



Stereospecific [2 + 2]-cross-photocycloaddition in a supramolecular donor–acceptor complex

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ABSTRACT

A bis(propylammonium) derivative of (*E*)-4-(4-mercaptostyryl)pyridine, which was synthesized for the first time, forms a highly stable bimolecular complex with a bis(18-crown-6 ether) derivative of (*E*)-stilbene in solution owing to ditopic coordination *via* hydrogen bonds. The complex formation results in much faster deactivation of the excited states of both compounds, which is explained by photoinduced electron transfer from the stilbene derivative to the styrylpyridinium dye. Despite this, the complexed olefins undergo [2 + 2]-cross-photocycloaddition upon selective excitation of the dye to afford solely the *syn*-cycloadduct. The *retro*-photocycloaddition occurs readily upon UV irradiation of the cycloadduct and leads to the initial bimolecular complex.

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Introduction

The [2 + 2]-photocycloaddition (PCA) reaction is one of the few classical photoreactions widely used in synthetic organic chemistry [1–3]. In particular, this reaction is applied as a key step in the synthesis of pharmaceuticals [4] and complex natural products [5], which greatly simplifies their synthesis and makes it possible to exclude the use of expensive and/or toxic reagents. Solid-state PCA reactions are also used in material chemistry and applied physics [6]. Intermolecular PCA reactions in solution are usually inefficient, due to short excited state lifetimes, and afford mixtures of cyclobutane isomers. To date, a variety of supramolecular approaches have been developed to control the efficiency and selectivity of the PCA reaction both in solution and in the solid state [7–11]. Most attention has been paid to auto-PCA, i.e. [2 + 2]-photodimerization, whereas supramolecular cross-PCA reactions remain less studied [12]. This especially concerns the reactions between electron-donor and electron-acceptor olefins, when photoinduced intermolecular electron transfer can be a competing process. In this case, it is rather difficult to predict the PCA

efficiency, because both competing photoreactions are significantly dependent on the geometric properties of the supramolecular assemblies.

Previously, we studied the photophysical and photochemical behavior of the supramolecular donor–acceptor complex between bis(18-crown-6)stilbene (*E*)-**1** (Scheme 1) and a bis(propylammonium) derivative of (*E*)-1,2-di(4-pyridyl)ethylene, formed owing to ditopic coordination *via* hydrogen bonds [13]. It was found that ultrafast conversion from the lowest-energy local excited states of the complexed olefins to the intermolecular charge-transfer excited state ($\tau < 0.3$ ps), followed by back electron transfer to the ground state ($\tau = 0.54$ ps), completely suppresses all other photochemical processes, including the expected cross-PCA reaction.

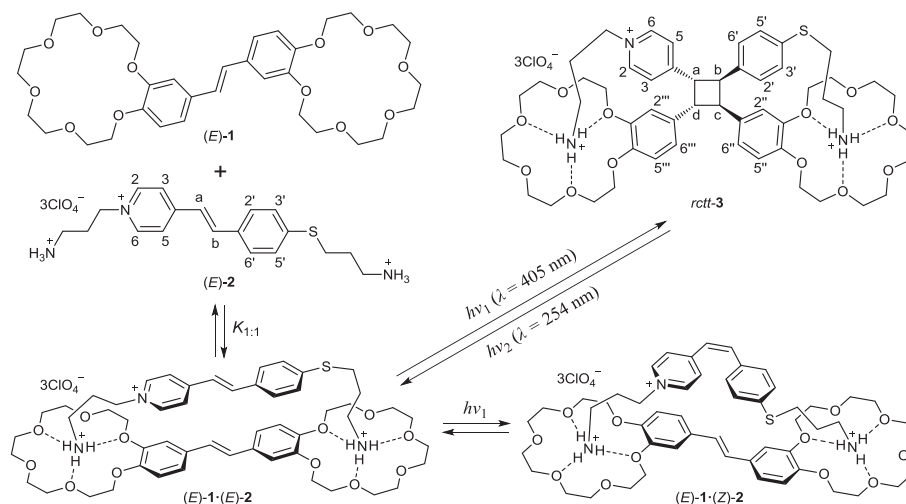
Herein, we report the synthesis of a bis(propylammonium) derivative of (*E*)-4-(4-mercaptostyryl)pyridine (compound (*E*)-**2**, Scheme 1) having weaker electron-acceptor properties than its dipyrindylethylene analogue mentioned above; in addition, we report the initial results of spectroscopic studies and quantum chemical calculations of the supramolecular donor–acceptor complex formed between compounds (*E*)-**1** and (*E*)-**2** in solution.

Results and discussion

The styrylpyridinium dye (*E*)-**2** was synthesized by quaternization of (*E*)-4-(4-methylthiostyryl)pyridine [14] with excess 3-bro-

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Scheme 1. Formation and photoreactions of supramolecular complex (E)-1·(E)-2 in MeCN.

mopropan-1-ammonium bromide, followed by treatment with HClO₄ (see ESI for details). The transalkylation of the methylthio group in the styrylpyridine occurred in parallel with quaternization of the pyridine nitrogen, but at a lower rate. Stilbene (E)-1 was prepared by the facile and efficient method reported previously [15].

The complexation of (E)-1 with (E)-2 was studied by spectrophotometric titration in MeCN containing 3% H₂O (ESI, Fig. S1). The titration spectra were well fitted to the single equilibrium shown in Scheme 1. The stability constant $K_{1:1}$ for the complex (E)-1·(E)-2 was estimated to be approximately 10^{6.6} mol⁻¹ dm³. This value is three orders of magnitude higher than the $K_{1:1}$ value of 10^{3.5} mol⁻¹ dm³ measured for the complex between benzo-18-crown-6 ether and the EtNH₃⁺ ion in the same solvent (ESI, Fig. S2). This strongly indicates the ditopic coordination of (E)-1 with (E)-2 leading to pseudocyclic complex (E)-1·(E)-2 (Scheme 1).

Fig. 1 shows the absorption spectra of (E)-1, (E)-2, and (E)-1·(E)-2. The main spectral and photochemical characteristics of compounds (E)-1 and (E)-2 in the free and complexed forms are given in Table 1 (see also the spectral data in ESI, Figs. S3–S5).

The formation of complex (E)-1·(E)-2 causes a red shift of the lowest-energy absorption band of dye (E)-2 and a significant decrease in the intensity of this band. The absorption band of

stilbene (E)-1 shows a small blue shift. The fluorescence quantum yields of (E)-1 and (E)-2, as well as the E → Z photoisomerization quantum yield of (E)-2 [16], decrease greatly, which suggests much faster deactivation of the local excited states of both olefins in complex (E)-1·(E)-2. The most probable reason for this is photoinduced electron transfer from stilbene (E)-1 to dye (E)-2. This hypothesis is strongly supported by the quantum chemical calculations presented below.

It was also found that the formation of complex (E)-1·(E)-2 induces a stereospecific cross-PCA reaction giving solely the *syn*-cycloadduct (*rctt*-3, Scheme 1). The quantum yield of this photoreaction in MeCN, as measured upon selective excitation of the dye with 405 nm light, is approximately 8 × 10⁻⁴ (ESI, Fig. S6). Despite the low quantum yield, prolonged irradiation of complex (E)-1·(E)-2 led to almost complete conversion of the dye to cross-cycloadduct *rctt*-3, which was characterized by NMR spectroscopy and mass-spectrometry (ESI). The signals of the cyclobutane ring protons in the ¹H NMR spectrum of *rctt*-3 in DMSO-*d*₆ (Fig. 2) manifest as four doublets of doublets. The vicinal coupling constants calculated for this ABCD spin system, ³J_{trans-ab} = 7.5 Hz, ³J_{cis-bc} = 10.2 Hz, ³J_{trans-cd} = 7.2 Hz, and ³J_{cis-da} = 10.3 Hz, are typical of the *rctt* isomers of 1,2,3,4-tetra(het)aryl-substituted cyclobutanes [17,18]. It should be noted that the NH₃⁺ proton signals in the ¹H NMR spectrum of *rctt*-3 are significantly narrowed and shifted upfield by approximately 0.6 ppm in comparison with free dye (E)-2, which points to the intramolecular coordination of the ammonium groups with the crown ether moieties [19].

It was found that cyclobutane *rctt*-3 readily undergoes the *retro*-PCA reaction upon irradiation with 254 nm light, leading predominantly to the initial complex (E)-1·(E)-2 (ESI, Fig. S7).

The molecular structures of (E)-1, (E)-2, and (E)-1·(E)-2 in MeCN were studied by density functional theory (DFT) calculations using the hybrid M06-2X functional [20] and the SMD solvation model [21]. The electronic transition energies for these three species were calculated by time-dependent DFT (see ESI for computational details). We analyzed a variety of conformations of complex (E)-1·(E)-2 with both the *syn*- and *anti*-orientations of the two olefinic bonds with respect to each other. On the whole, the *anti*-conformers were slightly more stable. For example, the difference in the Gibbs free energy in solution between the most stable *syn*- and *anti*-conformers of (E)-1·(E)-2 (Fig. 3) was calculated to be 0.47 kcal mol⁻¹ in favor of the latter. The olefinic bonds in the most stable *syn*-conformer are almost parallel to each other, and the distance between them is only 3.57 Å. The structure of this conformer is consistent with the topochemical criteria for PCA [22,23].

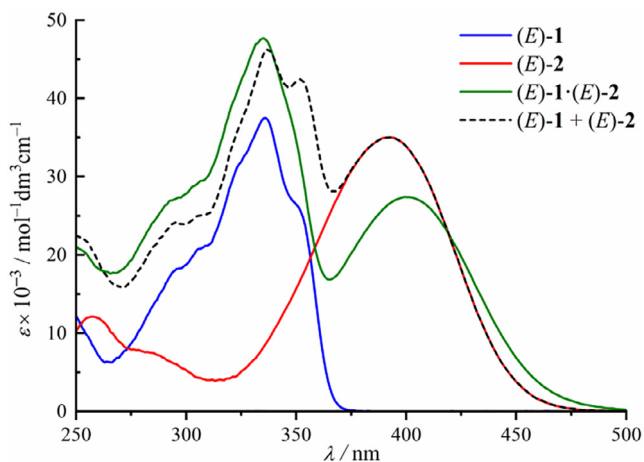


Fig. 1. Absorption spectra of (E)-1, (E)-2, and (E)-1·(E)-2 in MeCN containing 3% H₂O; the dashed curve is the sum of the spectra of (E)-1 and (E)-2.

Table 1
Spectral and photochemical characteristics of stilbene (*E*-1) and dye (*E*-2) in free forms and in complex (*E*-1)·(*E*-2).^a

Species	λ_{abs}	$\epsilon \times 10^{-3}$	λ_{fl}	φ_{fl}	φ_{E-Z}
Free (<i>E</i> -1)	336	37.5	386	0.30	0.24
Complexed (<i>E</i> -1)	335	–	386	0.02	–
Free (<i>E</i> -2)	392	35.0	552	0.20	0.34
Complexed (<i>E</i> -2)	400	27.4	562	0.03	0.05

^a In MeCN at ambient temperature; data for uncomplexed (*E*-1) are taken from Ref. [13]; λ_{abs} is the position of the absorption maximum, nm; ϵ is the molar absorptivity at λ_{abs} , $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$; λ_{fl} is the position of the fluorescence maximum in the corrected spectrum, nm; φ_{fl} is the fluorescence quantum yield; φ_{E-Z} is the *E* → *Z* photoisomerization quantum yield.

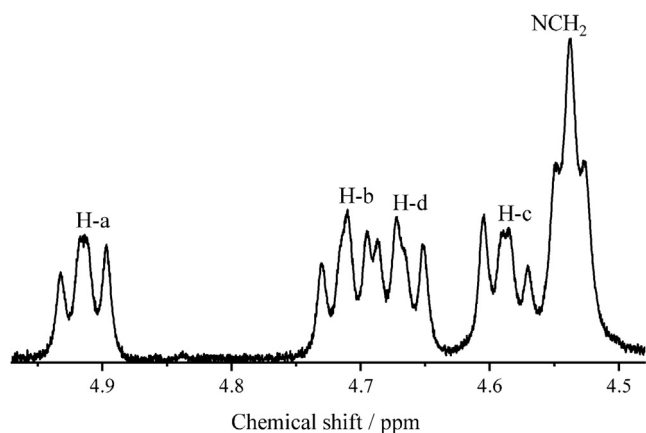


Fig. 2. ¹H NMR spectrum of *rctt*-3 (the region of cyclobutane ring protons, 500 MHz, DMSO-*d*₆).

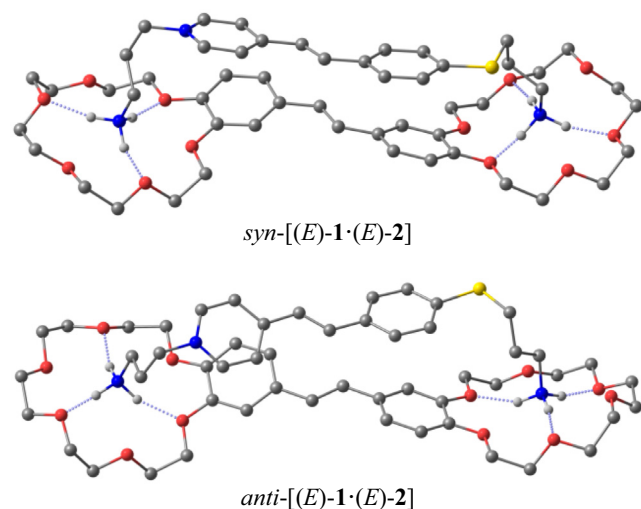


Fig. 3. DFT calculated structures of the most stable *syn*- and *anti*-conformers of complex (*E*-1)·(*E*-2) in MeCN; hydrogen atoms are not shown, except those of the ammonium groups.

Fig. 4 shows the theoretical parameters of low-energy electronic transitions in the most stable conformers of compounds (*E*-1) and (*E*-2) and in the most stable *syn*-conformer of complex (*E*-1)·(*E*-2). The predicted changes in the π – π^* transitions of (*E*-1) and (*E*-2), due to the formation of complex (*E*-1)·(*E*-2), are in good agreement with the experimentally observed shifts in the absorption spectra. In addition, the calculations predict that the S_0 – S_1 transition in this complex is related to the electron transfer from stilbene (*E*-1) to dye (*E*-2) (ESI, Fig. S8). This corroborates the assumption that the observed fast deactivation of the local excited

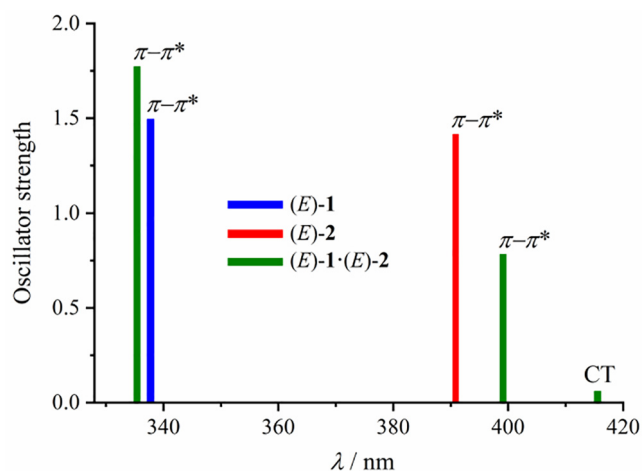


Fig. 4. Parameters of low-energy electronic transitions in the most stable conformers of (*E*-1) and (*E*-2) and in the most stable *syn*-conformer of complex (*E*-1)·(*E*-2). The λ parameters were obtained by subtracting 0.2 eV from the transition energies calculated by time-dependent DFT.

states in complex (*E*-1)·(*E*-2) is due to photoinduced electron transfer (in other words, due to internal conversion to the charge-transfer excited state). The absorption band associated with the intermolecular charge-transfer transition in (*E*-1)·(*E*-2) is unobservable in the experimental spectrum because it is overlapped with the broad and much more intense band associated with the lowest-energy local π – π^* transition in dye (*E*-2). It should be noted that the parameters of electronic transitions calculated for different *syn*- and *anti*-conformers of (*E*-1)·(*E*-2) are close to each other (ESI, Fig. S9).

Conclusion

In summary, the bis(crown ether)-containing stilbene (*E*-1) and the styrylpyridinium dye (*E*-2) form a highly stable two-deck bimolecular complex in MeCN due to ditopic coordination *via* hydrogen bonds. The complex formation results in much faster deactivation of the excited states of both olefins, which is explained by photoinduced electron transfer from the stilbene derivative to the dye. Despite this, the complexed olefins undergo the [2 + 2]-cross-photocycloaddition reaction upon selective excitation of the dye to afford solely the *syn*-cycloadduct (cyclobutane *rctt*-3). To the best of our knowledge, compound *rctt*-3 is the first representative of a 1-pyridyl-2,3,4-triphenyl cyclobutane derivative. Since both competing photoprocesses, photoinduced electron transfer and photocycloaddition, are dependent on the geometric properties of the supramolecular assemblies, it would be interesting to investigate how the length of the alkylammonium spacers affects the photoreactivity of complex (*E*-1)·(*E*-2). At present, we are carrying out the corresponding studies.

The results of this work can be used for the targeted design of photoactive supramolecular assemblies and in the development of new methods for the synthesis of cyclobutanes using [2 + 2]-cross-photocycloaddition reactions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.tetlet.2018.11.077>.

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