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Formation of a supramolecular charge-transfer complex. Ultrafast excited state dynamics and quantum-chemical calculations

Valery V. Volchkov, ^(D)*^a Mikhail N. Khimich, ^(D)* Mikhail V. Rusalov, ^(D)* Fedor E. Gostev, ^b Ivan V. Shelaev, ^b Viktor A. Nadtochenko, ^(D)* Artem I. Vedernikov, ^c Sergey P. Gromov, ^{a,c} Alexandra Ya. Freidzon, ^(D)* Michael V. Alfimov^c and Mikhail Ya. Melnikov ^(D)*

The formation of a supramolecular complex of bis(18-crown-6)stilbene (1) and 4,4'-bipyridine with two ammoniopropyl *N*-substituents (3) and the substitution reaction between 1·3 and alkali and alkaline-earth metal perchlorates have been studied using absorption, steady-state fluorescence, and femtosecond transient absorption spectroscopy. The formation of $1 \cdot (M^{n+})_2$ complexes in acetonitrile was demonstrated. The weak long-wavelength charge-transfer absorption band of 1·3 completely vanishes upon complexation with metal cations because of disruption of the pseudocyclic structure. The spectroscopic and luminescence parameters, stability and substitution constants were calculated. The relaxation scheme of the 1·3 singlet state excited by a 25 fs laser pulse was proposed. It includes very fast vibrational relaxation and direct ($\tau_{CT-d} = 0.32$ ps) and back ($\tau_{CT-b} = 0.51$ ps) electron transfer resulting in complete fluorescence quenching. The quantum-chemistry calculations revealed the species taking part in the ET process and elucidated the mechanism of relaxation of the excited complex.

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Introduction

The first ultrafast spectroscopic investigation of electron photo-transfer in donor–acceptor complexes using transient absorption and fluorescence spectroscopy was carried out by the Mataga group for pyrene-pyromellitic dianhydride (PMDA) systems.¹ Later, various donor–acceptor systems connected by single covalent bonds $(D-A)^{2,3}$ or flexible carbohydrate chains $(D-b-A)^{4,5}$ have been studied. Initially, decreasing the exponential dependence (instead of the bell-shaped one) between the driving force $-\Delta G_{\rm IP}$ and charge recombination rate constants was shown for contact D–A complexes in acetonitrile.² It was found that variation of electronic coupling and the distance between

^aChemistry Department, M. V. Lomonosov Moscow State University, 1-3 Leninskie Gory, Moscow 119991, Russian Federation. Fax: +7 (495) 9328846;

Tel: +7 (495) 9391671; E-mail: volchkov_vv@mail.ru

^bN. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,

Fax: +7 (495) 9361255; Tel: +7 (495) 9350116

^dNational Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoye shosse 31, Moscow 115409, Russia the D and A units can influence the process of their separation and recombination. Usually charge separation in such systems correlates with solvent relaxation time, but sometimes it occurs more rapidly. In many cases the excited state relaxation kinetics are bi-exponential. Non-exponential kinetics can be observed when charge transfer is solvent controlled or accompanied by possible intramolecular conformational changes.⁶ When single bond deformation within the complex affects the averaged interchromophore D–A angle, spectral-kinetic parameters are considerably dependent upon viscosity.⁷ Numerous studies in this field are presented in an extensive review.⁸

However, the transient absorption studies of D-b-A complexes, wherein the donor is connected with the acceptor *via* several hydrogen bonds, are scarce. We continue the studies of the thermodynamic and photophysical properties of the complexes between (*E*)-bis(18-crown-6)stilbene (1), alkaline and alkaline-earth metal cations and the dynamics of photoinduced electron transfer in the hydrogen-bonded donor-acceptor complexes of bis(18-crown-6)stilbene with the ammonioalkyl derivatives of (*E*)-1,2-di(4-pyridyl)ethylene (4, 5), 4,4'-bipyridine (2, 3) and 2,7-diazapyrene.⁹⁻¹¹ Their high thermodynamic stability is achieved *via* cooperative intermolecular coordination of both NH₃⁺ acceptor groups with two crown-ether fragments of the donor. Variations of the inter-

⁴ Kosygina str., Moscow 119991, Russian Federation. Fax: +7 (499) 1378357; Tel: +7 (495) 9397347

^cPhotochemistry Center, FSRC "Crystallography and Photonics", Russian Academy of Sciences, 7A-1 Novatorov str., Moscow 119421, Russian Federation.

chromophore distances in such bi- and trimolecular complexes D·A and D·A·D influence the intensities of charge-transfer (CT) absorption bands¹² and the parameters of intramolecular electron transfer.^{9,10} Variations in the electron-withdrawing abilities of the central acceptor moiety and the length of ammonioalkyl fragments affect spectral-luminescence parameters, stability, substitution, and dissociation constants. Similar to the related bis(crown-ether) derivatives of distirylbenzene,¹³ the complexes of bis-crown stilbene may be viewed as fluorescent chemosensors. In this work we established the stoichiometry of the substitution reaction between complex 1·3 and alkaline and alkaline-earth metal cations. The substitution constants were calculated for cations (strong and weak competitors). A relaxation scheme was proposed for the excited singlet state of 1·3.

Experimental

The structural formulas of compounds 1–5, C12 and complexes 1·2 and 1·3 are shown in Chart 1. An efficient synthesis of stilbene 1 is described in ref. 14. The syntheses of acceptor compounds 2 and 3 as well as compounds 4 and 5 are described in ref. 15, 14 and 16, respectively. ¹H NMR spectra were obtained with a Bruker DRX500 instrument. 1,1'-Bis (3-ammoniopropyl)-4,4'-bipyridinium tetraperchlorate (1·3) 1H NMR (MeCN- d_3 , 500.13 MHz, 25 °C) d: 2.41, (m, 4H, 2 CH_2CH_2N , 3.13 (m, 4H, 2 CH_2NH_3), 4.72 (t, J = 7.7 Hz, 4H, 2 CH_2N), 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).

Steady-state absorption and fluorescence spectra were obtained at 298 K with a Shimadzu-3100 spectrophotometer, as well as with PerkinElmer LS-55 and Elumin-2M spectrofluorimeters. The fluorescence quantum yields were determined by comparing the areas under the corrected fluorescence spectra of degassed solutions of the samples and that of quinine bisulfate in 1 N H₂SO₄ ($\Phi_f = 0.546$).¹⁷ The solutions were degassed by bubbling nitrogen through them for 15 min, except for quinine bisulfate in 1 N H₂SO₄. The details of transient spectra measurements were described in our previous publication.¹⁸ The corrected transient absorption spectra were subjected to a global fitting procedure based on the alternatingvariable descent method supposing triexponential decay. The global fitting procedure implies that the resulting characteristic times, unlike the pre-exponential factor or the constant term, do not depend on the detection wavelength. The calculation was performed using the set of experimental data for the 400-800 nm range from 0 to 3 ps. The procedure implied minimization of the root-mean-square deviations between the experimental and theoretical data matrices, calculated by variation of the characteristic times τ_i . The calculations were carried out using a script composed of standard MATLAB 6.0 functions. The average uncertainty was \sim 5%. The deconvolution was not carried out. Spectral grade purity (Merck) Li, Na, K, Mg, Ca, and Ba perchlorates were dehydrated by drying in vacuo (0.01 mm Hg) at 200 °C for 5 h in a VacuCell



Chart 1 Structures of 1–5, C12, and 1'–3' and complexes 1.2, 1.3, and 1'-3'.

apparatus. All measurements were carried out with freshly prepared solutions in acetonitrile (Fisher, HPLC gradient grade, water content 0.0021%) and freshly distilled butyronitrile (Merck) at 298 K.

The fluorescence spectra of **1** and **1**·3 in butyronitrile at 77 K were recorded on an Elumin-2M spectrofluorimeter using a specially designed micro-Dewar vessel. The substitution constants were calculated with the "Equilibrium" program based on a multivariable nonlinear least-squares method.¹⁹ The stability constant of **1**·3 was determined by means of a guest-competitor titration method. Average uncertainty amounted to

~10%. To avoid minor dissociation of complex 1·3 caused by traces of water in acetonitrile, the fluorescence spectra of the $1\cdot3$ /MeCN/metal perchlorate system were obtained in solutions of $1\cdot3$ with a 4-fold excess of acceptor 3.

Quantum chemical calculations were performed using the GAMESS $(US)^{20,21}$ program package with the 6-31G(d,p) basis set. The geometry of the complex in its ground state was optimized by means of DFT; its excited states were optimized by means of TDDFT. We used a BHHLYP functional with empirical dispersion correction version 3 with Becke-Johnson damping²² for the ground state; the excited states were optimized without dispersion correction. The environmental effects were included via the solvation model density continuum model.²³ The $S_0 \rightarrow S_n$ absorption, emission, and $S_1 \rightarrow S_n$ absorption spectra were calculated using the Firefly v.8.2 program package²⁴ by means of the state-averaged complete active space self-consistent field (SA-CASSCF)²⁵⁻²⁹ improved by second-order quasi-degenerate perturbation theory (XMCQDPT2).³⁰ The spectra were calculated for a model system $1' \cdot 3'$ consisting of 1,2-bis(3,4-dimethoxyphenyl)ethene (1') as a donor, 1,1'-dimethyl-4,4'-bipyridinium (3') as an acceptor, and two ammonium cations. The geometrical parameters of the model system were the same as those of the entire complex in the corresponding state. The environmental effects were included via the dielectric polarizable continuum DPCM model.³¹ The active space included 8 electrons in 12 orbitals. The density matrix was averaged over 11 lowest singlet states (XMCQDPT2//SA(11)-CASSCF(8,12)/6-31G(d,p)/DPCM). The charge distributions in the ground and excited states of the complex were found from the Mulliken charges on the donor and acceptor fragments.

Results and discussion

Ground state complexation and substitution reactions

The addition of **3** to solutions of **1** in acetonitrile induces weak hypsochromic and pronounced hypochromic shifts in the absorption spectra.

The broad absorption band of a very low intensity appears in the long-wave region. It was attributed to the charge-transfer (CT) band (Fig. 1). Within the error of 0.002 absorbance units, the absorption spectra of the main band have 3 linearly independent components. Mainly pseudocyclic complex 1:1 is formed in diluted solutions at low concentrations of reactants.

$$\mathbf{1} + \mathbf{3} \stackrel{K_1}{\leftrightarrow} \mathbf{1} \cdot \mathbf{3} \tag{1}$$

According to quantum-chemical calculations, the aromatic donor and acceptor moieties of 1·3 are non-planar in the ground state (Fig. 2). The BHHLYP/6-31G(d,p) optimized dihedral angle between the two pyridyl fragments of viologen is \sim 39°, which agrees with the X-ray crystal data.¹⁵

The calculation of the $S_0 \rightarrow S_n$ transition parameters of 1'.3' by XMCQDPT makes it possible to verify that the CT state is not an artifact. The calculation (Table 1) allows us to assign the $S_0 \rightarrow S_1$ transition to the charge transfer (CT) from the



Fig. 1 Absorption spectra of 1.3×10^{-5} M 1/MeCN/3 at 0, 1.13×10^{-6} , 2.75×10^{-6} , 4.78×10^{-6} , 7.10×10^{-6} , 9.64×10^{-6} , 1.23×10^{-5} , and 1.3×10^{-5} M of 3 (curves 1 to 8). CT band of 1·3 at 1.3×10^{-5} M of 3, T = 298 K. Inset: Fluorescence spectra of 1.3×10^{-5} M 1/MeCN/3 at 0, 5.7×10^{-8} , 1.14×10^{-7} , 1.69×10^{-7} , 3.31×10^{-7} , 6.31×10^{-7} , 1.16×10^{-6} , 1.98×10^{-6} , 2.60×10^{-6} , 3.09×10^{-6} , 3.47×10^{-6} , and 6.95×10^{-6} M of 3 (curves 1 to 12). $\lambda_{exc} = 300$ nm (isosbestic point), T = 298 K.



Fig. 2 Structures of 1.3 in the ground (S₀), charge transfer (CT) and local excited (LE) states.

HOMO localized on the donor to the LUMO localized on the acceptor (Chart 2). The charge distribution in $1' \cdot 3'$ changes upon excitation from +0.07 (stilbene)/+1.93 (viologen) to +0.99/+1.01. Electron transfer transforms the donor and the acceptor into radical cations.

The BHHLYP/6-31G(d,p) optimized structure of the CT state of the complex is more planar than the ground-state one. The inter-chromophore distance slightly increases.

 $\label{eq:table_$

| Parameter | S ₀ | CT | LE |
|--------------------------------|----------------|-------|----------------------|
| $\theta_{\rm vv}, \circ$ | 39 | 6 | 38 |
| θ_{ss}, \circ | 30 | 19 | 11 |
| $\Theta_{\rm vs}, \circ$ | 22/46 | 7/13 | 12/17 |
| $l_{\rm D-A}$, Å | 4.17 | 4.23 | 5.4 |
| $\Delta E_{\rm CT}$, eV | 1.89 | 0.82 | 1.33 |
| $\Delta E_{\rm LE}, {\rm eV}$ | 4.13 | 3.80 | 3.63 |
| f _{CT} | 0.007 | 0.008 | 9.6×10^{-5} |
| $f_{\rm LE}$ | 0.88 | 1.16 | 1.27 |

 $\theta_{\rm vv}$ is the angle between two pyridyl rings (planes V1 and V2); $\theta_{\rm ss}$ is the angle between two phenyl rings (planes S1 and S2); $\theta_{\rm vs}$ are the angles between phenyl and pyridyl rings (planes V1 and S1 and V2 and S2, respectively); and $l_{\rm D-A}$ is the D-A distance. $\Delta E_{\rm CT}$ is the energy gap between the S₀ and CT states in the geometry of the S₀ state (second column), in the geometry of the CT state (third column); and in the geometry of the S₀ and LE states in the geometry of the S₀ state (second column), in the geometry of the CT state (third column), and in the geometry of the LE state (fourth column) $\Delta E_{\rm LE}$ is the energy gap between the S₀ and LE states in the geometry of the S₀ state (second column), in the geometry of the CT state (third column), and in the geometry of the LE state (fourth column) calculated for the model complex 1'·3'. $f_{\rm CT}$ and $f_{\rm LE}$ are the corresponding oscillator strengths.



The formation of the complex is accompanied by fluorescence quenching, which is typical of the process of electron transfer (Fig. 3). Spectral shifts of any kind were absent. The calculated fluorescence spectrum of the model stilbene 1' exhibits a strong $S_1 \rightarrow S_0$ band at 341 nm, while the $S_1 \rightarrow S_0$ transition in the model complex 1'.3' is almost forbidden. The fluorescence quantum yield for 1.3 is quite low which can be explained by a small (~0.8 eV) calculated S_1 - S_0 energy gap and low oscillator strength resulting in efficient nonradiative deactivation.

Usually such complexes demonstrate high thermodynamic stability ($\log K_1 > 7$). Therefore, to obtain an amended value for the constant we employed spectrofluorimetric competition titration. Log K_1 was calculated with eqn (2):

$$\log K_1 = \log K_c - \log K_s \tag{2}$$

where K_1 is the stability constant, while K_c is the formation constant for complex **1**·**C12** in reaction (3) $(\log K_c = 8.59)^{15}$ and K_s is the substitution constant of complex **1**·3 with acceptor **C12** in reaction (4) (Fig. 3, inset).

$$\mathbf{1} + \mathbf{C12} \stackrel{K_{\mathbf{c}}}{\leftrightarrow} \mathbf{1} \cdot \mathbf{C12} \tag{3}$$

$$\mathbf{1} \cdot \mathbf{3} + \mathbf{C12} \stackrel{K_{\mathrm{s}}}{\leftrightarrow} \mathbf{1} \cdot \mathbf{C12} + \mathbf{3} \tag{4}$$

The value of $\log K_s = -0.91$ was obtained by the analysis of fluorescence spectra for 1.3/MeCN/C12 in reaction (4). The



Chart 2 The orbitals of $1' \cdot 3'$ with the largest contribution to the LE and CT transitions.

initial 4-fold excess of acceptor **3** was taken into consideration. The substitution constant was calculated with eqn (5):

$$\frac{c^{1C12}}{c_{\max}^{1C12}} = \frac{1}{2c_0^{DA}} \left(-(c_0^A + K_s[C12]) + \sqrt{(c_0^A + K_s[C12])^2 + 4K_sc_0^{DA}[C12]} \right)$$
(5)

where $c^{1C12}/c_{\text{max}}^{1C12}$ represents the ratio of current to maximum concentrations of 1·C12, attained at the excess of C12; c_0^{A} and c_0^{DA} represent the initial concentrations of 3 and 1·3, respectively. Since 1·3 exhibits a very weak fluorescence ($\Phi_{\text{f}} < 0.001$), we took the ratio under the fluorescence spectra of 1·3/MeCN/ C12 as $c^{1C12}/c_{\text{max}}^{1C12}$. The required log $K_1 = 9.5$ (9.15, ¹H NMR titration¹⁵) was calculated using eqn (2). Despite the high stability of 1·3, the stability constants of complexes 1 : 1 and



Fig. 3 Fluorescence spectra of the system: **1**-3/MeCN/C12 at ~7.4 × 10⁻⁶ M of 1, ~3.0 × 10⁻⁵ M of 3, and 0, 6.11 × 10⁻⁶, 1.81 × 10⁻⁵, 3.54 × 10⁻⁵, 6.03 × 10⁻⁵, 9.14 × 10⁻⁵, 1.27 × 10⁻⁴, 1.66 × 10⁻⁴, 2.13 × 10⁻⁴, 2.73 × 10⁻⁴, 3.53 × 10⁻⁴, and 9.22 × 10⁻⁴ M of C12 (curves 1 to 12). λ_{exc} = 342 nm (isosbestic point), T = 298 K. Inset: Ratio of areas under fluorescence spectra vs. concentration of acceptor, S_{max} – the same area with the acceptor in excess. The smooth curve depicts the theoretical dependence fitted using Eq. 5.

1:2 between stilbene **1** and 1-(3-ammoniopropyl)-4-methylpyridinium diperchlorate are moderate (log $K^{1:1} = 4.6$, log $K^{1:2} =$ 2.9).¹⁴ Alkali and alkaline-earth metal cations possess a larger affinity to bis-crown cavities than ammonium; therefore they displace it during the substitution.

The addition of Ba, Ca, K, Li, Na, and Mg perchlorates to solutions of 1·3 in acetonitrile induces noticeable blue and hyperchromic shifts of the main absorption band. For Ba, Ca, and K perchlorates we observed indistinct isosbestic points, while for Li, Na, and Mg perchlorates clear-cut isosbestic points were detected. In both cases the weak CT band of 1·3 is completely quenched. The character of quenching is not linear, which implies that this is a stepwise process. In all the cases the presence of three types of complexes (1·3, 1·M^{*n*+}, and 1·(M^{*n*+})₂) was confirmed by means of the Wallace–Katz method.³² In all systems but 1·3/MeCN/KClO₄, the absorption spectra have 3 linearly independent

components. It allows us to propose the following reaction mechanism:

$$\mathbf{1} \cdot \mathbf{3} + \mathbf{M}^{n+\frac{K_{S1}}{\leftrightarrow}} \mathbf{1} \cdot \mathbf{M}^{n+} + \mathbf{3}$$
(6)

$$\mathbf{1} \cdot \mathbf{M}^{n+} + \mathbf{M}^{n+\frac{K_{S2}}{\leftrightarrow}} \mathbf{1} \cdot (\mathbf{M}^{n+})_2.$$
⁽⁷⁾

As the complexes $1 \cdot M^{n+}$ and $3 \cdot 1 \cdot M^{n+}$ are intermediates, they exist in solutions only in trace amounts. Spectral-thermodynamic parameters of the product $1 \cdot (M^{n+})_2$ are shown in Table 1.

Comparing the reported $\log K_s^{1:2}$ values with related ones published earlier for reaction (8)¹¹ (Table 2), it is apparent that substitution constants of **1**·3 are lower than the corresponding stability constants of $1 \cdot (M^{n+})_2$

$$\mathbf{1} + 2\mathbf{M}^{n+} \stackrel{K_{\mathbf{a}}^{1::2}}{\longleftrightarrow} \mathbf{1} \cdot (\mathbf{M}^{n+})_2.$$
(8)

Obviously it can be interpreted as a requirement for ammonium to be rejected from the bis-crown cavities. The most significant decrease in the values of the constants is observed for Ca²⁺ and Ba²⁺. Nevertheless, they remain strong competitors. At low concentrations of salts the absorption spectra at the 334 nm band and also the fluorescence spectra of the 10^{-5} M $1\cdot3$ /MeCN/2.5 × 10^{-4} M Ca(ClO₄)₂ and 10^{-5} M $1/MeCN/2.5 \times 10^{-4}$ M Ca(ClO₄)₂ and 10^{-5} M $1/MeCN/2.5 \times 10^{-4}$ M Ca(ClO₄)₂ systems are identical. This indicates the detachment of two ammonioalkyl acceptor chains from the bis-crown during the substitution. As with the stability constants, the smallest substitution constants were obtained for compact Li⁺ and Mg²⁺ cations. In fact the absorption spectra of the 8.4×10^{-6} M $1\cdot3/MeCN/0.5$ M LiClO₄ and 8.4×10^{-6} M 1/MeCN/0.5 M LiClO₄ systems are different (Fig. 4).

Apparently, with Li^+ being a weaker competitor, it gives a lower product yield of the product $(1 \cdot (\text{Li}^+)_2)$. This was also supported by the fluorescence spectra. Upon increasing the LiClO₄ concentration up to 0.5 M the fluorescence intensity maximum in the first system amounts to only 42% of that for the second system (Fig. 4, inset). For the K⁺ and Na⁺ cations with more prominent acceptor abilities, the yield of $1 \cdot (\text{M}^{n+})_2$ is higher.

The fluorescence spectra of **1**·3 in a low temperature glassy matrix of PrCN do not exhibit a noticeable increase in intensity and the appearance of a distinct oscillatory structure at 77 K,

Table 2 Absorption maxima (ε_a^{max}), molar absorption coefficients at the absorption maxima (ε_a^{max}), substitution constants (log $K_s^{1:2}$) for **1**·3 and stability constants (log $K_a^{1:2}$) for **1** in MeCN at 298 K, the diameter of metal cation

| Salt | λ_a^{\max} 1:2, nm | $\varepsilon_{\rm a}^{\rm max} \times 10^{-4} 1 : 2, {\rm M}^{-1} {\rm cm}^{-1}$ | $\log K_{\rm s}^{1:2}$, M ^{-2 a} | $\log K_{\rm a}^{1:2}$, M ⁻² , ¹¹ | Diameter of metal cation, Å |
|--------------------|----------------------------|---|--|--|-----------------------------|
| LiClO ₄ | 332 | 3.38 | 2.0 | 3.7 | 1.36 |
| $NaClO_4$ | 333 | 3.77 | 5.6 | 7.8 | 1.94 |
| KClO ₄ | 332 | 3.41 | 6.6 | 7.1 | 2.66 |
| $Mg(ClO_4)_2$ | 329 | 3.53 | 3.5 | 3.7 | 1.32 |
| $Ca(ClO_4)_2$ | 329 | 3.51 | 4.3 | 15.6 | 1.98 |
| $Ba(ClO_4)_2$ | 329 | 3.39 | 4.4 | 16.7 | 2.68 |

^{*a*} Due to negligible absorption of 3 in the 330–400 nm range, $\log \xi_a^{1:2}$ was calculated for the following scheme: $\mathbf{1} \cdot \mathbf{3} + 2\mathbf{M}^{n+} \leftrightarrow \mathbf{1} \cdot (\mathbf{M}^{n+})_2$. 1 in MeCN: $\lambda_a^{\max} = 336 \text{ nm}, e_a^{\max} = 3.57 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}, \lambda_f^{\max} = 386 \text{ nm}, \Phi_f = 0.4$. 3 in MeCN: $\lambda_a^{\max} = 259 \text{ nm}, e_a^{\max} = 2.69 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}, \lambda_f^{\max} = 354 \text{ nm}, \Phi_f = 0.034$. $\mathbf{1} \cdot \mathbf{3}$ in MeCN: $\lambda_a^{\max} = 335 \text{ and } 492 \text{ nm}$ (CT band), $e_a^{\max} = 3.08 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and 208 M⁻¹ cm⁻¹ (CT band), $\log K_1 = 9.5, \Phi_f < 0.001$.



Fig. 4 Absorption spectra of 1/MeCN (1), 1/MeCN/0.5 M LiClO₄ (2), 1·3/ MeCN (1'), and 1·3/MeCN/0.5 M LiClO₄ (2'). The concentrations of 1 and 1·3 are 8.85 × 10⁻⁶ M, *T* = 298 K. Inset: Fluorescence spectra of 1/MeCN (1), 1/MeCN/0.5 M LiClO₄ (2), and 1·3/MeCN/LiClO₄ at 0, 1.923 × 10⁻², 5.357 × 10⁻², 8.333 × 10⁻², 0.1094, 0.1377, 0.1667, 0.1988, 0.2312, and 0.5 M of LiClO₄ (curves 1' to 10'). λ_{exc} = 335 nm, the spectra are normalized to equal absorbance at λ_{exc} , [1] = [1·3] = 8.85 × 10⁻⁶ M, *T* = 298 K.

as opposed to **1**. It points to a barrier-less electron transfer process, which does not require significant adjustments in the solvation shell.

Transient absorption spectroscopy

To describe the evolution of the transient spectra of **1** and **1**·3, mono- and polyexponential models were used, respectively. The differential optical densities $\Delta D(\lambda, t)$ of **1** in acetonitrile, either free or fully complexed with **3**, were measured after excitation with a 25 fs, 330 nm pump pulse (close to the isosbestic point) in the 500 ps time range. The evolution of the spectra for stilbene **1** in the range of 0 to **1** ps can be described as an emergence of a single broad band with its peak at 561 nm. In the range of 1 to 6 ps this band does not change noticeably. Then, in the range of **5**–500 ps the band undergoes mono-exponential decay with the characteristic time of 0.325 ns. The transient spectra of **1**·3 on the femtosecond-picosecond time scale in the 425–775 nm range at excitation in the main absorption band are shown in Fig. 5.

The evolution of the spectra involves three stages. During the first 150 fs, a broad single band with its peak at 566 nm arises. Then, up to 0.6 ps the band is subjected to quenching with a monotonous blue shift of up to 43 nm. After that we observe gradual quenching without shifts in the 0.6–3 ps range.

A theoretical calculation of $S_1 \rightarrow S_n$ absorption spectra of a model complex and its components (stilbene 1', viologen 3', and their radical cations) led us to the following scheme of the processes that take place after the 1.3 complex is excited to its most intense absorption band (Fig. 6).

The complex is excited to the LE state localized on stilbene (the experimental absorption wavelength is 330 nm; the calculated value is 315 nm). The calculation of the model complex



Fig. 5 Differential absorption of $1.3 (\sim 1.4 \times 10^{-4} \text{ M})$ in MeCN. The time increments: (a) 0.02 ps (0-0.15 ps); (b) 0.1 ps (0.15-1.95 ps). Arrows depict the direction of the time axis.



Fig. 6 Relaxation pathways for the excited singlet state of 1.3.

shows an intense $S_1 \rightarrow S_n$ absorption band from the LE state localized on stilbene (the calculated value is 586 nm) in the wavelength range of interest (400–800 nm), which corresponds to the calculated $S_1 \rightarrow S_n$ absorption bands at 559 and 585 nm in the model stilbene 1' and to the experimentally observed band at 566 nm.

The increasing absorption in this range during 150 fs after excitation can be explained by the relaxation of the vibrationally excited LE* state to the minimum of the LE state through chromophore vibrations and solvent reorganization.

$$LE^* \rightarrow LE(k_1)$$

This relaxation rate can be explained by a rather long decoherence time, ~ 100 fs in the LE state due to the proximity of

the minima of the ground and LE states.³⁴ A further blue shift of the band corresponds to the charge transfer and absorption of the CT state of the model complex (calculated value 500 nm), which corresponds to the $D_0 \rightarrow D_n$ absorption of the radical cation of the model stilbene 1' (the calculated value is 506 nm and the experimental value is 523 nm). According to our calculation, a radical cation of the model viologen 3' also absorbs in this region (560–580 nm, $D_0 \rightarrow D_n$) with low intensity, which explains an incomplete decay of the band at 550–570 nm simultaneously with the onset of the blue-shifted band.

The potential energy surface of the CT state is located in the vicinity of the LE minimum. The energy gap between these surfaces is small enough to make the nonradiative transition from the LE to the CT state faster than emission from the LE state. The experiment shows that no stilbene luminescence is observed in the complex; therefore, the complex, indeed, directly goes from the LE to the CT surface. According to Tully's surface hopping concept³⁵ this transition does not have to take place immediately near the LE minimum. The hopping probability in a given point of the potential energy surface depends on the nonadiabatic coupling and nuclear velocity in this point. In a system with a sloped conical intersection³⁶⁻³⁸ between the LE and CT surfaces, this probability does not have to exhibit a clear-cut maximum. Therefore, one cannot separate a vertical downward transition from the LE minimum to the CT* from the following CT* \rightarrow CT relaxation. We believe that hopping from the LE to CT surface occurs simultaneously with the relaxation of the CT state, and these processes can be described with a single effective constant. Hence, this process includes charge transfer followed by viologen planarization and solvent reorganization.

$$LE \rightarrow CT^* \rightarrow CT (k_2)$$

Next, the CT state nonradiatively relaxes through back electron transfer. As a result, the absorption from the stilbene and viologen radical cations completely decays. This process is the slowest one. As in the case of LE to CT hopping, hopping from CT to the ground state surface takes place simultaneously with relaxation to the ground state minimum through viologen twisting and solvent reorganization.

$$CT \rightarrow GS^* \rightarrow GS(k_3)$$

This corresponds to complete decay of transient absorption.

Therefore, the evolution of the photoinduced absorption spectra of the complex can be described by the following differential equations:

$$\frac{\mathrm{d}[\mathrm{LE}]^*}{\mathrm{d}t} = -k_1[\mathrm{LE}]^* \tag{9}$$

$$\frac{\mathrm{d[LE]}}{\mathrm{d}t} = k_1 [\mathrm{LE}]^* - k_2 [\mathrm{LE}] \tag{10}$$

$$\frac{\mathrm{d}[\mathrm{CT}]}{\mathrm{d}t} = k_2[\mathrm{LE}] - k_3[\mathrm{CT}] \tag{11}$$

Solving these equations leads us to the following expressions for differential absorption of each state:

$$\Delta D_{\mathrm{LE}^*}(\lambda, t) = \varepsilon'_{\mathrm{LE}^*}(\lambda) \cdot e^{-k_1 t}$$
(12)

$$\Delta D_{\rm LE}(\lambda, t) = \frac{\varepsilon'_{\rm LE}(\lambda) \cdot k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$
(13)

$$\Delta D_{\rm CT}(\lambda, t) = \frac{k_1 k_2 \varepsilon'_{\rm CT}(\lambda)}{(k_1 - k_2)(k_1 - k_3)(k_2 - k_3)} \\ \left((k_2 - k_3)e^{-k_1 t} - (k_1 - k_3)e^{-k_2 t} + (k_1 - k_2)e^{-k_3 t} \right)$$
(14)

where each of the three arrays: $\varepsilon'(\lambda) = \varepsilon(\lambda) \times [\text{LE}^*_0]$ is, in fact, a spectrum of each intermediate state.

The absorption spectra of the three intermediates, namely LE*, LE, and CT (Fig. 7), were determined by a global fitting procedure applied to the whole dataset of 425-750 nm and 0-2.2 ps. Their effective lifetimes were found to be 60, 320, and 510 fs. Fig. 8 shows the decay kinetic plots of complex 1.3 at the front, peak, and tail of the spectrum as well as the corresponding concentration curves of LE*, LE, and CT states (Fig. 8, inset). Fig. 9 shows the potential energy scans of the complex $1' \cdot 3'$ with respect to the inter-chromophore distance for two complex geometries: the closed-shell state (CS, obtained by unrelaxed scan of the ground-state structure) and the charge-transfer state (CT, obtained by unrelaxed scan of the charge-transfer structure and representing a biradicaloid state). The chromophores in the CS geometry (full lines) are twisted, while in the biradicaloid geometry (broken lines), they are planar. At a larger distance between the chromophores, a more planar structure of the CT state is preferred. At a relatively large distance, which is not accessible in a complex bonded by short alkyl linkers, state flipping can occur and the CT' state can become lower than the CS' state. As for the nonplanar structure, the closed-shell ground state is the lowest



Fig. 7 The absorption spectra of intermediates resulting from the excitation of the complex 1-3.



Fig. 8 Time plot of the transient absorption spectra of 1.3 in MeCN at 500 nm (a), 566 nm (b), and 650 nm (c) in the 0–2.3 ps range. Smooth curves represent global fitting. Inset: Time plot of LE*, LE, and CT states of 1.3 derived from Fig. 6.



Fig. 9 Energy of complex 1'·3' in the closed shell ground state (CS, CS'), biradicaloid charge-transfer excited (CT, CT'), and locally excited (LE, LE') states vs. D–A distance (XMCQDPT2 calculation). Solid and broken lines stand for nonplanar and planar conformations of chromophores, respectively.

one at any inter-chromophore distances. At large distances the planar CT' and non-planar CS states are quasi-degenerate. This quasi-degeneration favors the efficient nonradiative conversion from the CT to the closed-shell ground state.

So, we can suggest the following relaxation mechanism: a twisted LE state, whose geometry only slightly differs from the geometry of the CS ground state, is quasi-degenerate with the planar biradicaloid CT state at a distance of 3–4 Å, which is quite affordable with short alkyl linkers. This quasi-degeneration causes fast LE \rightarrow CT relaxation. Quasi-degeneration of the planar CT state with either the planar CS' state or the twisted CS state is achieved at the distances of 9 Å or longer, which are not affordable with short alkyl linkers. This explains relatively slow CT \rightarrow GS relaxation.

Table 3 Interchromophore distance (l_{D-A}), frequency (ν_{max}) and peak extinction coefficient (ε_{max}) of CT absorption bands, and electron back-transfer time ($\tau_{\text{CT-b}}$) in the related complexes in MeCN at 298 K

| | $\iota_{\mathrm{D-A}}, \pi$ | M CIII | cm ¹ | $\tau_{\rm CT-b}$, fs |
|------------------------------------|--|--|--|--|
| -(CH ₂) ₂ - | 3.6 | 160 | 18 900 | 400 |
| $-(CH_2)_3-$ | 4.15 | 210 | 20 3 0 0 | 510 |
| $-(CH_2)_2-$ | 3.62 | 331 | 18 500 | 400 |
| -(CH ₂) ₃ - | 3.82 | 375 | 19700 | 540 |
| | -(CH ₂) ₂ - -(CH ₂) ₃ - -(CH ₂) ₂ - -(CH ₂) ₃ - | $\begin{array}{ccc} -(CH_2)_{2^-} & 3.6 \\ -(CH_2)_{3^-} & 4.15 \\ -(CH_2)_{2^-} & 3.62 \\ -(CH_2)_{3^-} & 3.82 \end{array}$ | $\begin{array}{ccccc} -(CH_2)_{2^-} & 3.6 & 160 \\ -(CH_2)_{3^-} & 4.15 & 210 \\ -(CH_2)_{2^-} & 3.62 & 331 \\ -(CH_2)_{3^-} & 3.82 & 375 \end{array}$ | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ |

In the series of bis(crown)stilbene complexes with two different acceptors (bipyrydil and bipyridilethylene derivatives), the alkyl chain lengths of the acceptors and the interchromophore D–A distances correlate to some extent with the charge transfer parameters $S_0 \rightarrow CT$ and $CT \rightarrow S_0$ (Table 3). As the alkyl chain increases from two to three methylene links, the molar extinction coefficient and the frequency of the $S_0 \rightarrow CT$ transition slightly increase together with the electron back-transfer time, which can be associated with the increased donor–acceptor distance.

Conclusion

An efficient substitution reaction takes place upon the interaction of donor-acceptor complex 1·3 with alkali and alkalineearth metal perchlorates in acetonitrile. The reaction results in the substitution of two ammonioalkyl linkers by metal cations with the formation of the fluorescing product $1 \cdot (M^{n+})_2$. The thermodynamic and kinetic parameters of 1·3 and $1 \cdot (M^{n+})_2$ were determined. Complex 1·3 may be viewed as an optical sensor for metal cations. The subpicosecond characteristic times of direct and back electron transfer in the supramolecular complex 1·3 were determined by means of femtosecond transient absorption spectroscopy. The nature of the excited states of 1·3 is elucidated and a reliable mechanism of photoinduced charge transfer and further relaxation is suggested with the use of quantum chemical calculations.

Conflicts of interest

There are no conflicts to declare.

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