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Photo-sensitized donor-acceptor molecular systems with carbonyl-containing viologen

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The viologen 1,1'-bis[2-(4-methoxyphenyl)-2-oxoethyl]-4,4'-bipyridine-1,1'-diium bromide containing carbonyl units, is studied as an acceptor in photo-sensitized donor-acceptor molecular systems formed in liquid solutions. The photo-electrical properties of the molecular systems are examined by impedance measurements. The results obtained show a photo-electrical response of the viologen-containing donor-acceptor complexes that may be of interest for solar energy utilizing.

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1. Introduction

Viologens and various their derivatives are very attractive for light conversion applications, where the reversible electron transfer (ET) and the redox properties of these compounds are widely exploited [1–5]. In particular, in view of the need of efficient energy saving and conservation, the research on viologen-constituted photoelectro-chemical systems and materials, particularly photoactive in the visible ET Donor-Acceptor (DA) systems, is of special interest for solar energy technology and applications of concentrated photons [1,6,7]. Photolytic excitation of complexes formed from viologen (acceptor) and electron-donating molecule can result in ET and in a formation of photo-generated free radicals (Fig. 1). A recombination of the D-A radical ion pair ($D^{\cdot+}/A^{\cdot-}$) and spontaneous ET can turn the system back to its ground state. Thus, both processes are related to the well known reversible intramolecular ET mechanism [8] controlled by the viologen molecule [1,2].

The photochemistry of the DA complexes on the base of viologen derivatives in the solutions and solid state has been investigated in detail over many years. Upon visible light illumination, such molecular systems containing viologens are able to absorb a considerable amount of energy, e.g. 60 – 70 kcal.mol^{-1}, and the energy stored by formation of ion radicals can be significant, e.g. of about 20 kcal.mol^{-1} [9,10]. As known, the energy balance of the reversible photo-reaction (Fig. 1) depends on the donor ionization potential, electron affinity of the electron acceptor, as well as on the electronic energy of both ground and excited states of the ETDA complex [8,11,12].

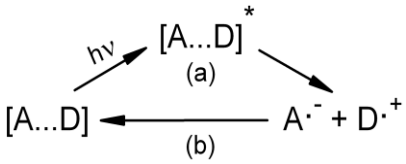

Fig. 1. Schematic illustrating the reversible electron transfer after a photolytic excitation of ground-state charge-transfer DA complex, in which the acceptor molecule (A) is a viologen compound: (a) light-induced electron - transfer reaction; (b) spontaneous back-electron- transfer at darkness.

In a preliminary study [13] we reported on the synthesis and characterization of modified 1,1'-disubstituted 4,4'-bipyridinium viologens aimed to be employed as electron acceptor molecules in photochemical ETDA systems for combined solar energy conversion and storage. The 1 and 1' substituents include simple aromatic rings and alkyl groups, as well as carbonyl groups. The inclusion of the polar C=O groups in the molecular structure of the viologen molecule gives rise to the charge separation and stabilization of viologen in polar media [14]. Moreover, one can expect that the electron-attracting properties of carbonyl group should enhance the electron affinity of the viologen. In the present study, we deal with such a carbonyl-containing viologen, namely 1,1'-bis[2-(4-methoxyphenyl)-2-oxoethyl]-4,4'-bipyridine-1,1'-diium bromide. Photo-electrical properties of DA molecular systems based in this viologen are reported, as probed under light illumination close to solar irradiation conditions.

2. Experimental

The synthesis and characterization of the viologen 1,1'-bis[2-(4-methoxyphenyl)-2-oxoethyl]-4,4'-bipyridine-1,1'-diium bromide (Fig. 2) have been reported elsewhere [13]. Briefly, this compound was prepared in an anhydrous *N*,*N*-dimethylformamide (DMF) under nitrogen atmosphere by the reaction of 4,4'-bipyridine with 1-(4-methoxyphenyl)-2-chloethan-2-one solved in dried DMF. The temperature of reaction was kept at 20° C, the yield was 78.4 %. Aromatic rings and methyl groups, as well as carbonyl groups, were introduced into the symmetrical molecular structure of the viologen. The produced viologen exhibited photophysical properties suitable for light-conversion applications [13]. The compound was stable and highly soluble in water, ethanol and other protic polar solvents, as well as in dipolar aprotic solvents, such as DMF and acetonitrile (CH_3CN). Also, the viologen was stable upon solar irradiation conditions.

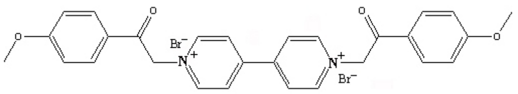

Fig. 2. Chemical structure of the carbonyl-containing viologen 1,1'-bis[2-(4-methoxyphenyl)-2-oxoethyl]-4,4'-bipyridine-1,1'-diium bromide.

Three molecular complexes were studied in liquid solutions. The synthesized viologen was complexed with two aromatic amines, namely *o*-phenylenediamine and 1-naphthylamine (Aldrich). These compounds were used as donors because of the strong electron-donating ability owing to the amino group. Electron DA systems constituted from viologens and amines exhibit an efficient and reversible ET, e.g., like the one reported for an equilibrium mixture of l,l'-dimethyl-4,4'-dipyridinium dichloride and *p*-phenylenediamine [9]. Despite of the lack of electron-donating properties, benzophenone was also probed as a component of a photo-sensitized electron-transfer viologen-containing molecular system. The molecular complexes were build by mixing of solutions of the viologen and the second component. Aqueous CH_3CN (a mixture of CH_3CN and singly distilled water in a volume/volume ratio of 9:1) was used as a solvent. The effect of the aqueous CH_3CN on the energy balance of viologen/aminoaromatics DA systems in solutions has been established [9]. Being highly polar [19], this solvent should affect the ionization of the electron acceptor and the efficiency of the electronic transition and energy transfer process in DA solutions [12].

The photo-electrical response of the formed molecular systems was studied by impedance measurements on a Pt/EDA/Pt assembly using a computer-controlled multi-frequency LCR Meter HP 4274A. A voltage of 2 mV at frequency 100 kHz was applied on the platinum electrodes. The DA systems in solutions were illuminated with a white light (continuos 25 W tungsten filament lamp) passing through a Schott Glass bandpass filter GG495 (cut-off at 500 nm). The steady illumination was done for periods of ten minutes alternated with equal dark periods. All experiments in this work were carried out at room temperature.

3. Results and discussion

Being uncomplexed, the viologen compound and the second component of the molecular systems exhibited an ultraviolet absorption. Dissolved at concentration of 1.0×10^{-3} M in $CH_3CN:H_2O$ (9:1 vol/vol), the absorption maxima were as follows: 290 nm for the viologen, 253 nm for benzophenone, 300 nm for *o*-phenylenediamine, and 330 nm for 1-naphthylamine. Upon mixing the components, a molecular complex is formed whose absorption band appears in the visible. For example, Fig. 3 compares the absorption spectra of viologen, 1-naphthylamine and that of the composed DA complex. The latter is characterized by an absorption band with a maximum at ~ 555 nm which is widely red-shifted from the electronic absorption bands of the uncomplexed components.

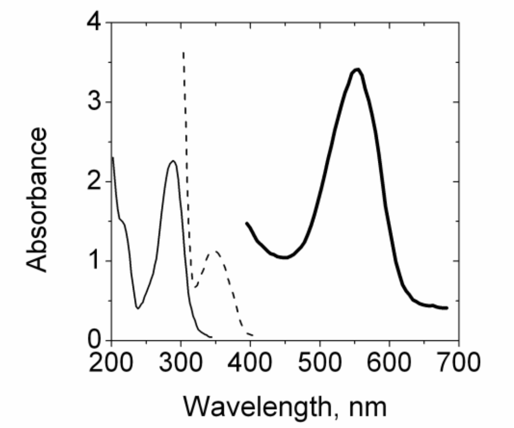

Fig. 3. Absorption spectra (20 ℃) of 1-naphthylamine (2×10^{-2} M in CH_3CN) (dashed line) and carbonyl viologen 1,1'-bis[2-(4-methoxyphenyl)-2-oxoethyl]-4,4'-bipyridine-1,1'-diium bromide at concentration 1.0×10^{-3} M in $CH_3CN:H_2O$ (9:1 vol/vol) (thin line). The absorption of DA charge-transfer complex formed from the viologen and 1-naphthylamine is shown with bold line.

The absorption bands of the other molecular complexes examined in the present work (Table 1) were also in the region of maximum solar intensity at the wavelength of yellow-green light, 500 – 600 nm, and did not overlap the absorption bands of isolated viologen and the second component.

Next we probed the ability of the molecular complexes in solutions to operate as photoactive systems upon repeated solar illumination. To examine the photo-induced charge separation and the reversibility of the electronic transition of the complexes, their photo-electrical response was studied by impedance measurements upon the alternation of illumination ($\lambda >$

500 nm) and dark. The electrical photocurrent measurements clearly indicate a reversible photo-electrical effect (Fig. 4). Further, one can compare the conductivity (Fig. 5 a) and capacitance (Fig. 5 b) of the solutions measured under the same conditions. Since the capacitance exhibits a negligible effect from the illumination, the reversible response of the illuminated complexes follows the conductivity component of the photo-induced current. Therefore, the photocurrent is due to photo-excitation into the new electronic band arising (charge-transfer (CT) band). The photoactive state should be the excited state from which electron transfer occurs (the CT state). Most probably, it is the first singlet state of the complex [9].

Table 1

Donor compound	Molar ratio D : A	λ_{max} [nm]	$E_{S0 \rightarrow S1}$ [kcal/mol]	σ_0 [μS]	$k_1 \times 10^{-3}$ [sec^{-1}]	$k_2 \times 10^{-3}$ [sec^{-1}]
1-Naphthylamine	1 : 2			130.12	4.84	3.02
				(0.09)	(0.12)	(0.04)
	1 : 1	555	51.6	143.6	5.52	3.39
				(0.1)	(0.12)	(0.14)
	2 : 1			231.12	4.8	3.3
				(0.23)	(0.13)	(0.19)
Benzophenone	1 : 1	575	49.8	129.93	6.83	3.05
				(0.04)	(0.1)	(0.18)
o-Phenylenediamine	1 : 1	582	49.2	175.77	5.52	3.32
				(0.14)	(0.16)	(0.19)

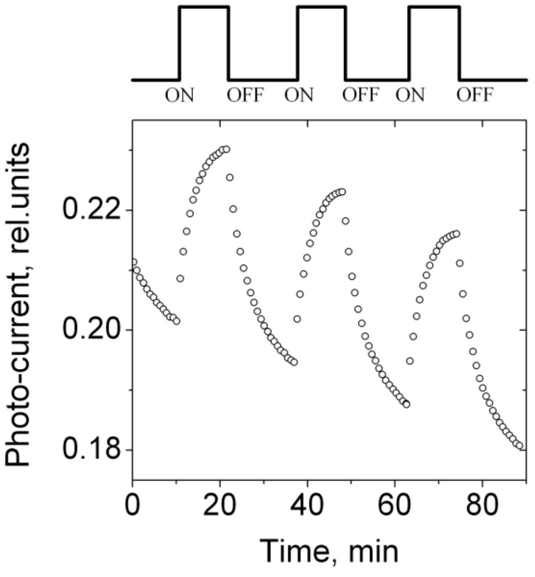

Fig.4. The photo-reversibility of electron DA complex formed from 1-naphthylamine and carbonyl viologen, both dissolved in $CH_3CN:H_2O$ (9:1 v/v) at concentrations 2.0 × 10^{-3} M and 1.0 × 10^{-3} M, respectively. The temperature was 22 °C. The illumination (white light, $\lambda > 500$ nm) is periodically switched-on and -off as shown on the top.

The photo-electrical measurements allows to be derived quantitative characteristics of photo-induced electrical response of the examined molecular systems, such as the stationary value of conductivity (σ_0) responsible for a complete energy-transfer process, as well as the rate constants (the increase rate constant, k_1, and the decay rate constant, k_2). Since the temporal variation of the conductivity of the measured systems was exactly fitted by a simple mono-exponential function, these characteristics can be readily evaluated (Table 1). The optimal photo-electrical response renders the high σ_0 and low values for the rate constants.

One can compare the effect of the donor component on the photo-induced conductivity and energy-conversion characteristics of ETDA systems having identical Donor-to-Acceptor (D:A) molar ratio. For the experimental results presented in Fig. 5 (a), this ratio was 1:1. As expected, the donor ability considerably affects the photo-induced energy transfer and photo-electrical properties of the ETDA systems. The donor ability can be related to the energy difference ($E_{S0 \rightarrow S1}$) between the ground and first excited singlet state of the DA complex.[11] The lower $E_{S0 \rightarrow S1}$ of a DA complex implies a better donor ability what improves the conductivity and the performance of the ETDA systems. It is seen from the obtained σ_0 (Table 1) that the donor *o*-phenylenediamine does form with the viologen a more efficient ETDA system than 1-naphthylamine.

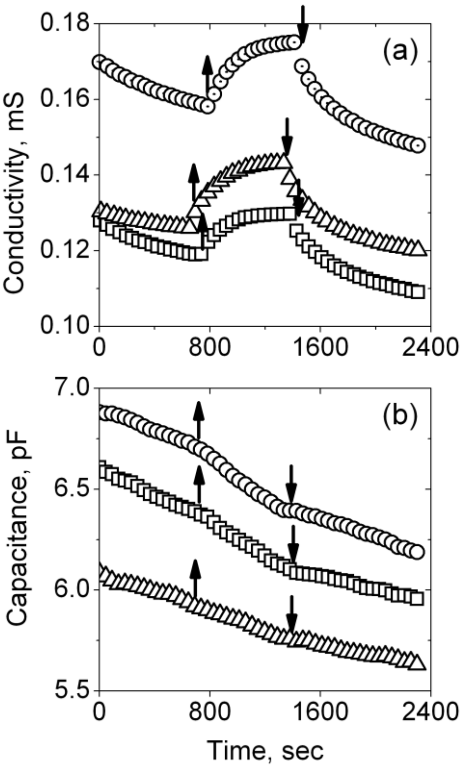

Fig.5. Time courses of the electrical conductivity (a) and capacitance (b) measured for molecular complexes upon switching-on (the up-arrows) and switching-off (down-arrows) of the illumination. The complexes formed in $CH_3CN:H_2O$ (9:1 v/v) are: o-phenylenediamine/viologen (circles); 1- naphthylamine/viologen (triangles) and benzophenone/viologen (squares). The viologen concentration was 1.0×10^{-3} M, the Donor-to-Acceptor molar ratio was 1:1 in the three cases, the temperature 22 °C.

Furthermore, the results for σ_0 correspond to the above mentioned relationship based on the $E_{S0\rightarrow S1}$ energy parameter and confirm that the energy transfer originates from a CT singlet state of the DA complexes. It should be noted that the kinetics of the processes shows that the reverse process (the charge recombination of the D-A radical ion pair ($D^{\cdot+}/A^{\cdot-}$) which occurs spontaneously, takes place in a longer time-scale ($k_2 < k_1$) indicating that a photo-sensitized energy-transfer cycle is achieved. This property is a premise for an efficient solar energy conversion. However, it should be noted the presence of some instability in the photo-electrical response of the examined molecular system, that may be a serious drawback for the energy conversion. For example, a 10 % decrease (from 0.20 to 0.18) of the intensity in three photocurrent cycles (in 80 min) was observed in the photocurrent experiment (recall Fig. 4). Most probably these changes are due to charge recombination. Another reason of the photocurrent decrease at each photochemical cycle could be the irreversible oxidation of the donor molecules.

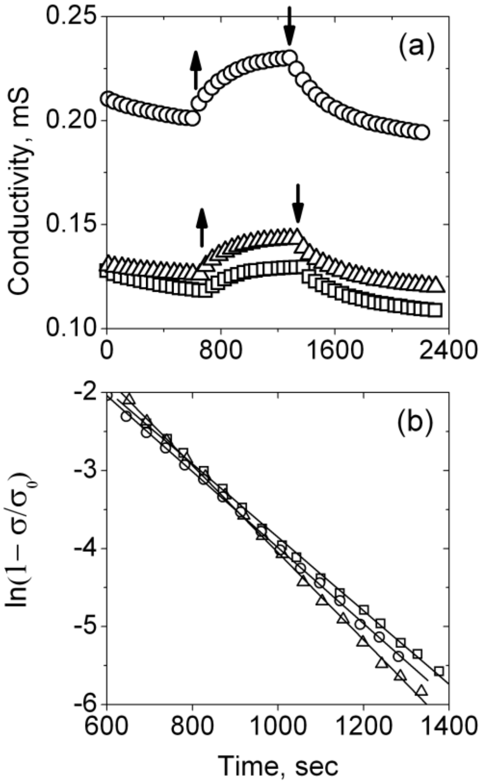

Fig.6. (a) The photo-electrical response of DA complexes formed from 1-naphthylamine and carbonyl viologen at various Donor-to-Acceptor molar ratio: 1:2 (squares), 1:1 (triangles) and 2:1 (circles) (all at 22 °C). The up-arrows indicate the switching-on of the illumination, the down-arrows – the switching-off. (b) Comparison of the time dependence of the relative change of the light-induced conductivity of these ETDA systems.

Generally, the stable photo-electrical response of ETDA system is defined from the stability of both viologen and viologen radical. Such a stability is attributable to the delocalization of the electrons throughout the π-framework of the vilogen molecule (radical). The inclusion of carbonyl groups in the symmetrical molecular structure of the viologen 1,1'-bis[2-(4-methoxyphenyl)-2-oxoethyl]-4,4'-bipyridine-1,1'-diium bromide between the 4,4'-bipyridinic units and phenyl rings gives rise to the stability of both viologen and viologen radical [14] and thereby improves the performance of ETDA systems formed by use of such a viologen compound.

By varying the D:A molar ratio, the photo-induced electrical response of the ETDA systems in solutions can be considerably changed. Fig. 6 (a) represents the photocurrent measured for 1-naphthylamine/viologen D-A pair at three values of this ratio (1:2, 1:1 and 2:1). In this case, the values of σ_0 (Table 1) indicate that the photo-excitation leads to a charge carriers generation whose efficiency increases with the increasing D:A molar ratio. Accordingly, the performance of the ETDA system is also improved. This result implies a correlation between the charge-transfer rate and the carrier concentration. Indeed, the time dependence of the relative change of the photo-induced conductivity of the examined DA systems at various D:A molar ratio was an exactly exponential function (Fig. 6 b), like a typical current-concentration dependence of a dilute electrolyte.

4. Conclusions

The results show that using suitable electron donor, photo-sensitized donor-acceptor systems can be formed by the carbonyl-containing viologen proposed here. The stable and highly soluble viologen compound 1,1'-bis[2-(4-methoxyphenyl)-2-oxoethyl]-4,4'-bipyridine-1,1'-diium bromide exhibits a significant photoactivity in solutions upon visible light illumination. Since the photo-excitation into the charge-transfer band of donor-acceptor complexes based on this viologen can be achieved with light in the region of maximum solar intensity, such photoactive molecular systems might have application in solar energy conversion and storage systems (by storing solar energy in the form of chemical products).

References

[1] P. M. S. Monk, The Viologens: Physicochemical Properties, Synthesis and Applications of the Salts of 4,4'- Bipyridine, John Wiley & Sons, Ltd., Chichester (1998).

[2] M. Nanasawa, in: J. C. Crano, R. J. Guglielmetti (eds.), Organic Photochromic and Thermochromic Compounds, Topics in Applied Chemistry, Vol. 1, Main Photochromic Families, Plenum Press, New York (1999), p. 341.

[3] E. Ziomek, W. G. Martin, R. E. Williams, in: V. T. D'Souza, J. Feder (eds.), The Bioorganic Chemistry of Enzymatic Catalysis: An Homage to Myron L. Bender, CRC Press, Boca Raton (1992), p. 185.

[4] K. Kuwabara, in: M. Zafar, A. Munshi (eds.), Handbook of Solid State Batteries & Capacitors, World Scientific Pub., Singapore (1995), p. 555.

[5] R. J. Lin, M. Kaneko, in: K. Sienicki (ed.), Molecular Electronics and Molecular Electronic Devices, Vol. I, CRC Press, Boca Raton (1992), p. 207.

[6] J. Rabani, in: E. Pelizzetti, M. Schiavello (eds.), Photochemical Conversion and Storage of Solar Energy: Proceedings of the Eighth International Conference on Photochemical Conversion and Storage of Solar Energy, Kluwer, Dordrecht (1991), p. 103.

[7] N. J. Turo, J. K. Barton, D. Tomalia, in: E. Pelizzetti, M. Schiavello (eds.), Photochemical Conversion and Storage of Solar Energy: Proceedings of the Eighth International Conference on Photochemical Conversion and Storage of Solar Energy, Kluwer, Dordrecht (1991), p. 121.

[8] J. S. Connoly, J. R. Bolton, in: M. A. Fox, M. Chanon (eds.), Photoinduced Electron Transfer, Elsevier, Amsterdam (1988), part D, p. 303.

[9] A. T. Poulos, C. K. Kelley, R. Simone, J. Phys. Chem. **85**, 823 (1981).

[10] J. G. Carey, J. F. Cairns, J. E. Colchester, J. Chem. Soc. D: Chem. Commun. 1280 (1969).

[11] R. S. Mulliken, W. B. Person, Molecular Complexes: A Lecture and Reprint Volume, Wiley-Interscience, New York (1969).

[12] Y. Nishimura, H. Misawa, H. Sakuragi, K. Tokumaru, Chem. Lett. **18**, 1555 (1989).

[13] N. Kirov, Ts. Philipova, M. Hadjieva, K. Ivanova, G. B. Hadjichristov, Compt. Rend. Acad. Bulg. Sci. **62**, 433 (2009).

[14] V. Ya. Shafirovich, E. E. Batova, P. P. Levin, in: E. Pelizzetti, M. Schiavello (eds.), Photochemical Conversion and Storage of Solar Energy: Proceedings of the Eighth International Conference on Photochemical Conversion and Storage of Solar Energy, Kluwer, Dordrecht (1991), p. 47.

[15] T. Ohba, S. Ikawa, Mol. Phys. **73**, 985 (1991).

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