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Photoinduced charge separation in dyads and triads containing a ruthenium(II)- or osmium(II)-bis-terpyridine photosensitizer covalently linked to electron donor and acceptor groups

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Abstract

Some supramolecular systems containing a photosensitizer (P) covalently linked to an electron acceptor (A) and/or an electron donor (D) are reported. The photosensitizer is $Ru(ttp)_2{}^{2+}$ or $Os(ttp)_2{}^{2+}$, A is MV^{2+} and D is PTZ or DPAA [ttp is 4'-(*p*-tolyl)-2,2'-6',2"-terpyridine, MV^{2+} is methyl viologen, PTZ is phenotiazine, and DPAA is di-*p*-anisylamine]. The spectroscopic properties and electrochemical behavior of these systems have been investigated. Thermodynamic and kinetic aspects for possible formation of photoinduced charge separated products are discussed.

1. INTRODUCTION

Photoinduced electron transfer processes in supramolecular species (dyads, triads, and tetrads) made of a photosensitizer (P) covalently linked to electron acceptor (A) and/or electron donor (D) groups are currently under study in several laboratories [1-6] in order to clarify the role played by factors like (i) energetics, (ii) distance and (iii) orientation of the interacting components, (iv) nature of interconnecting spacers and (v) solvent.

In such supramolecular assemblies an important requirement is that the component subunits maintain the electrochemical and spectroscopic properties of the free species, i.e. that the connecting spacers do not lead to strong intercomponent electronic perturbations [6]. In such cases it is possible to design and synthesize supermolecules where light absorption can result in sequential

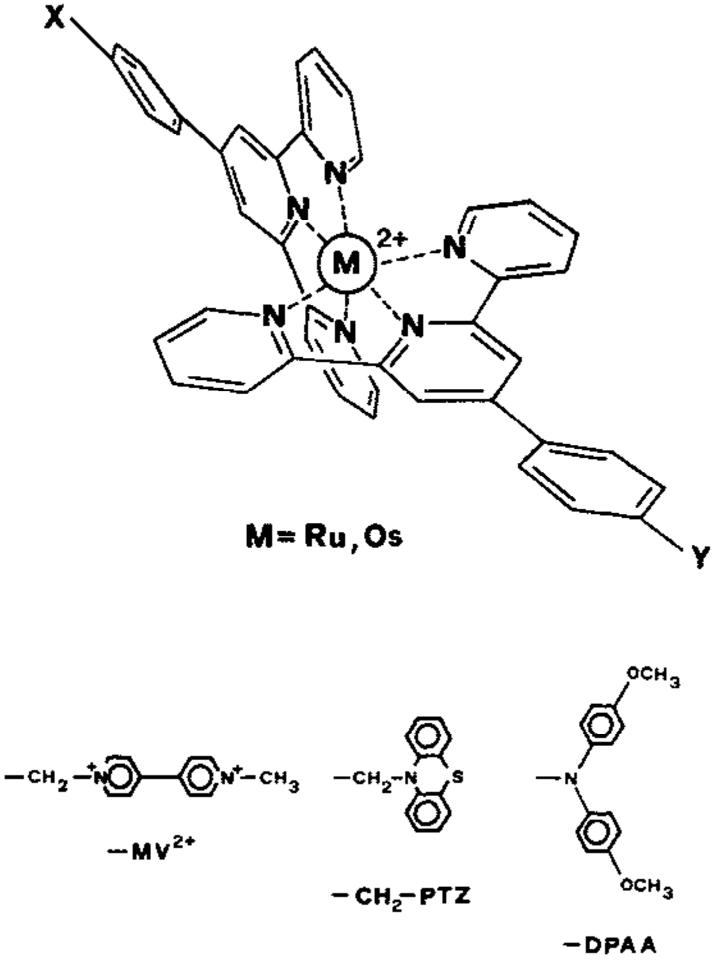

Figure 1. Schematic structure of the investigated systems. X is -CH_2-PTZ or DPAA; Y is -CH_2-MV^{2+}.

electron transfer steps, the final product being a transient charge separated (CS) state.

In this preliminary account we report some electrochemical and spectroscopic properties of dyads, D-P or P-A, and triads, D-P-A where the photosensitizer is $Ru(ttp)_2^{2+}$ or $Os(ttp)_2^{2+}$ [7], A is MV^{2+}, and D is PTZ or DPAA, see Figure 1. In the D-P-A triads the electron donor and acceptor groups are linked in opposite positions with respect to the photosensitizers, the edge-to-edge distance separation between D and A being 21 Å [7-9].

2. RESULTS AND DISCUSSION

2.1 Electrochemical behavior.

Table 1 collects room temperature electrochemical data for the investigated species in acetonitrile solvent [7-9]. The electrochemical waves of the dyads and triads can easily be assigned by comparison with the waves observed for the isolated components. Inspection of the reported values reveals that the electronic interaction between the various redox centers is negligible so that definition of the D-P, P-A, and D-P-A as supramolecular entities containing well defined components is satisfied.

2.2 Spectroscopic properties.

In Table 2 are listed room temperature absorption maxima for the two series of Ruthenium(II) [8] and Osmium(II) [7,9] complexes in acetonitrile solvent. The spectroscopy of the complexes is consistent with the assignement of the lowest optically allowed transition as metal-to-ligand charge transfer (^{1}MLCT), occurring at 490 nm for all complexes, except those containing DPAA. For the Osmium complexes, an additional band centered at about 670 nm is ascribed to direct singlet--->triplet absorption (ε ca 7000 M^{-1} cm^{-1}). These results are consistent with those from electrochemical data and suggest that P is little perturbed by the attachment of A or D groups, even if there is indication that when D = DPAA some conjugation exists between D and P.

2.3 Energy of the CS states.

In Figure 2 are schematized the energy levels for the DPAA-$Ru(ttp)_2^{2+}$-MV^{2+} and DPAA-$Os(ttp)_2^{2+}$-MV^{2+} triads. The levels have been drawn according to the luminescence maxima taken at 90 K (λ_{max} = 628 and 734 nm for Ru(ttp)$_2^{2+}$ [8] and Os(ttp)$_2^{2+}$ [9], respectively) and the electrochemical data obtained at room temperature, Table 1.

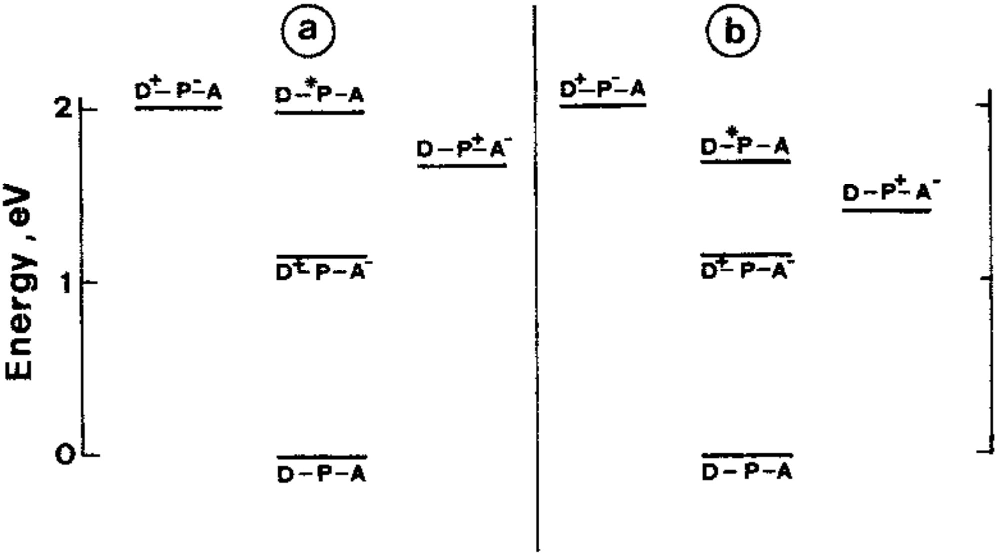

Figure 2 Energy level diagram for the triad systems: (a) DPAA-Ru(ttp)$_2^{2+}$-MV^{2+}; (b) DPAA-Os(ttp)$_2^{2+}$-MV^{2+}.

2.4 Quenching of the luminescence intensity and formation of CS species.

Ru(ttp)$_2^{2+}$ and the dyads and triads containing Ru(ttp)$_2^{2+}$ as a photosensitizer do not emit for T > 200 K. We have therefore examined their luminescent behaviour at 90 K, where the employed "nitrile" solvent is frozen, and at 150 K, where the solvent is fluid ["nitrile" is propionitrile-butyronitrile (4:5 v/v)]. Our findings indicate that in the frozen matrix there is no quenching while, at the higher temperature, quenching takes place in the DPAA-Ru(ttp)$_2^{2+}$ dyad and in the DPAA-Ru(ttp)$_2^{2+}$-MV^{2+} triad, but not in the Ru(ttp)$_2^{2+}$-MV^{2+}dyad [8]. An explanation for such behavior relies on a protective role played by A (i.e. MV^{2+})

Table 1
Electrochemical potentials and their assignments.[a]

	M^{3+}/M^{2+}	$DPAA^{+/0}$	$PTZ^{+/0}$	$MV^{2+/+}$	ttp/ttp$^-$
MV^{2+}				-0.44	
MePTZ[b]			+0.74		
MeDPAA[b]		+0.65			
$Ru(ttp)_2{}^{2+}$	+1.25	---	---	---	-1.24
$Ru(ttp)_2{}^{2+}$-MV^{2+}	+1.27	---	---	-0.36	-1.21
PTZ-$Ru(ttp)_2{}^{2+}$	+1.27	---	+0.79	---	-1.23
DPAA-$Ru(ttp)_2{}^{2+}$	+1.27	+0.77	---	---	-1.26
PTZ-$Ru(ttp)_2{}^{2+}$-MV^{2+}	+1.25	---	+0.76	-0.39	-1.24
DPAA-$Ru(ttp)_2{}^{2+}$-MV^{2+}	+1.26	+0.75	---	-0.40	-1.26
$Os(ttp)_2{}^{2+}$	+0.89	---	---	---	-1.17
$Os(ttp)_2{}^{2+}$-MV^{2+}	+0.90	---	---	-0.35	-1.20
PTZ-$Os(ttp)_2{}^{2+}$	+0.90	---	+0.76	---	-1.19
DPAA-$Os(ttp)_2{}^{2+}$	+0.94	+0.76	---	---	-1.24
PTZ-$Os(ttp)_2{}^{2+}$-MV^{2+}	+0.94	---	+0.78	-0.37	-1.17
DPAA-$Os(ttp)_2{}^{2+}$-MV^{2+}	+0.94	+0.75	---	-0.48	-1.21

[a] Acetonitrile solvent, room temperature. $E_{1/2}$ values in V, vs SSCE.
[b] Me is methyl.

Table 2
Ground state absorption maxima.[a]

	λ_{max}, nm (ε, M^{-1} cm^{-1})			
$Ru(ttp)_2{}^{2+}$	284(68000)	310(76000)	490(28000)	
$Ru(ttp)_2{}^{2+}$-MV^{2+}	285(98000)	311(79000)	491(32000)	
PTZ-$Ru(ttp)_2{}^{2+}$	285(75000)	310(84000)	490(31000)	
DPAA-$Ru(ttp)_2{}^{2+}$	284(63000)	310(81000)	502(39000)	
PTZ-$Ru(ttp)_2{}^{2+}$-MV^{2+}	284(112000)	310(83000)	491(32000)	
DPAA-$Ru(ttp)_2{}^{2+}$-MV^{2+}	285(83000)	310(77000)	504(43000)	
$Os(ttp)_2{}^{2+}$	286(58000)	314(68000)	490(26000)	667(6600)
$Os(ttp)_2{}^{2+}$-MV^{2+}	285(68000)	315(61000)	490(23000)	668(5700)
PTZ-$Os(ttp)_2{}^{2+}$	286(68000)	314(75100)	490(28000)	668(7100)
DPAA-$Os(ttp)_2{}^{2+}$	285(53000)	314(70000)	503(31000)	671(7800)
PTZ-$Os(ttp)_2{}^{2+}$-MV^{2+}	287(66000)	315(56900)	491(24000)	669(6700)
DPAA-$Os(ttp)_2{}^{2+}$-MV^{2+}	280(81000)	314(79000)	504(40000)	672(9200)

[a] Acetonitrile solvent, room temperature.

through formation of P^+-A^- and subsequent reformation of *P-A. Transient absorption spectroscopic studies of DPAA-Ru(ttp)$_2$$^{2+}$-MV^{2+} show that a CS state, D^+-P-A^-, is involved in the deactivation of D-*P-A. This state, which is estimated to lie at 1.1 eV, lives less than 100 ns.

For the dyads and triads containing Os(ttp)$_2$$^{2+}$ as a photosensitizer, luminescence can be detected in the temperature range 90 to 295 K [7,9]. For this series of supermolecules, thermodynamics is only favourable to an initial CS step involving the P-A moiety, see Fig 2. For DPAA-Os(ttp)$_2$$^{2+}$-MV^{2+}, formation of D^+-P-A^- is followed by fast charge recombination leading to the D-P-A ground state [9].

More detailed results and a thorough discussion of the various systems will be reported elsewhere. [8,9]

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