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ARTICLES

Tuning the Charge-Separated Lifetimes of Ruthenium(II)polypyridyl-Viologen Dyads and Ruthenium(II)polypyridyl-Viologen Triads by the Formation of Supramolecular Assemblies with Crown Ethers

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The synthesis and photophysical properties of a ruthenium dyad (**4**) and triad (**5**) are reported. Both biomimetic systems are physical models for the photosynthetic reaction center. They consist of a ruthenium(II)-polypyridyl sensitizer featuring chemically attached 3,3′-dimethyl-4,4′-viologen and 4,4′-viologen electron acceptors. The binding of the chemically attached electron acceptors by the three structurally different crown ethers, $DB_{30}C_{10}$, BBO_5O_5, and AAO_5O_5, offers a remarkable tool for the enhancement of the lifetimes of the charge separated states (τ_{CS}), up to a factor of 2×10^4. The drastic increase in the lifetimes observed can be explained by a decrease in the reorganization energy λ due to the presence of the crown ether units bound to the viologen acceptor.

Introduction

A large number of covalently linked dyads and triads of varying geometry and rigidity, equipped with electron donors and acceptors capable of photoinduced electron transfer, have been explored as models for the photosynthetic reaction center (RC).[1−5] Such *D−A, *D−A_1−A_2, and D−*D−A (*D = photoexcited donor; D = donor; A, A_1, A_2 = acceptors) structures are schematically shown in Figure 1,[6−11] where in many cases *D is a Ru(II) diimine complex.[12−20] Whereas many systems are aimed at structural models for the photosynthetic reaction center, some were especially designed to achieve long lifetimes of the charge separated states formed upon photoexcitation. Possible future uses of these donor−acceptor assemblies include solar energy conversion[21,22] and in biomedical applications.[23]

The work presented here is concerned with the tuning of the photophysical properties of two ruthenium-polypyridyl-based covalently linked assemblies, one dyad and one triad, by supramolecular complexation with three crown ethers, which differ in size and structure. The implications of our work can be most easily understood in analogy to the photosynthetic reaction center. Therefore, we will discuss it accordingly.

A remarkable feature of the photosynthetic reaction center (RC) lies in its utilization of only one of the two nearly identical electron transfer (ET) pathways available from the excited state of the special pair to the Q_A and Q_B quinone acceptors[24,25] (Figure 1).

Although supramolecular donor/acceptor systems have proven useful in the investigation of long-lived charge separation, only a few can be utilized in the modeling of the dual ET pathways found in the reaction center.[24] These systems possess two chemically identical acceptors tethered to the donor, A−*D−A (Figure 2 a,b), thus providing a bifurcated pathway for the photoinduced electron transfer. One A−*D−A supramolecular assembly previously reported is of particular importance owing to the similarity in the spatial arrangement of the donor and acceptors compared to that in the RC.

We investigated the photophysical behavior of a bifurcated dyad, $[Ru(dmbpy)_2(di\text{-}V^{2+}\text{-}bpy)]^{6+}$ (dmbpy = 4,4’-dimethyl-2,2’-bipyridine), and a triad, $[Ru(dmbpy)_2(di\text{-}(dmV^{2+}\text{-}V^{2+}\text{-}bpy)]^{10+}$. Both extended ruthenium(II) complexes are of the type $[Ru^{II}(dmbpy)_2(di\text{-}X\text{-}bpy)]^{4+}$, where the structure of ligand di-X-bpy in the complex is shown in Figure 3 and possesses either

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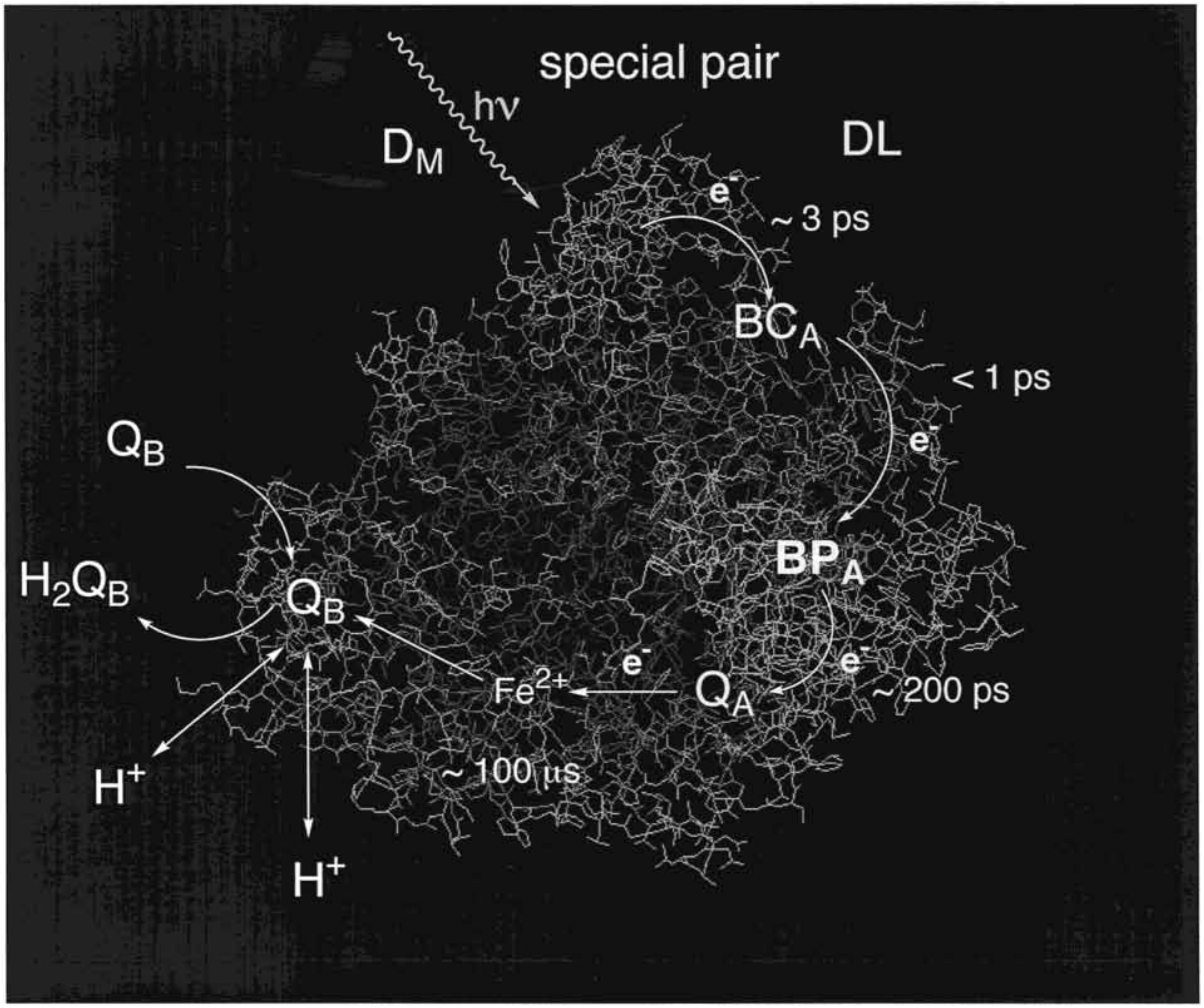


Figure 1. Reaction center (blue) of *Rhodobacter sphaeroides* including protein matrix (a) and simplified reaction center compounds (b) (D_M and D_L and B_{CA} and B_{CB} = bacterio chlorophylls, BP_X and BP_B = phycophytins, Q_A and Q_B = quinones).

a chain of two 4,4′-dialkyl viologens, in case of the dyad, or two linked 3,3′-dimethyl-4,4′-dialkyl viologen-4,4′-dialkyl viologens when the triad is employed.[26] UV-absorption and fluorescence data of **4** and **5** are summarized in Table 1.

The binding of the chemically attached 4,4′-dialkyl viologen units at the end of the branches of the dyad and the triad by three different crown ethers creates a series of physical model systems for the photochemical reaction center and allows a comparison of electron transfer rates in the presence and absence of the crown ethers. Here we present the tuning of the observed lifetimes of the charge-separated states of the ruthenium dyad (**4**) and the ruthenium triad (**5**) by interaction with the three crown ethers $DB_{30}C_{10}$ (**6**), BBO_5O_5 (**7**), and AAO_5O_5 (**8**) (Figure 4). The goal of this work consists of the design of a long-lived artificial model system for the photosynthetic reaction center.

Experimental Section

Chemicals. All reagents were purchased from Aldrich, all solvents from Fluka, except ethanol (Roth).

Synthesis. The synthesis of (**4**) is described below (Scheme 1); that of (**5**) has been published.[27]

4,4′-Bis[(4,4′-bipyridinium-1-ethylcarboxylic acid)] Bromide (1). A 2.00 g (1.04×10^{-2} mol) amount of 4,4′-bipyridine dihydrate was dissolved in toluene (30 mL) at 90 °C. Then 2.00 g of 3-bromopropionic acid (1.31×10^{-2} mol), dissolved in toluene (10 mL), was added dropwise over 5 h. The reaction mixture was stirred at 60 °C for further 12 h. The reaction product, 4,4′-bis[(4,4’-bipyridinium-1-ethylcarboxylic acid)] bromide (**1**) precipitated slowly. The yellow precipitate was filtered off from the hot mother liquor, washed twice with hot toluene, and then with diethyl ether at room temperature.

4,4′-Bis[(4,4′-bipyridinium-1-ethylcarboxylic acid)] Hexafluorophosphate (2). Compound (**1**) was dissolved at 293 K in as little H_2O as possible and then added dropwise to a saturated solution of NH_4PF_6 (10 mL). The colorless precipitate was filtered off and then washed three times with H_2O. After drying overnight at 313−320 K, a yield of 2.55 g (65%) of (**2**) (mp 178 °C) was obtained. ^1H NMR(d^6-DMSO): $\delta = 3.13$ (t, $^3J = 6.7$ Hz, 2H); 4.83 (t, $^3J = 6.7$ Hz, 2H); 8.03 (d, $^3J = 6.0$ Hz, 2H); 8.62 (d, $^3J = 6.2$ Hz, 2H); 8.87 (d, $3J = 6.0$ Hz, 2H); 9.23 (d, $^3J = 6.4$ Hz, 2H) ppm. ^{13}C NMR (d^6-DMSO): $\delta =$ 34.29; 56.08; 121.98; 124,94; 125.10; 140.90; 145.74; 145.95; 150.76; 151.02; 152.48; 171.54 ppm. $C_{13}H_{13}N_2O_2PF_6$ (374.23 g mol^{-1}) calc.: C, 41.72; H, 3.50; N, 7.49. Found: C, 41.67; H, 3.60; N, 7.55.

4,4′-Bis[(4,4′-bipyridinium-1-ethylcarboxylic acid-1′-yl)-methyl]-2,2′-bipyridine Hexafluorophosphate (3). A 1.00 g (2.70×10^{-3} mol) amount of (**2**), dissolved in DMF (10 mL), was heated under N_2 to 120 °C. Then, 0.35 g (1.00×10^{-3} mol) of 4,4′-bis(bromomethyl)-2,2′-bipyridine,[27] dissolved in DMF (10 mL), was added dropwise. The reaction mixture was stirred at 120 °C for 12 h. The lemon yellow precipitate was filtered off the

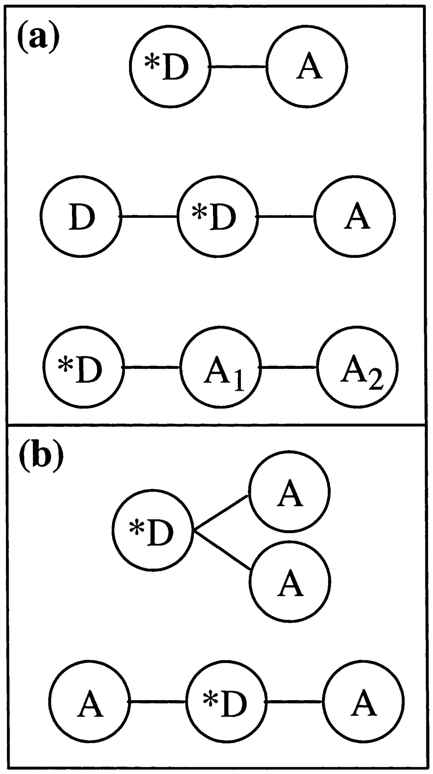
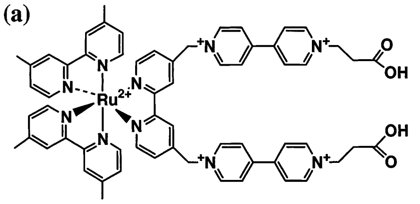
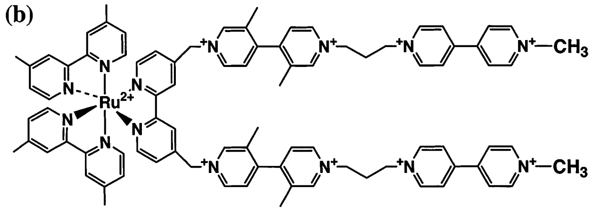


Figure 2. General schemes of photoelectron-transfer assemblies: (a) monodirectional; (b) bifurcated.



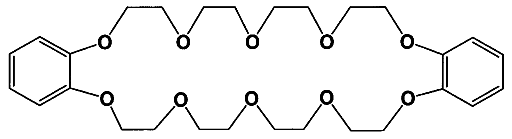
$[Ru(dmbpy)_2(di\text{-}V^{2+}\text{-}bpy)]^{6+}$ (**4**)



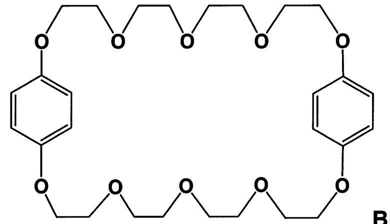
$[Ru(dmbpy)_2(di\text{-}(dmV^{2+}\text{-}V^{2+}\text{-}bpy))]^{10+}$ (**5**)

Figure 3. Ruthenium dyad (**4**): $[Ru(dmbpy)_2(di\text{-}V^{2+}\text{-}bpy)]^{6+}$ and ruthenium triad (**5**): $[Ru(dmbpy)_2(di\text{-}(dmV^{2+}\text{-}V^{2+}\text{-}bpy)]^{10+}$ were employed in our experiments.

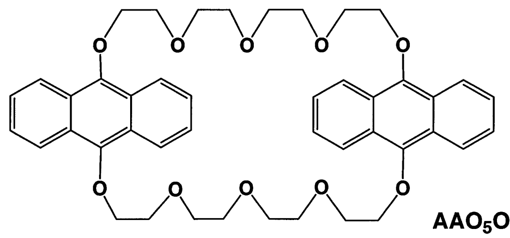
hot mother liquor and washed three times with cold DMF/toluene (50:50, v/v). The dry precipitate was then dissolved in H_2O and precipitated as hexafluorophosphate as already described in the synthesis procedure for (**2**). A 0.52 g (yield: 43%) sample of the colorless precipitate (**3**) (mp 239 °C) was obtained. ^{1}H NMR (d^6-DMSO): $\delta = 3.16$ (t, $^3J = 6.4$ Hz, 4H); 4.90 (t, $^3J = 6.4$ Hz, 4H); 6.10 (s, 4H); 7.59 (d, $^3J = 4.8$ Hz, 2H); 8.61 (s, 2H); 8.74 (d, $^3J = 6.4$ Hz, 4H); 8.79 (d, $^3J = 4.8$ Hz, 2H); 8.81 (d, $^3J = 6.6$ Hz, 4H); 9.38 (d, $^3J = 6.4$ Hz, 4H); 9.55 (d, $^3J = 6.6$ Hz, 4H) ppm. ^{13}C NMR (d^6-DMSO): $\delta = 34.29$; 56.67; 62.11; 120.33; 123.77; 126.22; 127.16; 143.93; 146.11; 146.23; 148.68; 149.43; 150.21; 155.34; 172.33 ppm. $C_{38}H_{36}N_6O_4P_4F_{24}$ (374.23 g mol^{-1}) calc.: C, 37.39; H, 2.97; N, 6.89. Found: C, 37.54; H, 3.14; N, 6.99.



$DB_{30}C_{10}$ (**6**)



BBO_5O_5 (**7**)



AAO_5O_5 (**8**)

Figure 4. Crown ethers employed in this work: (**6**) $DB_{30}C_{10}$; (**7**): BBO_5O_5; (**8**): AAO_5O_5 to be bound to the viologen subunits.

*Bis(4,4′-dimethyl-2,2′-bipyridine)(4,4′-bis[(4,4′-bipyridinium-1-ethylcarboxylic acid-1′-yl)-methyl]-2,2′-bipyridine) Ruthenium(II) Hexafluorophosphate (**4**).* A 0.20 g (3.0×10^{-4} mol) portion of (**3**) and a 0.14 g (3.0×10^{-4} mol) portion of *cis*-bis(4,4′-dimethyl-2,2′-bipyridine) ruthenium(II) dichloride[27] were dissolved in EtOH/H_2O (50:50 v/v, 70 mL) and stirred at 90 °C under N_2 in the dark. The solvent was removed in a vacuum. The dark residue was dissolved in H_2O and filtered. The filtrate was then extracted using CH_2Cl_2 (30 mL). The extraction procedure was repeated until the CH_2Cl_2 phase was colorless. The water phase was removed in a vacuum and then redissolved using H_2O (2 mL). The reaction product was purified by descending column chromatography employing silica gel ($d = 1$ cm, $l = 10$ cm) and a mixture of MeOH, H_2O, and saturated NH_4Cl in H_2O (4:5:1, v/v/v) as the mobile phase. The purified product was evaporated in vacuum and dissolved in 2-propanol (5 mL). NH_4Cl was removed by filtration. 2-Propanol was removed in vacuum. The red residue was dissolved in H_2O (1 mL) and further purified by column chromatography employing Sephadex G-15 as stationary and H_2O as mobile phases. Finally, the red product was precipitated as hexafluorophosphate according to the synthesis procedure for (**2**) to give 0.27 g (53%) yield (mp > 252 °C (dec)). ^{1}H NMR (d^6-DMSO): $\delta = 2.52$ (s, 12 H); 3.11 (t, $^3J = 6.1$ and 5.8 Hz, 4H); 4.86 (t, $^3J = 5.8$ and 6.1 Hz, 4H); 5.95 (s, 4H); 7.21 (m, 4H); 7.42 (d, $^3J = 6.1$ Hz, 2H); 7.46 (d, $^3J = 5.5$ Hz, 2H); 7.49 (d, $^3J = 5.6$ Hz, 2H); 7.84 (d, $^3J = 6.1$ Hz, 2H); 8.35 (m, 8H); 8.41 (d, $^3J = 6.6$ Hz, 4H); 8.60 (s, 2H); 9.01 (d, $^3J = 6.5$ Hz, 4H); 9.05 (d, $^3J = 6.6$ Hz, 4H) ppm. ^{13}C NMR (d^6-DMSO): $\delta = 21.22$; 35.05; 58.69; 63.41; 125.91; 125.56; 127.89; 128.76; 128.30; 129.31; 142.86; 147.12; 147.40; 151.00; 151.57; 151.85; 152.00; 151.41; 152.09; 153.42; 157.26; 157.34; 158.67; 171.73 ppm. $C_{74}H_{84}N_{10}O_4RuP_6F_{36}$ (2148.41 g mol^{-1}) calc.: C, 41.37; H, 3.94; N, 6.52. Found: C, 41.51; H, 4.13; N, 6.61.

Synthetic steps for the preparation of compound (**4**): (a) in toluene, heat; (b) in water; saturated aqueous solution of NH_4PF_6; (c) DMF, heat; (d) saturated aqueous solution of NH_4PF_6; (e) in ethanol/water (50:50,v/v), heat. The overall yield was found to be ca. 15%.

SCHEME 1

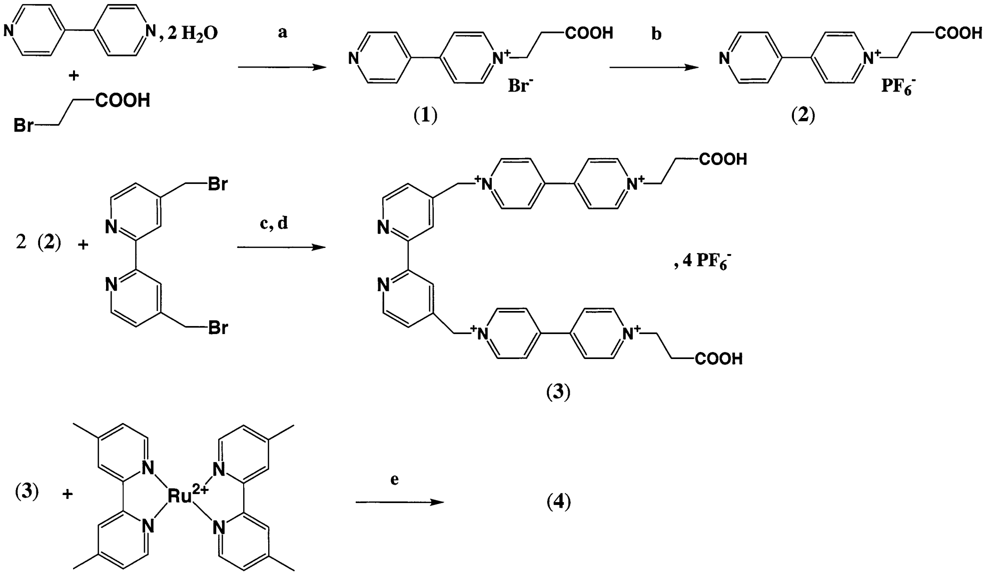


TABLE 1: Absorption and Emission Parameters of $[\mathrm{Ru(dmbpy)_2(di\text{-}V^{2+}\text{-}bpy)}]^{6+}$ (4) and $[\mathrm{Ru(dmbpy)_2(di\text{-}(dmV^{2+}\text{-}V^{2+}\text{-}bpy))}]^{10+}$ (5)

Ru(II) complex	MLCT$_1$ [nm]	lg ϵ	MLCT$_2$ [nm]	lg ϵ	λ_{ex} [nm]	λ_{em} [nm]	ϕ_l
(**4**)	477	4.19	449	4.17	466	642	0.0005
(**5**)	437	4.08			461	621	$<10^{-5}$

Bis(4,4′-dimethyl-2,2′-bipyridine)(4,4′-bis[(3,3′-dimethyl-4,4′-bipyridinium-1-propyl-1”-4,4’-bipyridinium-1′”-methyl-1′-yl)-methyl]-2,2′-bipyridine) Ruthenium(II) Hexafluorophosphate (5). This compound was synthesized according to published procedures.[27] The dibenzo-crown ether (**6**) (dibenzo-30-crown-10, $\mathrm{DB_{30}C_{10}}$) was purchased from Aldrich. Compound (**7**), (1,4,-10,13,20,23,26,29,32-decaoxa[13.13])-(1,4)-benzophan, $\mathrm{BBO_5O_5}$, was prepared following a published procedure.[28a] Compound (**8**) (1,4,10,13,20,23,26,29,32-decaoxa[13.13])-(9,10)-anthracenophan, $\mathrm{AAO_5O_5}$, was synthesized according to a procedure previously published.[28b]

Instrumentation. *Electrochemical Equipment and Experimental Conditions*. All electrochemical experiments were performed using a computer controlled EG&G Princeton Applied Research potentiostat/galvanostat (model 263A) and the EG&G M270 software. $\mathrm{Ru(bpy)_3Cl_2/Ru(bpy)_3(ClO_4)_2}$ was used as an electrochemical standard.[29] Cyclic voltammograms and differential pulse voltammograms (DPV, 50 mV pulse height) were taken using a glassy carbon working electrode vs SSCE reference electrode (sodium saturated calomel electrode) and a platinum sheet auxiliary electrode. All measurements were performed in 0.50 M $\mathrm{Na_2SO_4}$ in water.

Laser Instrumentation and Experimental Conditions. For the recording of laser transients, an EAI/LP900S1 nanosecond laser flash system (Edinburg Analytical Instruments Ltd.) Nd:YAG pulse width ~4 ns was employed. All laser measurements were performed in acetonitrile (HPLC grade). The ruthenium dyads (**4**) and triads (**5**) were HPLC purified prior to taking the photophysical measurements. The optical density at the excitation wavelength ($\lambda = 532$ nm) was 0.10 in 1 cm quartz cuvettes ($c \approx 2 \times 10^{-5}$ M) unless otherwise noted. The crown ethers (**6**), (**7**), and (**8**) were added from stock solutions of $c = 1.0$ M such that the resulting concentrations in the cuvettes were 1×10^{-1} M in order to ensure complete 1:1 complexation during the photophysical experiments. All samples were degassed by at least three consequent freeze−pump−thaw cycles. C,H,N,S analyzer: LECO Instruments GmbH; UV−vis: Hewlett-Packard 8452.

Quantum efficiencies were estimated by using the ferrioxalate actinometer (using $\Phi_{\mathrm{Fe2+}} = 0.0082$ at $\lambda_{\mathrm{exc}} = 532$ nm) under exactly the same experimental conditions as during the laser excitation experiments. A detailed description of this actinometer was published earlier.[30]

Results and Discussion

Redox Potentials and Binding of the Crown Ethers. In Table 2 the redox potentials of the employed ruthenium dyad (**4**) and triad (**5**) and the binding constants of the crown ethers (**6**, **7**, **8**) to the viologen branches of (**4**) and (**5**), which were determined by ^{1}NMR titrations, are summarized. It is clear from Table 2, that the accessible binding constants of the crown ethers (**6**) and (**7**) are rather small, since they do not exhibit a measurable influence in the measured redox potentials of (**4**) and (**5**) in the presence of all three crown ethers in acetonitrile. However, the changes in the lifetimes of the charge separated state, which resulted from the relatively weak complexation by the crown ethers, were remarkable indeed, especially when $\mathrm{DB_{30}C_{10}}$ (**6**) and $\mathrm{BBO_5O_5}$ (**7**) were employed. The binding constant for crown ether (**8**) was not measurable.

Before we shall consider in detail the strong impact of crown ether complexation on the lifetimes of charge separation within the ruthenium dyad (**4**) and triad (**5**), the principal geometry of the crown ether binding to the viologen branches of the supramolecular ruthenium−polypyridyl complexes will be discussed. The results from molecular modeling using MM2+ with an enhanced set of parameters for the calculation of octahedral metal complexes are shown in Figure 5. In agreement with the findings from NMR spectroscopy, the ruthenium dyad (**4**) (not shown) and the ruthenium triad (**5**) form strictly 1:1 complexes with the crown ethers employed (**6**), (**7**), and (**8**). This behavior offers the opportunity to study a physical model system for the photosynthetic reaction center: It is of great interest, how complexation by crown ethers influences the lifetimes of charge separated states of the supramolecular ruthenium complexes employed and thus introduces a significant selectivity of only one branch in photoelectron transfer reactions. To date, these mechanisms are barely understood. At the same

TABLE 2: Redox Potentials of the Employed Ruthenium Complexes [Ru(dmbpy)$_2$(di-V^{2+}-bpy)]$^{6+}$ (4) and [Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy))]$^{10+}$ (5) and Complexation Constants of Three Crown Ethers DB$_{30}$C$_{10}$ (6), BBO$_5$O$_5$ (7) and AAO$_5$O$_5$ (8) with Both Ruthenium Complexes (4) and (5)

Ru complex	solvent	E$_0$ (vs SHE) Ru$^{3+/2+c)}$	E$_0$ (vs SHE) MV$^{2+/1+c)}$	E$_0$ (vs SHE) dmMV$^{2+/1c)}$	E$_0$ (vs SHE) MV$^{1+/0c)}$	E$_0$ (vs SHE) dmMV$^{1+/0c)}$	DB$_{30}$C$_{10}$ (**6**) K [L mol^{-1}]	BBO$_5$O$_5$ (**7**) K [L mol^{-1}]	AAO$_5$O$_5$ (**8**) K [L mol^{-1}]
(**4**)	H$_2$O^a	1314	−257		−686				
(**4**)	acetonitrile^b	1310	−210		−640		146 ± 8	249 ± 22	*d*
(**5**)	H$_2$O^a	1273	−358	−592	−723	−980			
(**5**)	acetonitrile^b	1270					156 ± 12	188 ± 20	*d*

[a] Electrolyte: 0.10 M K$_2$SO$_4$; working electrode: glassy carbon; reference electrode: Hg/Hg$_2$SO$_4$/K$_2$SO$_4$(sat.); auxiliary electrode: Pt; argon 4.8. [b] Electrolyte: 0.10 M N(CH$_3$)$_4$PF$_6$; working electrode: Pt; reference electrode: Hg/Hg$_2$Cl$_2$/KCl(sat.); auxiliary electrode: Pt; helium 4.6. [c] vs standard hydrogen electrode (SHE) in mV. [d] CIS-shifts from the NMR-titrations did not permit to calculate a clear result.

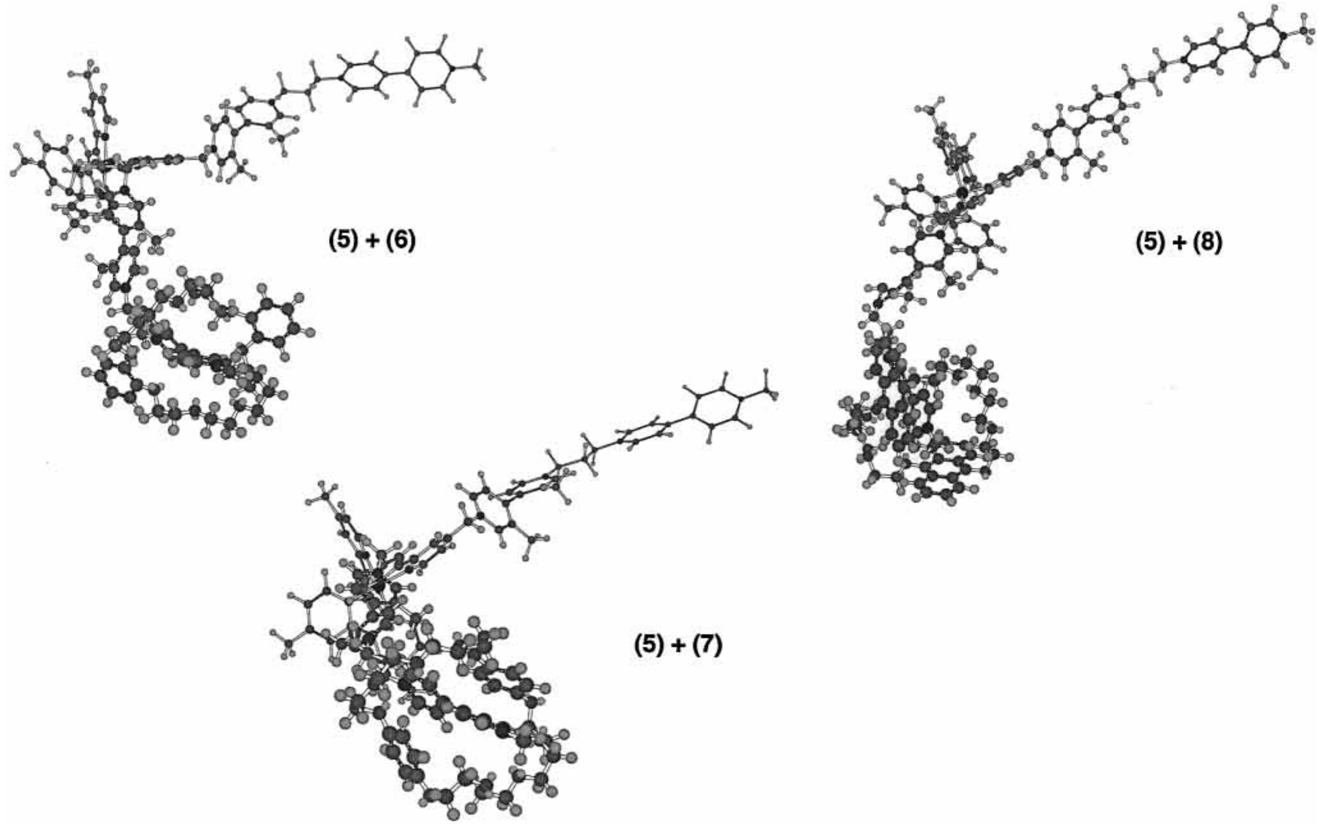


Figure 5. Graphic representation of the MM2+ calculations of crown ether complexation of the ruthenium triad (**5**). ((**6**): DB$_{30}$C$_{10}$; (**7**): BBO$_5$O$_5$; (**8**): AAO$_5$O$_5$).

time, the increase of the lifetimes of the charge separated states by several orders of magnitude offers a great application potential as indicated above. The most striking result from NMR and molecular modeling is that all three crown ethers, regardless of their particular structures and sizes, are bound exclusively to the 4,4′-viologen units of the ruthenium dyads (**4**) and triads (**5**). Furthermore, in all three cases investigated the binding of the crown ether can be regarded as symmetrical with regard to the 4,4′-bipyridinium guest, although small deviations exist. Therefore, crown ether complexation can be achieved at the terminal position of the designed photoredox chain Ru(L$_3$)$^{2+*}$−[3,3′-dimethyl-4,4′-viologen]-[4,4′-viologen], where the greatest influence by the bound crown ether is to be expected.

Time-resolved absorption measurements indicate that the complexation of the ruthenium triad (**5**) by the three crown ethers investigated has a remarkable effect on the observed lifetimes of the charge separated states. The lifetime of charge separation (τ_{cs}) of the ruthenium-triad (**5**) in the absence of any crown ether was 21 ± 3 ns (back transfer rate constant $k_{BT} = 4.76 \times 10^7\ s^{-1}$). This value is in agreement with earlier findings.[21] For the ruthenium dyad (**4**) an even faster back electron transfer was observed, with $k_{BT} \approx 2 \times 10^8\ s^{-1}$, consistent with a lifetime of the charge separated state of approximately 5 ± 1 ns. When the anthracene-containing crown ether AAO$_5$O$_5$ (**8**) was added to (**5**), the decay became biexponential with τ_{cs} values of 110 ± 6 ns (88%) and 155 ± 7 ns (12%). An even greater enhancement of the lifetime of the charge separated state was observed when the benzo-crown ethers DB$_{30}$C$_{10}$ (**6**) and BBO$_5$O$_5$ (**7**) were added to solutions of [Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy))]$^{10+}$ (**5**), resulting in τ_{cs} of 0.114 s ($k_{BT} \approx 8.8\ s^{-1}$) and $\tau_{cs} = 0.107$ s ($k_{BT} \approx 9.3\ s^{-1}$), respectively. For the interaction of the three crown ethers with the ruthenium dyad (**4**), a strikingly similar experimental trend was found. The measured lifetimes of the charge separated state, as well as the approximate quantum efficiencies of charge separation are summarized in Table 3. From the comparison of the complexation constants, K, listed in Table 2 and the lifetimes in Table 3, it becomes immediately clear that there is no straightforward correlation between the two. Therefore, a more complex model is developed below.

Concentration Dependence of the Lifetimes of the Charge Separates States. Figure 7 shows a strong concentration

TABLE 3: Lifetimes of Charge Separation (τ_{CS}), Rate Constants of Back-Electron Transfer (k_{BT}) and Approximate Quantum Efficiencies of Charge Separation (ϕ_{CS}) of [Ru(dmbpy)$_2$(di-V^{2+}-bpy)]$^{6+}$ (4) and [Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy))]$^{10+}$ (5) Complexed with DB$_{30}$C$_{10}$ (6), BO$_5$O$_5$ (7) or AAO$_5$O$_5$ (8) in Acetonitrile, Measured after Laser Excitation at $\lambda = 532$ nm

	DB$_{30}$C$_{10}$ (**6**)			BBO$_5$O$_5$ (**7**)			AAO$_5$O$_5$ (**8**)		
Ru complex	$\tau_{CS} \times 10^6$ s	k_{BT} [s^{-1}]	ϕ_{CS} [a]	$\tau_{CS} \times 10^6$ s	k_{BT} [s^{-1}]	ϕ_{CS} [a]	$\tau_{CS} \times 10^6$ s	k_{BT} [s^{-1}]	ϕ_{CS}
(**4**)[b]	32 ± 2	3.1×10^1	~0.1	104 ± 4	9.6×10^0	~0.1	0.11 ± 0.02	9.1×10^3	~0.1
(**5**)[c]	114 ± 7	8.8×10^0	~0.4	107 ± 3	9.3×10^0	~0.4	0.11 ± 0.01 (88%) 0.15 ± 0.01 (12%)	1.2×10^4	~0.4

[a] ϕ_{cs} = dn (MV$^{+\cdot}$)/P$_a$ (dn: mols of photoreduced 4,4′-viologen acceptor; P$_a$: mol photons per laser pulse). [b] $\tau_{CS} = 5 \pm 1 \times 10^9$ s. [c] $\tau_{CS} = 21 \pm 3 \times 10^9$ s.

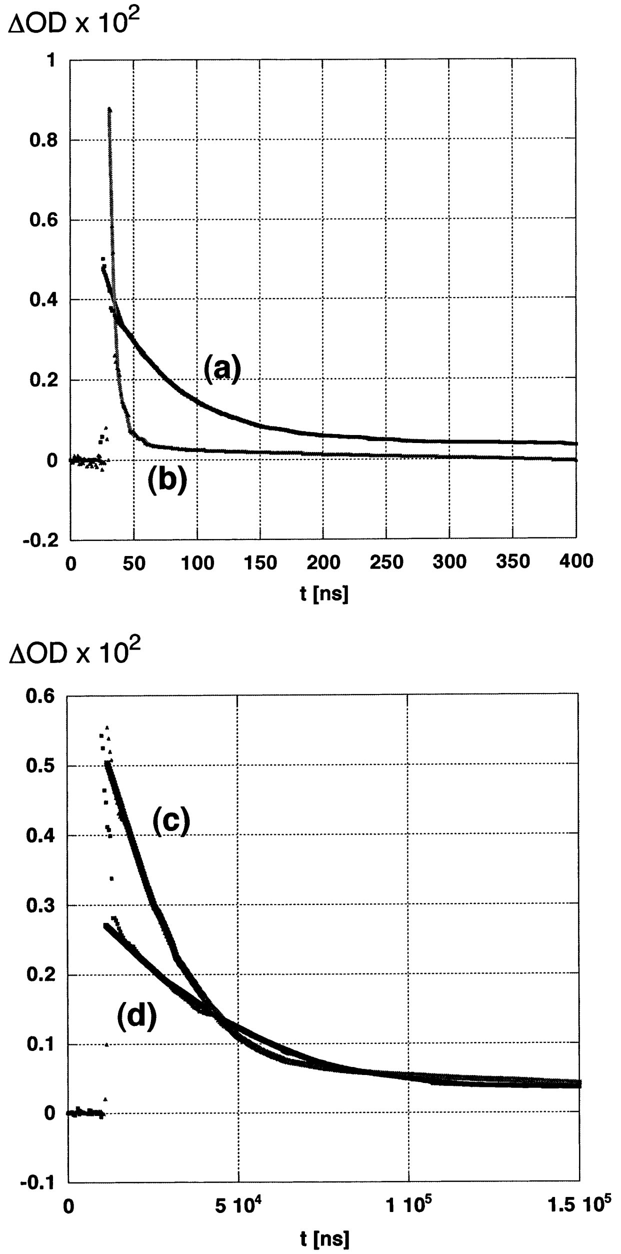


Figure 6. Time-resolved absorption: difference of optical density ΔOD of the 4,4′-viologen cation radical (MV$^{+\cdot}$) formed upon laser-excitation at $\lambda = 532$ nm. (a) [Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy))]$^{10+}$ (**5**); (b) [Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+} -bpy))]$^{10+}$ (**5**) + AAO$_5$O$_5$ (**8**) (1:5000); (c) [Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy))]$^{10+}$ (**5**) + DB$_{30}$C$_{10}$ (**6**) (1:5000); (d) [Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy))]$^{10+}$ (**5**) + BBO$_5$O$_5$ (**7**) (1:5000); [crown ether: 0.10 M].

dependence of the observed lifetimes of the charge transfer states. It is clear that there is a large decrease in τ_{cs} with increasing concentration of the ruthenium dyad (**4**) and triad (**5**). In all experiments, the crown ether concentration remained constant at 0.10 M. The decrease of τ_{cs} is consistent with the opening of a new deactivation pathway, because the intermolecular distances between the supramolecular assemblies become smaller with increasing concentrations of (**4**) and (**5**), thus increasing intermolecular back electron transfer. This effect is especially pronounced in these systems, because the intramolecular back electron transfer is remarkably slow within the supramolecular crown ether assemblies of (**4**) and (**5**). On the basis of this finding, it is clear that the lifetime measurements of the charge-separated states must be performed at defined concentrations of the ruthenium complexes.

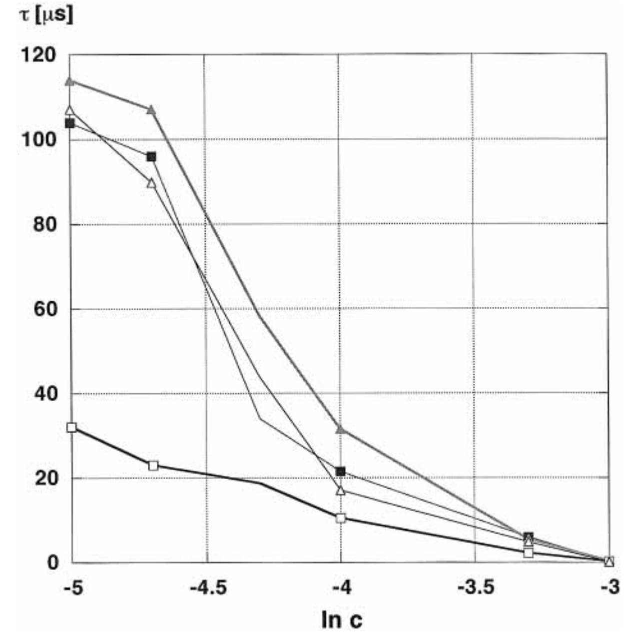


Figure 7. Concentration dependence of the lifetimes of the charge-separated states of four supramolecular complexes as a function of their concentration ($c_{(crownether)}$ = 0.10 M; c$_{(4)}$ and c$_{(5)}$ are plotted vs τ_{cs}: (▲)-[Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy))]$^{10+}$ (**5**) + DB$_{30}$C$_{10}$ (**6**); (△)[Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy))]$^{10+}$ (**5**) + BBO$_5$O$_5$ (**7**); (■)[Ru(dmbpy)$_2$-(di-V^{2+}-bpy)]$^{6+}$ (**4**) + BBO$_5$O$_5$ (**7**); (□)[Ru(dmbpy)$_2$(di-V^{2+}-bpy)]$^{6+}$ (**4**) + DB$_{30}$C$_{10}$ (**6**).

Excited-State Spectra of the [Ru(dmbpy)$_2$(di-V^{2+}-bpy)]$^{6+}$ (4) and [Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy))]$^{10+}$ (5) in interaction with DB$_{30}$C$_{10}$ (6); BBO$_5$O$_5$ (7); and AAO$_5$O$_5$ (8). The excited-state spectra of the ruthenium dyad (**4**) and triad (**5**), in the absence and in the presence of complexing crown ethers exhibit striking similarities. In the time window chosen for our time-resolved studies (5 ns > t > 200 μs), all excited-state spectra are consistent with the absorption spectra of the charge-separated state. The spectra were recorded point-by-point at 10 nm intervals. An overlay of the excited-state spectra of [Ru(dmbpy)$_2$(di-V^{2+}-bpy)]$^{6+}$ (**4**) in the absence of a complexing crown ether and in the presence of both DB$_{30}$C$_{10}$ (**6**) and BBO$_5$O$_5$ (**7**) is shown in Figure 8. Each of the excited-state

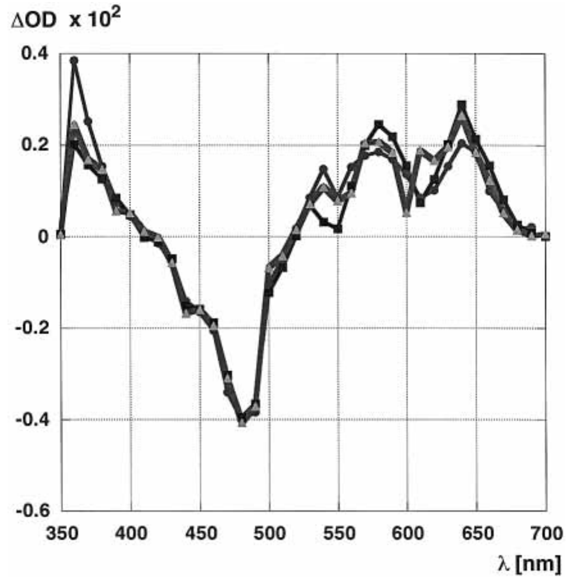


Figure 8. Absorption spectra of the charge-separated states of [Ru(dmbpy)$_2$(di-V^{2+}-bpy)]$^{6+}$ (**4**) and [Ru(dmbpy)$_2$(di-V^{2+}-bpy)]$^{6+}$ (**4**) in the presence of DB$_{30}$C$_{10}$ (**6**) and BBO$_5$O$_5$ (**7**) recorded 100 ns after laser excitation (λ_{exc} = 532 nm). (●)[Ru(dmbpy)$_2$(di-V^{2+}-bpy)]$^{6+}$ (c = 2.0 × 10^{-5} M); (■)[Ru(dmbpy)$_2$(di-V^{2+}-bpy)]$^{6+}$ (c = 2.0 × 10^{-5} M) + BBO$_5$O$_5$ (c = 0.10 M); (▲)[Ru(dmbpy)$_2$(di-V^{2+}-bpy)]$^{6+}$ (c = 2.0 × 10^{-5} M) + DB$_{30}$C$_{10}$ (c = 0.10 M).

spectra exhibited the absorption band at 360 nm, typical for donor substituted ruthenium(II)-polypyridyl complexes.[12] The observed bleach in the wavelength range between 420 and 520 nm, with the maximum at approximately 480 nm, is assigned to the ground-state MLCT absorption of the ruthenium−polypyridyl complex possessing three 2,2′-bipyridine ligands with substituents in 4,4′-position.[12] The third typical feature is the absorption maximum of the reduced propyl-methyl-substituted 4,4′-viologen (MV$^{+\cdot}$) at 640 nm.[31] Note that the absorption peak around 580 nm is still of unknown origin. In agreement with the results from electrochemistry and NMR spectroscopy, the presence of complexing crown ethers does not lead to remarkable changes in the time-resolved absorption spectra. From this finding we can conclude that only relatively weak interactions between the 4,4′-viologens and each of the employed crown ethers are operative.

The time resolved absorption spectra of the ruthenium triad [Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy))]$^{10+}$ (**5**) is shown in Figure 9 under the same conditions utilized for (**4**) in Figure 8. The spectra shown in Figure 9 are very similar to those in Figure 8, leading to the same assignment discussed above for (**4**). Note that the VIS-absorption spectrum of the singly reduced 3,3′-dimethyl-4,4′-viologen (3,3′-dmp-4,4′ V$^{+\cdot}$) features only a very small absorption coefficient ($\epsilon_{(615\ \mathrm{nm})}$ = 35 cm^2 mmol^{-1}),[32] thus, its time-resolved absorption cannot be detected when two 4,4′-viologen (4,4′ V$^{+\cdot}$) units are present with $\epsilon_{(630\ \mathrm{nm})} \approx$ 13.000 cm^2 mmol^{-1} [31] in [Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy))]$^{10+}$ (**5**). It should be noted that the irreversible reduction of (**5**) using triethylamine (TEA) as a sacrificial donor ($E_{ox} \approx$ 0.85 V (vs SHE)) results in a an excited-state spectrum that is very similar to that recorded in the presence of crown ethers (**6**), (**7**), and (**8**). In that particular case, a quasi-permanent reduction of the attached 4,4′-viologens was observed (τ_{CS} = 2.1 × 10^{-4} s).

Discussion

It is apparent from Table 3 that complexation of the ruthenium dyad (**4**) and triad (**5**) with crown ethers of varying structures led to a remarkable enhancement of the lifetimes of the charge-separated states. However, the complexation was determined to be weak by NMR titrations and electrochemical measurements. One possible explanation for the extremely long lifetimes observed for the charge separated states could be the oxidation of the crown ethers by the photochemically excited ruthenium−polypyridyl complexes (**4**) and (**5**). Electrochemical investigations of the crown ethers DB$_{30}$C$_{10}$ (**6**) and BBO$_5$O$_5$ (**7**) in H$_2$O and acetonitrile[33] demonstrated that both possess an oxidation potential of E^0_{ox} = 1.44 V (vs SHE). Therefore, the possibility that the photooxidized Ru^{3+}-polypyridyls (E^0_{ox} = 1.31 V (**4**) and E^0_{ox} = 1.27 V (**5**) (vs SHE)) are able to react with the crown ethers (**6**) and (**7**) can be excluded. Furthermore, a reductive pathway (reduction of the photoexcited Ru^{2+*} by crown ethers to Ru^{1+}, followed by electron transfer to the 4,4′-viologen acceptor) can also be ruled out given the relatively low oxidation potential of Ru^{2+*} ($E_{\mathrm{Ru}^{2+*}/\mathrm{Ru}^{1+}}$ = 0.63 V (**4**) and 0.59 V (**5**) (vs SHE)). These electrochemical results prove that crown ether oxidation does not occur in our laser flash experiments. It can also be excluded that the branch of the bifurcated electron-transfer pathway, which is complexed by

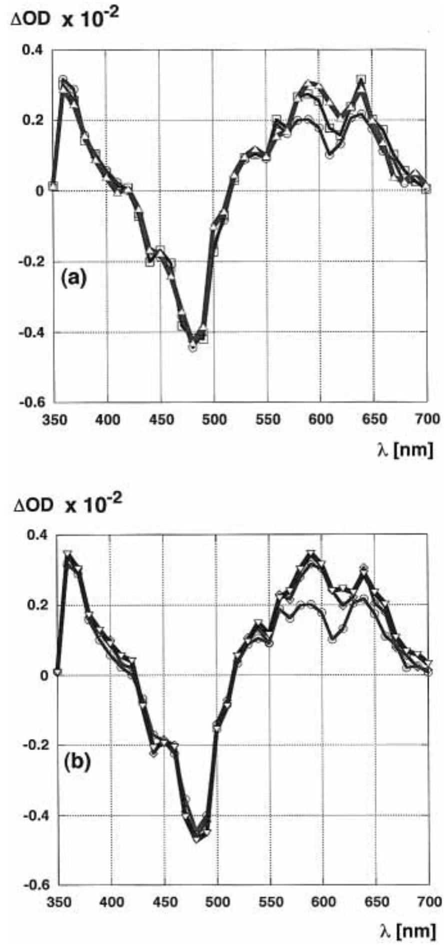
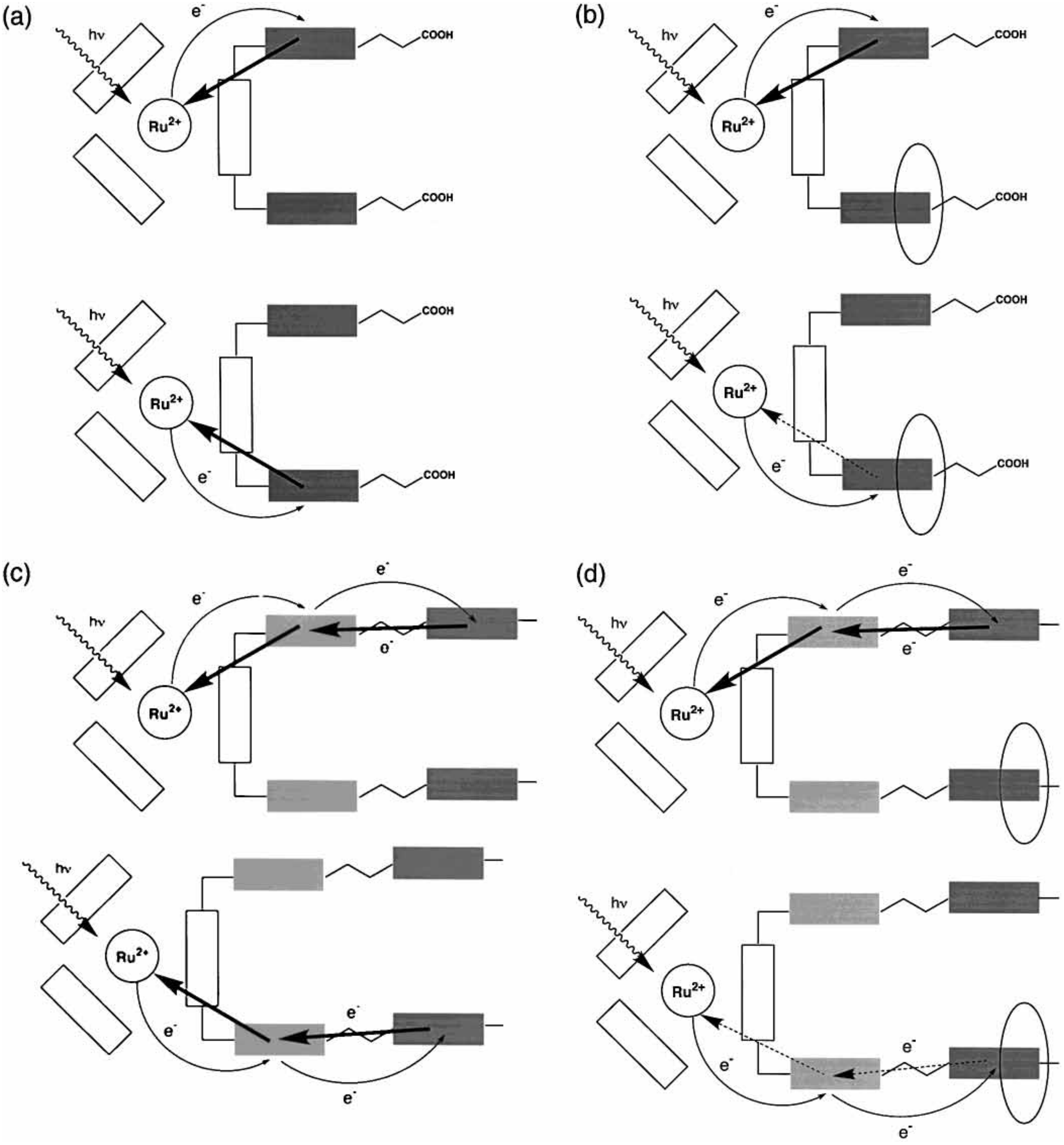


Figure 9. Absorption spectra of the charge-separated states of [Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy))]$^{10+}$ (**5**) and [Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy))]$^{10+}$ (**5**) in the presence of DB$_{30}$C$_{10}$ (**6**), BBO$_5$O$_5$ (**7**), AAO$_5$O$_5$ (**8**), and triethylamine (TEA) recorded 100 ns after laser excitation (λ_{exc} = 532 nm). (a) (○)[Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy)]$^{10+}$ (**5**) (c = 2.0 × 10^{-5} M); (□)[Ru(dmbpy)$_2$(di-V^{2+}-bpy)]$^{6+}$ (c = 2.0 × 10^{-5} M) + BBO$_5$O$_5$ (c = 0.10 M); (△)[Ru(dmbpy)$_2$(di-V^{2+}-bpy)]$^{6+}$ (c = 2.0 × 10^{-5} M) + DB$_{30}$C$_{10}$ (c = 0.10 M). (b) (○)[Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy)]$^{10+}$ (**5**) (c = 2.0 × 10^{-5} M); (◇)[Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy)]$^{10+}$ (c = 2.0 × 10^{-5} M) + AAO$_5$O$_5$ (c = 0.10 M); (▽)[Ru(dmbpy)$_2$(di-(dmV^{2+}-V^{2+}-bpy)]$^{10+}$ (c = 2.0 × 10^{-5} M) + triethylamine (c = 0.10 M).

SCHEME 2



the added crown ether,does not take the electron from the photoexcited state, since no apparent change in the redox potential could be detected.

In Scheme 2(a,b,c,d) the working paradigm of our supramolecular assemblies is shown. [Ru(dmbpy)$_2$(di-V^{2+}-bpy)]$^{6+}$ (**4**) shows no selection of one pathway over the other, because the ruthenium dyad is symmetrical. Therefore, the photoinduced electron transfer proceeds with exactly the same probability to each of the two attached 4,4′-viologen acceptors. We will report shortly that visible excitation leads to fast electron transfer from the Ru^{2+}* metal center to one of the 4,4′-viologens with rise times of $\sim$1−2 ps ($\lambda_{\mathrm{exc}} = 450$ nm, fwhm $\sim$ 200 fs).[23] Then, the back-electron transfer proceeds partially through bond and partially through space within 5 ns. The lifetime of the charge separated state of (**4**) in the absence of a complexing crown ether is typical of other dyads[34,35] and triads[36] previously reported.

As discussed above, the presence of a crown ether does not change the electrochemical properties of either the Ru(II) electron donor or the covalently attached acceptors. Therefore, we have to assume that the photoinduced reduction proceeds equally to both attached 4,4′-viologen units in the absence and presence of the crown ethers. It can be assumed that the kinetics of the back-electron transfer of the branch that is not complexed by the crown ether remains unchanged. The lifetime of the charge separated state of the crown ether complexed branch increases up to a factor of 2×10^4, however. Because we can rule out effects such as crown ether induced changes in the redox potential of photodonor and acceptor, the most likely explanation of such a drastic difference is a change in the reorganization energy λ. Within the rise time of 1−2 ps, no drastic conformational changes of the crown ether bound to the 4,4′-viologen acceptor can occur. Therefore, its presence should lead to a decrease of the reorganization energy λ of this particular acceptor. In accordance with the classic Marcus theory,[37,38] a decrease of the reorganization λ energy will lead to a consequent increase of the lifetime of the charge separated state and the back reaction is expected to be in the inverted region ($\Delta G = -1.55-1.60$ eV). Unfortunately, at the present time, the small number of data points prevents a full analysis.

The photophysical behavior of $[\mathrm{Ru(dmbpy)_2(di\text{-}(dmV^{2+}\text{-}V^{2+}\text{-}bpy))}]^{10+}$ (**5**) is very similar to that of $[\mathrm{Ru(dmbpy)_2(di\text{-}V^{2+}\text{-}bpy)}]^{6+}$ (**4**). In the ruthenium triad (**5**), it is also expected that both photoredox pathways are equally utilized. The presence of 3,3′-dimethyl-4,4′-viologen ($E^0_{\mathrm{red}} = -0.79$ V (vs SHE)) in the center of the redox chain, facilitates directed electron transfer to the attached 4,4′-viologen. The back-electron transfer can then proceed through bond or through space, or a combination of both. However, the flexibility of the C3 spacer between the two viologens does not permit the exact elucidation of the actual back-electron transfer pathway. The lifetime of the charge-separated state ($\tau_{\mathrm{CS}} = 21 \pm 1.7$ ns) is slightly greater than that of $[\mathrm{Ru(dmbpy)_2(di\text{-}V^{2+}\text{-}bpy)}]^{6+}$ due to the larger geometric extension of $[\mathrm{Ru(dmbpy)_2(di\text{-}(dmV^{2+}\text{-}V^{2+}\text{-}bpy))}]^{10+}$.

$[\mathrm{Ru(dmbpy)_2(di\text{-}(dmV^{2+}\text{-}V^{2+}\text{-}bpy))}]^{10+}$ (**5**) complexed with each of the three crown ethers employed $\mathrm{DB_{30}C_{10}}$ (**6**), $\mathrm{BBO_5O_5}$ (**7**), and $\mathrm{AAO_5O_5}$ (**8**) represents the largest supramolecular system discussed here. Its photophysical behavior is similar to that of $[\mathrm{Ru(dmbpy)_2(di\text{-}V^{2+}\text{-}bpy)}]^{6+}$ in the presence of the crown ethers. Especially the complexation of (**5**) with $\mathrm{DB_{30}C_{10}}$ (**6**) and $\mathrm{BBO_5O_5}$ (**7**) resulted in an increase in the observed lifetimes τ_{CB} to 114 μs and 107 μs, respectively, by factors of approximately 5500. These lifetimes are smaller than achieved by Gust, Moore, et al. by a factor of 3 [39] and approximately 3 times greater than those observed with a tetrad.[40] $\mathrm{AAO_5O_5}$ (**8**) is markedly less efficient than (**6**) and (**7**), presumably because of its very weak binding affinity.

Conclusion

Our experiments demonstrate that the ruthenium dyad (**4**) and triad (**5**) are promising physical model systems for the photosynthetic reaction center. The complexation of the chemically attached 4,4′-viologens by the crown ethers $\mathrm{DB_{30}C_{10}}$ (**6**), $\mathrm{BBO_5O_5}$ (**7**), and $\mathrm{AAO_5O_5}$ (**8**) led to remarkable increases of the lifetimes of the charge-separated states (τ_{CB}) up to a factor of 2×10^4 for $[\mathrm{Ru(dmbpy)_2(di\text{-}V^{2+}\text{-}bpy)}]^{6+}$ complexed by $\mathrm{BBO_5O_5}$ (**7**) and 5500 for $[\mathrm{Ru(dmbpy)_2(di\text{-}(dmV^{2+}\text{-}V^{2+}\text{-}bpy))}]^{10+}$ in the presence of $\mathrm{DB_{30}C_{10}}$ (**6**). The drastic observed changes may be caused by a decrease of the reorganization energy λ at the acceptor due to the presence of a bound crown ether.

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