Optics and Spectroscopy, 2022, Vol. 130, No. 5

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Molecular Photonics of 3,3'-diethyl-9-methylthiacarbocyanine Monomers and Dimeric Complexes with Cucurbit[8]uril

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Received November 30, 2021
Revised November 30, 2021
Accepted January 11, 2022

A comparative study of the spectral-luminescent and spectral-kinetic properties of 3,3'-diethyl-9-methylthiacarbocyanine (MTCC) and 3,3'-diethylthiacarbocyanine (TCC) and their complexes with cucurbit[8]uril in aqueous solution was carried out. Dimeric complexes of TCC with cucurbit[8]uril consist of trans-isomers and exhibit only delayed fluorescence while dimeric complexes of MTCC consist of cis-isomers and exhibit both delayed fluorescence and phosphorescence in water. The dimeric complexes of MTCC and TCC with cucurbit[8]uril participate in the electron phototransfer reaction where the dimeric complex of MTCC exhibits a greater ability to enter into photooxidation reactions.

Keywords: polymethine dyes, trans-cis isomerization, cucurbiturils, absorption, fluorescence, triplet-triplet absorption, electron phototransfer.

DOI: 10.21883/EOS.2022.05.54436.3-22

Introduction

It is known [1–3] that for monomers of thiacarbocyanine dyes, a characteristic feature is the existence in solutions of an equilibrium between *trans*- and *cis*-isomers, the position of which depends on the structure of the molecule and the polarity of the solvent. For unsubstituted thiacarbocyanines, for example, for 3,3′-diethylthiacarbocyanine (TCC), the *trans*-isomer [4] is stable. In this case, the *trans*→*cis* transition is sterically hindered, and the solvent polarity does not affect the position of the *trans*⇄*cis* equilibrium. At the same time, for alkylmesosubstituted thiacarbocyanine (3,3′-diethyl-9-methylthiacarbocyanine (MTCC)) there is equilibrium between *trans*- and *cis*-isomers [3], whose position depends on the polarity of the solvent. As polarity of the solvent increases, equilibrium shifts towards the *cis*-isomer [5]. It is also known that thiacarbocyanines exhibit the ability to aggregate [6–8] with formation of dimers as the simplest supramolecular systems [8,9]. Thus, equilibrium of monomer⇄dimer TCC shifts towards dimers with increasing dye concentration in water. Along with *trans*-*cis*-photoisomerization, polymethine dye monomers participate in redox reactions involving the triplet state [10]. Polymethine dimers are capable of electron transfer reactions in the triplet state [11–13]. Thus, for anionic thiamono- and thiatrimethine dyes, the product of one-electron oxidation of dimers in the triplet state is a dimeric anion-radical of the dye, which, due to instability, spontaneously dissociates in $10-30\,\mathrm{s}$ [13] into a neutral radical and dye anion. At the same time, a characteristic feature of polymethine dyes is the ability to form complexes with cavitand molecules and, in particular, with molecules of cucurbit[7,8]urils [14–16]. In the article [16], it has been shown that *trans*-TCC forms 2:2 dimeric complexes with cucurbit[8]uril (CB8), which are capable of intercombination transition to the triplet state. The relatively long lifetime of dimeric complexes in the triplet state ($\tau_T \sim 1\cdot10^{-4}\,\mathrm{s}$) allows them to be used in triplet-triplet (T-T) energy transfer [17,18] and in the reaction of electron phototransfer [19].

In the present article, we carried out a comparative study of the spectral-luminescent and spectral-kinetic properties of MTCC and TCC and their dimeric complexes with CB8 in aqueous solutions.

Experimental procedure

The studies were carried out with polymethine dyes — MTCC-iodide and TCC-iodide, synthesized at NIIKHIM-PHOTOPROEKT. CB8 (Aldrich) was used as a cavitand, *n*-nitroacetophenone and 1,4-dinitrobenzene (Aldrich) were used as electron acceptors. The measurements were carried out in methanol, ethanol, acetonitrile (Aldrich) and in water purified using the Direct−Q3 Millipore system. Taking into account the limited solubility of the dye in water, the solutions were prepared by adding a saturated solution of the dye in dimethyl sulfoxide (Aldrich) to an aqueous solution of $2-5\,\mu$l. Absorption spectra were recorded on an Agilent 8453 spectrophotometer. Luminescence measurements were performed on a Cary Eclipse spectrofluorimeter. The spectra of delayed fluorescence and phosphorescence were recorded 100 μs after stopping of emission of the flash-tube as an excitation source (spectrofluorimeter option). The T-T absorption spectra and triplet state deactivation kinetics were measured using an ns-laser photolysis setup [20–22]. Dye solutions were irradiated with yttrium-aluminum garnet (Nd:YAG, „Solar", $\lambda = 532$ nm) laser pulses with pulse duration of 10 ns and energy up to 70 μJ. Removal of atmospheric oxygen was achieved by purging the solution with gaseous argon. Spectral-luminescent measurements were performed at room temperature.

Results and discussion

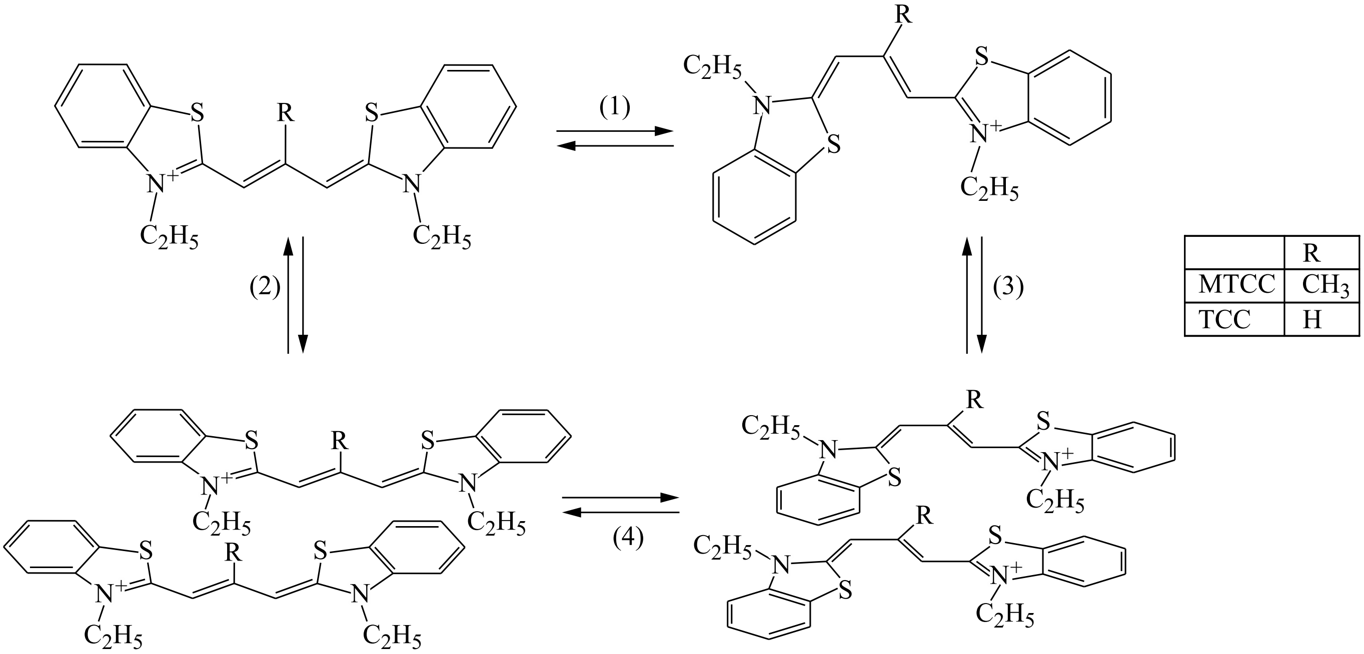
For MTCC and TCC monomers, the existence of four bound equilibria is fundamentally possible (Scheme 1): between *trans*- and *cis*-monomers (1), *trans*-monomers and *trans*-dimers (2), *cis*-monomers and *cis*-dimers (3), *trans*- and *cis*-dimers (4).

In diluted aqueous solution, as in a polar medium, MTCC molecules are predominantly in the form of *cis*-monomers, while in low polar solvents (chloroform, dichloroethane, dioxane) MTCC molecules are present in the form of the *trans*-isomer [3,5]. Figure 1 shows the normalized absorption spectrum of MTCC in water with a maximum at 540 nm and a shoulder at 504 nm, the absorption of which increases with increasing dye concentration. The maximum at 540 nm refers to the *cis*-isomer, while the shoulder results from the superposition of the absorption bands of the *cis*-dimer and the dye *cis*-monomer (equilibrium 3, Scheme 1). With increase in the concentration of MTCC in water up to $1.2 \cdot 10^{-5}$ mol/l, increase in absorption at 504 nm is observed due to increase in the concentration of the dimer. The value of the MTCC dimerization constant (K_d) calculated based on the Harris-Hobbs [23] ratio is $1.1 \cdot 10^5$ l/mol. In methanol, the dye dimers dissociate into solvated monomers (Fig. 1). In contrast to MTCC, TCC molecules exist as the *trans*-isomer in solvent of different polarity [3].

In this article, we measured the fluorescence and fluorescence excitation spectra of MTCC in water, shown in Fig. 2. The position of the maximum of the fluorescence excitation spectrum (548 nm) differs from the position of the maximum of the absorption spectrum (Fig. 1), which confirms the existence of two forms, one of which (*cis*-isomers) does not fluoresce. The *cis*-dimers of MTCC also do not exhibit fluorescence, like the non-fluorescent dimers of TCC, which consist of *trans*-isomers [8,24].

The presence of CB8 in aqueous solution of MTCC leads to significant changes in the absorption and fluorescence spectra of MTCC as a result of the formation of complexes. Figure 3 shows the absorption spectra of MTCC in water in the absence and presence of CB8. When CB8 is added to the dye solution, the absorption of MTCC at 540 nm decreases with a simultaneous increase in absorption at 520 nm, related to the dimeric complexes 2[MTCC@CB8] and shifted by 16 nm to the short-wavelength region relative to the MTCC dimers in water. According to [16,18], the 2[MTCC@CB8] complex has a composition of 2:2.

Figure 4 shows the fluorescence spectra of MTCC measured in the absence (spectrum *1*) and in the presence (spectrum *2*) of CB8 upon excitation of luminescence in the absorption band of dimeric complexes of MTCC with CB8 (520 nm). The spectrum *1* with a maximum at



	R
MTCC	CH_3
TCC	H

Scheme 1.

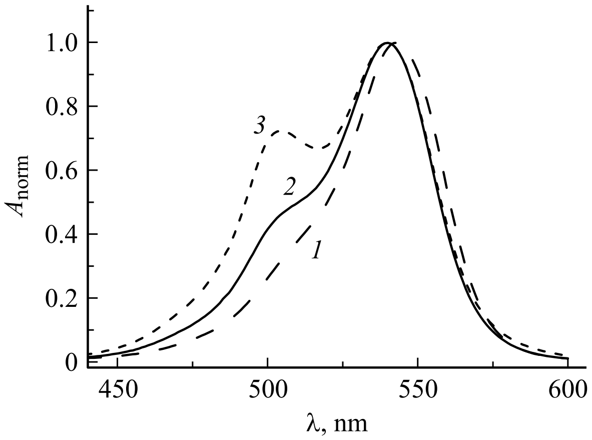


Figure 1. Normalized absorption spectra of MTCC in methanol (*1*) at concentration of $5 \cdot 10^{-6}$ mol/l and in water at concentration of $5 \cdot 10^{-6}$ (*2*) and $1.2 \cdot 10^{-5}$ mol/l (*3*).

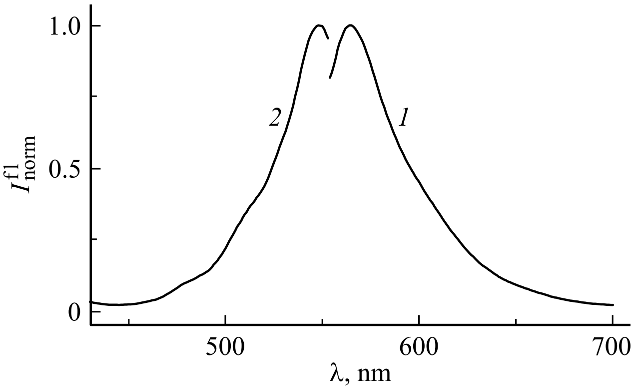


Figure 2. Normalized spectra of fluorescence (*1*, excitation at $\lambda_{\text{ex}} = 540$ nm) and fluorescence excitation (*2*, observation at $\lambda_{\text{obs}} = 564$ nm) of MTCC in water ($1.3 \cdot 10^{-6}$ mol/l).

565 nm refers to the fluorescence of MTCC monomers. The spectrum *2* is characterized by three maxima, of which the maximum at 604 nm refers to the fluorescence of dimeric complexes of MTCC with CB8, and the maxima at 670 and 705 nm — to phosphorescence. Measurement of the phosphorescence spectrum of a deoxygenated MTCC solution in the presence of CB8 (Fig. 4, spectrum *3*) confirmed the correct assignment of the bands at 670 and 705 nm to the phosphorescence of dimeric complexes. The shoulder at 600 nm in the phosphorescence spectrum is due to the delayed fluorescence of dimeric complexes of MTCC with CB8. The lifetime of the phosphorescence of dimeric complexes, measured in a deoxygenated solution at room temperature at 676 and 707 nm, is $2.8 \cdot 10^{-4}$ s. The coincidence of the lifetime measured in 2 maxima confirms the presence of 2 maxima in the phosphorescence spectrum of the dimer complex. It is important to emphasize that, according to [16], dimeric complexes consisting of *trans*-TCC and CB8 exhibit exclusively delayed fluorescence, the lifetime of which is $1.5 \cdot 10^{-2}$ s.

In the article, spectral-kinetic measurements of intermediate products of laser excitation of MTCC monomers in organic solvents (methanol, ethanol, acetonitrile), as well as dimers and their dimeric complexes with CB8 in water were also carried out. Upon laser excitation of aqueous solutions, short-term reversible changes in the absorption spectra were observed due to the intercombination transition to the triplet state. Figure 5 shows the difference absorption spectra of deoxygenated MTCC solution in ethanol measured at different time intervals after the laser pulse. The negative maximum at 550 nm reflects depletion of the main level of MTCC monomers, while the positive maximum at 620 nm refers to T-T-absorption of MTCC monomers. Spectral changes at $\lambda < 470$ nm are also related to T-T-absorption. The lifetime of monomers in the triplet state is $9.5 \cdot 10^{-6}$ s (Fig. 5, insertion).

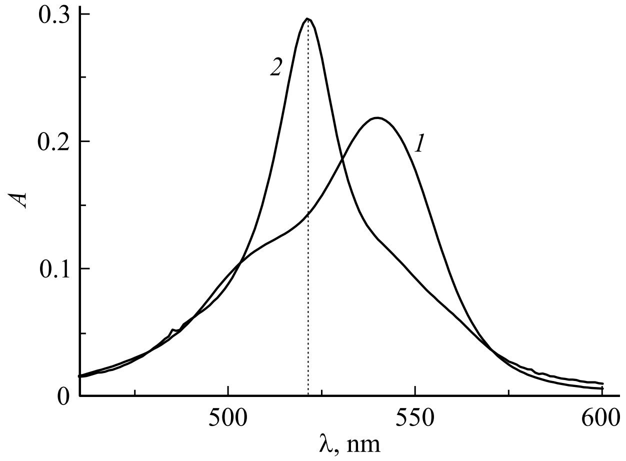


Figure 3. Absorption spectra of MTCC ($1.6 \cdot 10^{-6}$ mol/l) in the absence (*1*) and in the presence (*2*) of CB8 ($2.5 \cdot 10^{-5}$ mol/l) in water.

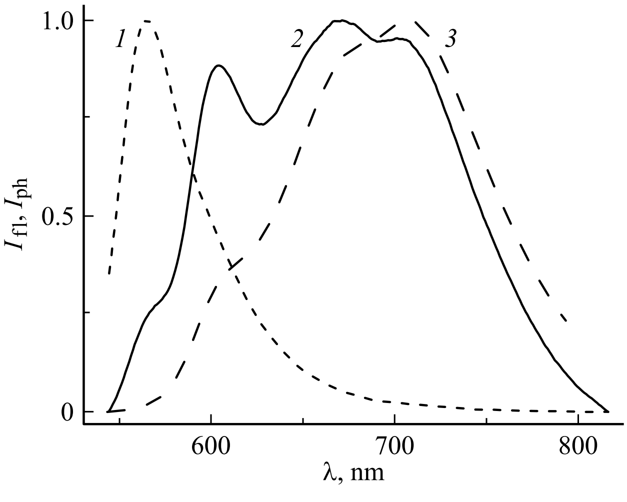


Figure 4. Normalized fluorescence spectra of MTCC solutions in the absence (*1*) and in the presence (*2*) of CB8 and the phosphorescence spectrum of deoxygenated MTCC solution in the presence of CB8 (*3*). Concentrations of MTCC — $1.6 \cdot 10^{-6}$ mol/l, CB8 — $2.5 \cdot 10^{-5}$ mol/l; $\lambda_{\text{ex}} = 520$ nm.

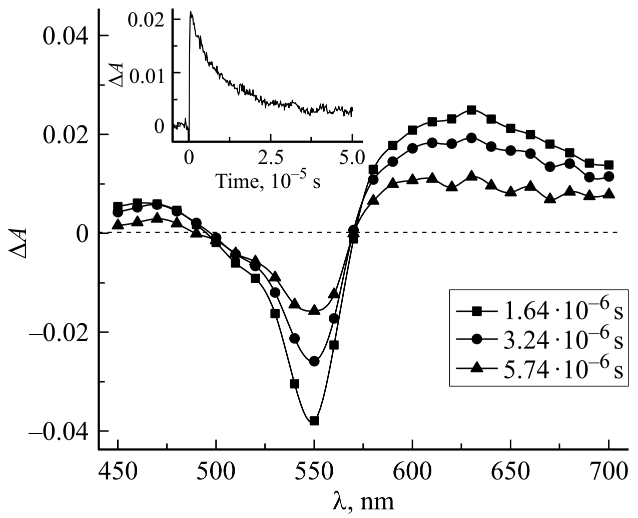


Figure 5. Time-resolved difference T-T-absorption spectra of deoxygenated MTCC solution in ethanol. MTCC concentration is $1.3 \cdot 10^{-4}$ mol/l. In the frame — spectra measurement time. In the insertion — the kinetics of deactivation of the triplet state of the dye at 650 nm.

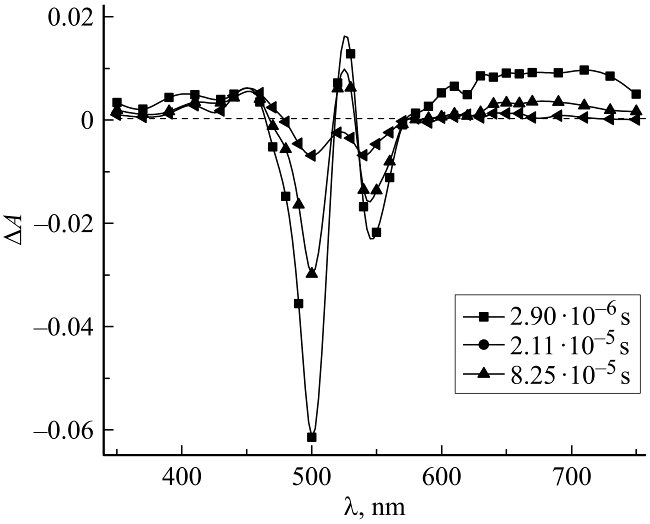


Figure 6. Time-resolved difference T-T-absorption spectra of deoxygenated aqueous MTCC solution. MTCC concentration is $1.3 \cdot 10^{-4}$ mol/l. In the frame — spectra measurement time.

The difference absorption spectrum of aqueous solution of MTCC (Fig. 6) is characterized by the presence of positive and negative maxima. The negative maxima at 500 and 550 nm reflect bleaching of the bands of dimers and monomers, respectively, due to depletion of the main levels. The maximum at 525 nm refers to T-T-absorption of the dye dimers. The broad band ($\lambda > 620$ nm) is a superposition of T-T-absorption spectra of MTCC monomers and dimers. In aqueous solution, the lifetime of MTCC monomers in the triplet state is $4 \cdot 10^{-5}$ s, of dimers — $1 \cdot 10^{-5}$ s.

Figure 7 shows the difference T-T-absorption spectra of deoxygenated aqueous solution of MTCC in the presence of CB8. The spectra are characterized by the presence of positive and negative maxima. The bands at 550 nm and $\lambda > 620$ nm are related to T-T-absorption of dimeric complexes of MTCC with CB8. In the T-T-absorption spectrum of the complex, a shift of the maximum to the long-wavelength region by 25 nm with respect to the T-T-absorption maximum of dimers is observed. The spectrum is similar to the T-T-absorption spectrum of the dimeric complex of TCC with CB8 and the T-T-absorption spectra of polymethine dimers [25]. The lifetime of the triplet state (τ_T) of the dimeric complex is $2.8 \cdot 10^{-4}$ s, coincides with the phosphorescence lifetime and noticeably exceeds τ_T of MTCC dimers.

In the present article, we observed electron transfer between the dimeric complexes of MTCC and TCC with CB8 in the triplet state and electron acceptors — *p*-nitroacetophenone (*p*-NAP) and 1,4-dinitrobenzene (DNB). The conclusion about the participation of the triplet state in the electron transfer reaction follows from the shortening of the triplet state lifetime of the dimer complex when adding an electron acceptor. Figure 8, *a* shows the kinetic curves for triplet state deactivation of dimeric complexes of MTCC with CB8 in the absence and presence of *p*-NAP. The value of the quenching rate constant k_q is $1.4 \cdot 10^9$ l·mol^{-1}s^{-1}. In the course of quenching, in the difference absorption spectrum of MTCC dimer complexes with CB8, a new absorption band appeared at 460 nm, related to the trication radical of MTCC dimer complexes as a result of one-electron oxidation of the MTCC dimer complex (Fig. 8, *b*, insertion). From Fig. 8, *b* it follows that the kinetic curve ΔA consists of three segments: *a–b*, *b–c* and *c–d*. The region *a–b* reflects a fast ($1 \cdot 10^{-8}$ s) increase in ΔA due to the occurrence of T-T-absorption of

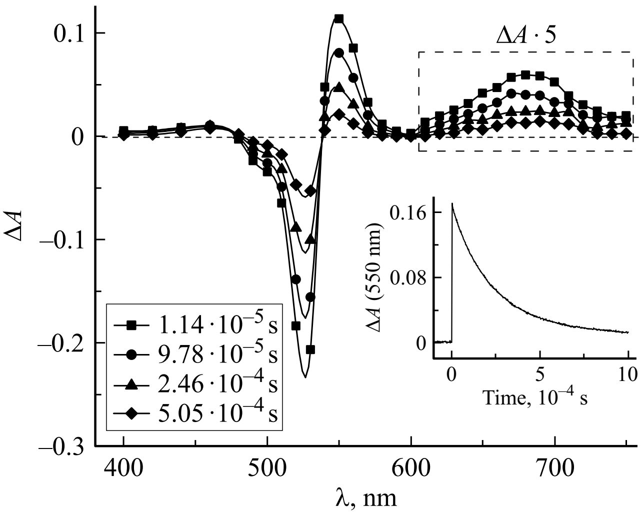


Figure 7. Time-resolved difference T-T-absorption spectra of aqueous solution of MTCC ($1 \cdot 10^{-4}$ mol/l) in the presence of CB8 ($5 \cdot 10^{-5}$ mol/l). In the insertion — the kinetic curve of deactivation of the triplet state of the dye at 550 nm. In the frame — spectra measurement time; in dashed frame — scale-up spectra ($\Delta\lambda = 610$-750 nm).

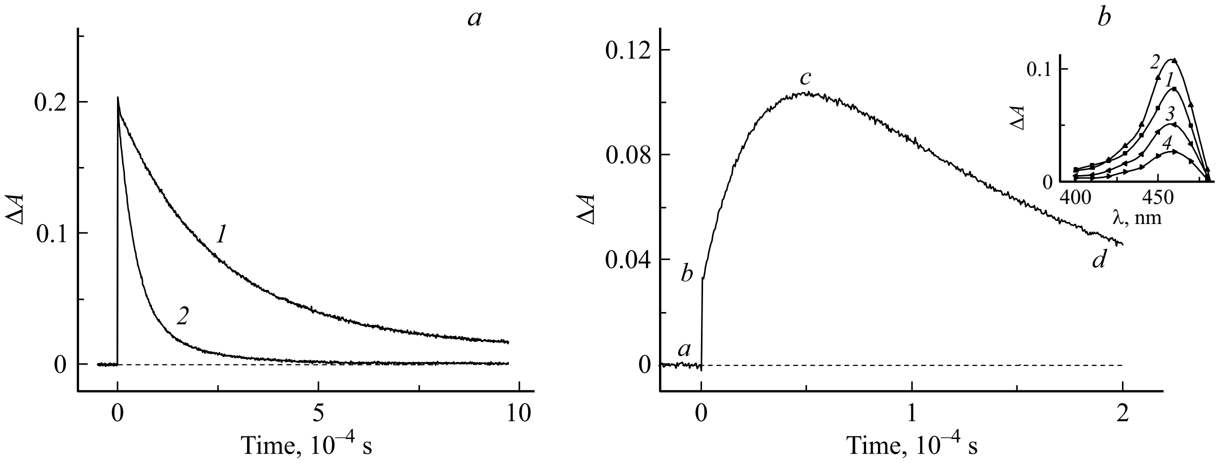


Figure 8. Kinetic curves of deactivation of the MTCC triplet state ($1 \cdot 10^{-5}$ mol/l) in the presence of CB8 ($2.5 \cdot 10^{-5}$ mol/l) at 550 nm (*a*) in the absence (*1*) and in the presence (*2*) of *n*-NAP. Kinetic curves of formation and death of the trication radical of the MTCC dimer in the complex with CB8 at 460 nm in the presence of *n*-NAP (*b*). The concentration of *n*-NAP is $1.2 \cdot 10^{-5}$ mol/l. The insertion shows the absorption spectra of the trication radical of the MTCC dimer complex, measured through $2.9 \cdot 10^{-6}$ (*1*), $1.31 \cdot 10^{-5}$ (*2*), $8.99 \cdot 10^{-5}$ (*3*) and $1.68 \cdot 10^{-4}$ (*4*) s.

dimeric complexes. The section *b–c* reflects a relatively slow ($5 \cdot 10^{-5}$ s) increase ΔA as a result of the electron transfer reaction between dimer complexes in the triplet state and *p*-NAP, leading to formation of a dimeric trication radical $2\text{MTCC}^{3+\bullet}$. The section *c–d* reflects the process of relatively slow decay of $2\text{MTCC}^{3+\bullet}$ with lifetime exceeding $2 \cdot 10^{-4}$ s.

Electron phototransfer occurs in the dimeric complexes of both MTCC and TCC with CB8. In this case, the quenching rate constant of the 2(TCC@CB8) triplet state with *p*-nitroacetophenone is $k_q = 8 \cdot 10^8\,\text{l·mol}^{-1}\text{s}^{-1}$, which is ~ 2 times less than the value k_q for 2(MTCC@CB8). A lower efficiency of photooxidation of dimeric complexes 2(TCC@CB8) compared to dimeric complexes 2(MTCC@CB8) is also observed in the reaction with DNB proceeding with triplet state quenching rate constants $k_q = 3 \cdot 10^9\,\text{l·mol}^{-1}\text{s}^{-1}$ and $k_q = 5.3 \cdot 10^9\,\text{l·mol}^{-1}\text{s}^{-1}$ for 2(TCC@CB8) and 2(MTCC@CB8) respectively.

Thus, the result of the study is discovery of features of the photophysical and photochemical properties of dimeric complexes of MTCC and TCTC with CB8. MTCC enters into the complex formation reaction with CB8 in the *cis*-form, while TCC — in the *trans*-form. Complexes of TCC with CB8 are characterized by the presence of delayed fluorescence, while complexes of MTCC with CB8 exhibit both delayed fluorescence and phosphorescence. The dimeric complexes of MTCC and TCC with CB8 are characterized by a one-electron oxidation reaction in the presence of an exogenous electron acceptor.

Funding

The study was performed with support of the Ministry of Science and Higher Education during works performing under the State Assignment of FSRC „Crystallography and Photonics“ of RAS.

Conflict of interest

The authors declare that they have no conflict of interest.

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