. The C═C stretching vibration of the alkene group does not contribute to either the SERS spectra of **2** and **4** or the Raman spectrum of **2**, since no additional band is observed in the 1640−1680 $cm^{-1}$ region as compared with the spectrum of **5**, the compound without alkene group. The 1640−1680 $cm^{-1}$ region is characteristic for the C═C stretching vibrations of the cis and trans disubstituted ethylenes.[7]

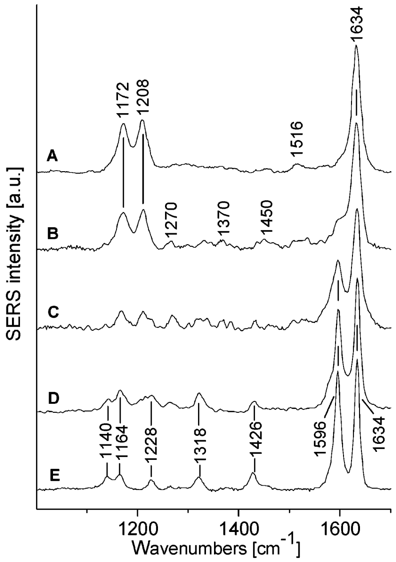

**Figure 4.** SERRS spectra of the CT complexes between **1** and **2** in acetonitrile at the **1**/**2** molar ratios of 1 (B), 2 (C), and 5 (D). Concentration of **2** in the mixtures was 50 μM. SERS spectra of free **2** (A) and **1** (E) at 1 mM concentration are shown for comparison. Spectra were normalized to the maximum. Contribution of solvent was subtracted.

The SERS spectra of **1** and **3** as well as the Raman spectrum of **1** contain two strong bands in the 1590−1650 $cm^{-1}$ region (Figure 3, Table 1), that are typical of many of the substituted benzenes, in particular, 1-substituted 3,4-dimethoxybenzenes.[8] The weak bands in the 1100−1500 $cm^{-1}$ region seem to be also related to the benzene modes and can be assigned using the results of the normal-mode analysis for 1-substituted 3,4-dimethoxybenzenes (Table 1). As in the case of **2** and **4**, the C═C stretching vibration of the alkene group is not observed in the spectra of **1** and **3**.

**3.2. SERS Study of CT Complex Formation.** Mixing **1** and **2** resulted in a considerable increase in SERS intensity and lowered the detection limit of spectra by 2 orders of magnitude as compared with that of the pure components. This fact indicates the formation of a complex between **1** and **2,** which absorbs light in the visible spectral region, that is, an intermolecular CT complex. Presence of the colored complexes enhanced additionally the SERS spectra (Figure 4, B-D) because of realization of surface-enhanced resonance Raman scattering (SERRS). Usually SERRS is several orders greater than SERS of noncolored molecules. This provides conditions for a selective detection of colored species even if they are present in small proportion as compared with noncolored molecules.

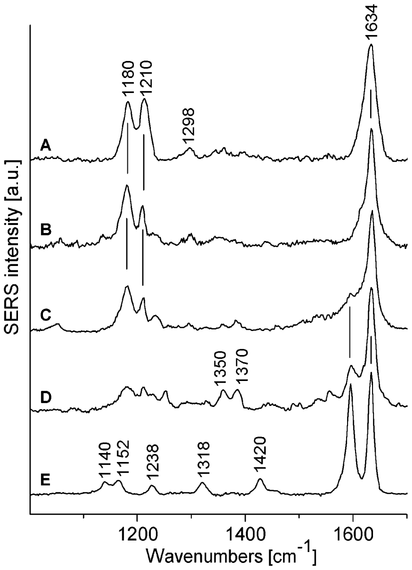

**Figure 5.** SERRS spectra of CT complexes between **1** and **5** in acetonitrile at the **1**/**5** molar ratios of 0.5 (B), 1 (C), and 2 (D). Concentration of **5** in the mixtures was 50 $\mu$M. SERS spectra of free **5** (A) and **1** (E) at 1 mM concentration are shown for comparison. Spectra were normalized to the maximum. Contribution of solvent was subtracted.

Varying widely a concentration of the components (0.01−1 mM), but keeping the molar excess of **2,** the SERRS spectrum of the CT complex between **1** and **2** was very similar to the spectrum of free **2** (Figure 4) except for extremely high intensity that changed proportionally to the concentration of the CT complex. The weak bands at 1270, 1370, and 1450 cm$^{-1}$ in the SERRS spectrum can be tentatively assigned to the in-plane C−H deformation ($\nu_3$, the $b_2$ symmetry group), ring stretching ($\nu_{14}$, the $b_2$ group), and ring stretching ($\nu_{19a}$, the $a_1$ group) modes of **2**, respectively. One can discern the unresolved traces of these bands in the SERS spectrum of **2**. An increase in a **1**/**2** molar ratio was accompanied by the gradual changes in the SERRS spectrum (Figure 4). The major changes included enhancement of the 1596 cm$^{-1}$ band and attenuation of the 1172 and 1208 cm$^{-1}$ bands. The SERRS spectrum of the **1**−**2** mixture at the molar ratio of 5 or higher became rather similar to the SERS spectrum of **1**. Spectral analysis revealed that at the excess of **1** the SERRS spectrum could be considered as a superposition of the signals from both components of the complex. Since a resonance character of the signal enhancement was preserved, a change of the CT complex structure was supposed. The increased contribution of the vibrational modes of **1** to the SERRS spectrum is consistent with the formation of a sandwichlike complex, [**1·2·1**], at the molar excess of **1** instead of the [**1·2**] complex dominating at the molar excess of **2**.

**3.3. Structural Features of the CT Complex Formation.** The compounds **3**−**5** were investigated in order to understand deeper the mechanism of CT and the structural features of the complexes. The alterations introduced in the structure of **3**−**5** as compared with **1** and **2** allowed a role of particular molecular moieties in the CT complex formation to be clarified.

It was impossible to detect any evidence of the CT complex formation between **2** and **3** or between **4** and **1**, whereas **1** and **5** formed a CT complex (Figure 5). The CT complex formation was again observed as resonance enhancement of SERS, but the enhancement factor was ca. 10-fold less than in the case of the complex between **1** and **2**. The SERRS spectrum of the CT complex between **1** and **5** at the molar excess of **5** was similar to the SERS spectrum of free **5** except for intensity (Figure 5A, B). An increase in the **1**/**5** molar ratio induced only moderate spectral changes, and they could not be interpreted as the alteration of the CT complex structure in favor of the [**1·5·1**] complex formation (Figure 5C, D). The origin of the changes is not clear. One may assume that the $CH_3$ antisymmetric and tertiary CH deformations of the methyl substituent give rise to the bands at 1370 and 1350 cm$^{-1}$, respectively, when the molar ratio increase induces tighter packing of adsorbed molecules and subsequent alteration in the orientation of the CT complex at the silver surface. At the same time, another interpretation cannot be excluded.

## 4. Discussion

The SERS spectroscopy study confirmed the formation of the CT complex between **1** and **2** found earlier by spectrophotometry.[4] The SERS spectroscopy data are in agreement with those of the absorption spectroscopy[5] concerning an existence of two types of the structurally different complexes, [**1·2**] and [**1·2·1**] (Figure 2). Both complexes are the CT complexes as follows from the resonance enhancement of SERS. Transition between two structures is controlled by the molar ratio of the components in solution. An excess of **2** promotes the [**1·2**] complex formation, whereas an excess of **1** stabilizes the [**1·2·1**] complex. Since the [**1·2**] complex dominates in an equimolar solution of **1** and **2** (Figure 4), its stability is higher than that of the [**1·2·1**] complex. Compounds **1** and **5** formed the 1:1 CT complex, which was considerably less stable than the [**1·2**] complex.

An analysis of the SERRS spectra of the CT complexes revealed two remarkable features: (i) the signals of **2** and **5** dominate in the [**1·2**] and [**1·5**] spectra, respectively, whereas the signal of **1** prevails in the [**1·2·1**] spectrum; (ii) the spectra of **2**, **5,** and **1** as constituents of the CT complexes are very similar to the SERS spectra of free compounds. Though a large contribution of **1** to the spectrum of the [**1·2·1**] complex looks reasonable because of its 2-fold molar excess over **2**, a reason of the negligible contribution of **1** to the [**1·2**] and [**1·5**] spectra is not evident. Considering a resonance character of the Raman signal of [**1·2**] ([**1·5**]) and following the resonance Raman theory,[9] one can suggest that a transient dipole moment, which predefines the relative intensities of the Raman bands, is localized on **2** (**5**). This can promote enhancement of the vibrational modes of **2** (**5**) solely. If so, enhancement of the modes of **1** should be interpreted as a considerable change in the transient dipole moment and its localization on going from [**1·2**] to [**1·2·1**].

Alternatively, the adsorption of [**1·2**] ([**1·5**]) on the SERS active surface via molecule **2** (**5**) can lead to selective enhancement of the vibrational modes of the molecule interacting directly with the surface. For example, selective enhancement of the benzo-15-crown-5 moiety modes was observed in the SERRS spectra of colored styryl dyes containing a benzo-15-crown-5 group and a benzothiazolium heteroaromatic residue with a sulfoalkyl or alkyl N-substituent.[10,11] This extreme selectivity was realized although a benzene $\pi$-electron system was only a part of the extended conjugated $\pi$-electron system responsible for a molecular electronic transition. These molecules adsorbed on the roughened silver electrode through the benzo-15-crown-5 moiety. Substitution of the benzo-15-crown-5 moiety with the benzo-18-crown-6 moiety changed the orientation of the molecule at the electrode and led to enhancement of the vibrational modes of other molecular groups, in particular, the benzothiazolium modes.[12] If the direct adsorption of **2** on the SERS-active surface accounts for the SERRS spectrum pattern of [**1·2**], then the direct adsorption of **1** and screening of **2** are responsible for enhancement of the vibrations of **1** in the spectrum of [**1·2·1**]. The last explanation is supposed to be more probable than the considerable change in the transient dipole moment.

Analysis of similarity between the SERS spectra of free compounds and the SERRS spectra of **1** and **2** as constituents of the CT complexes enables the features of CT to be clarified. Raman spectroscopy probes a vibronic structure of the ground state of molecules. A resonance Raman effect results in enhancement of Raman scattering because of the resonance of photons with the excited electronic state, but nevertheless, the spectrum reflects the ground-state structure. In this sense, the absence of changes in the spectra of **2** and **5** on going from the free state to the [**1·2**] and [**1·5**] CT complexes indicates that the ground-state vibronic structure of **2** (**5**) or, more exactly, the pyridinium moiety of **2** (**5**) is not altered in the complexes. As discussed below, the pyridinium moiety of **2** (**5**) is the acceptor center of the CT complex. An increase in electronic density should decrease a positive charge at the nitrogen atom of the pyridinium ring making its vibronic structure more similar to pyridine. Neutral pyridine derivatives are characterized by the $\nu_{8a}$ mode being 30−50 $cm^{-1}$ lower in frequency than the $\nu_{8a}$ vibration of the substituted pyridinium ions.[7] Thus, the $\nu_{8a}$ frequency of 4-methylpyridine varies in the SERS spectra from 1606 to 1612 $cm^{-1}$ depending on the electrode potential.[13] The unchanged frequency of the $\nu_{8a}$ mode in the [**1·2**] and [**1·5**] spectra demonstrates the lack of an electronic density shift from the donor, **1**, to the acceptor, **2** or **5**, in the ground state of the CT complex. Similarly, the nonperturbed vibrational spectrum of **1** in the [**1·2·1**] complex leads to the conclusion that the complex was not subjected to CT in the ground state. These experimental facts are in a strict accordance with the Mulliken's theory of CT complex[1] that describes ground (N) and excited (V) states of the CT complex between the donor (D) and the acceptor (A) with orthonormal wave functions $\Psi_N$ and $\Psi_V$:

$$\Psi_N = a\psi_0(D-A) + b\psi_1(D^+-A^-) \qquad (1)$$

$$\Psi_V = a^*\psi_1(D^+-A^-) - b^*\psi_0(D-A) \qquad (2)$$

Equations 1 and 2 state that the CT complex may be considered as a mixture of two structures: the nonbonding structure with the wave function $\psi_0(D-A)$, which means that intermolecular interactions occur without CT, and the CT structure with the wave function $\psi_1(D^{+-}A^-)$, which means that A accepted an electron density shifted from D. The SERRS data prove that a $\approx a^* \gg b \approx b^*$ in the case of the CT complexes studied here. It means that (i) in the ground state the [**1·2**], [**1·5**], and [**1·2·1**] complexes can be considered as usual molecular complexes; (ii) the shift of an electronic density from D to A occurs upon interaction of the molecular complex with a photon; and (iii) the profound shift of the electronic density from D to A is a property of the excited state.

Charge transfer was not observed for the **2**−**3** and **4**−**1** compositions. Therefore, the interaction just between the conjugated π-electron systems of stilbene and dipyridylethylene was not sufficient for association of the molecules, and the interactions between the ammonium groups of **2** and the crown ether moieties of **1** play a major role in stabilization of the molecular complex in the ground state. The formation of the CT complex between **1** and **5** confirms this conclusion. Besides, CT between **1** and **5** indicates that the ethylene group is not a key structural element for the realization of CT between **1** and **2**. One can conclude that the trisubstituted benzene ring of **1** is a donor center, whereas the neighboring pyridine ring of **2** or **5** is an acceptor center of the studied CT complexes. Binding of the ammonium group to the crown ether cycle seems to be not involved directly in CT.

Concerning the details of the [**1·2·1**] complex arrangement, a question arises if each ammonium group of **2** is bonded with the single crown ether cycle or with both adjacent cycles of **1**. The study of the **1**−**5** composition revealed that the formation of the [**1·5·1**] complex is hardly possible. Therefore, the ammonium group has poor ability to coordinate with two crown ether cycles simultaneously. Accordingly, the [**1·2·1**] complex is stabilized because of the interaction of one ammonium group with the crown ether cycle of the first **1** molecule and the interaction of another ammonium group with the crown ether cycle of the second **1** molecule (Figure 2). The model of one bonding center per a pair of molecules is consistent with a lower stability of the [**1·2·1**] complex in comparison with [**1·2**] having two bonding centers.

Each of the [**1·2**] and [**1·2·1**] complexes contains two preorganized equivalent donor−acceptor pairs formed by the trisubstituted benzene and pyridine rings. At the same time, only one pair is supposed to participate in CT upon the excitation with low intensity light. Currently, it is not clear if the second donor−acceptor pair can take part in a secondary charge transfer, when the complex stays in the excited state. Additional experiments with a pulsed excitation seem to be required to resolve this question.

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