Light-induced electron transfer in simple and supramolecular Ru–polypyridine complexes

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Abstract. In artificial photosynthesis the chief research goal is to duplicate the function of the photosynthetic unit in nature but not its structural subunits. In this paper, light-induced electron-transfer processes of Ru–polypyridines as energy-storing systems, in the presence of suitable acceptors and catalysts, are described. New highly photostable photosensitizers are presented. A new approach using supramolecular (non-covalently) connected assemblies in addition to covalently linked systems for energy-storing processes is demonstrated. The use of classical and new Ru–complex assemblies in oxygen or hydrogen generation from water is dealt with. The efficiency of the new systems in the reduction of CO₂ to methane is presented.

Keywords. Electron transfer; supramolecular photochemistry; supramolecular Ru–polypyridine complexes.

1. Introduction

The photosynthetic unit has been characterized in *Rhodospseudomonas viridis* by Deisenhofer *et al* (1984, 1985) and Mathis (1990). This work has stimulated intensive photoinduced electron-transfer studies (Juris *et al* 1988). In the recent past, this field has developed extremely fast and is defined today as artificial photosynthesis. Researchers aim to duplicate nature's functions but not its molecular design (Creutz and Sutin 1975; Balzani *et al* 1978; Kiwi *et al* 1982; Seddon and Seddon 1984). The complicated connections and interrelations of the different components of such systems have led to the birth of a new field, supramolecular photochemistry (Balzani 1987; Balzani and Scandola 1990; Dürr and Schneider 1991). Natural as well as artificial photosyntheses possess, as primordial characteristics, efficient light harvesting units for the conversion of solar energy. The basic reaction to be realized is light-induced charge separation leading to the cleavage of water. In artificial photosynthesis this is achieved by sensitizers absorbing in the visible region of the solar spectrum by electron relays functioning as short-time reservoirs of chemical energy and redox active components that can be used for energy storage (Juris *et al* 1988). Catalysts play an important role in these processes concerned in lowering

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Figure 1. Artificial photosynthetic unit.

kinetic barriers of the dark reactions induced by the photochemical primary processes. The typical components for such an artificial photosynthetic unit are shown in figure 1. The energy to be stored in a photoelectron-transfer reaction is shown in figure 2. Following excitation an (S^*-R) pair is generated. Electron transfer then produces ($S^+ + R^-$). This pair can undergo a reaction on a catalyst to afford H_2 and O_2 from water or a competition reaction $S^+ + R^-$ to SR occurs, the so-called back reaction. This leads to annihilation of the stored energy or, in other words, to waste of energy. In order to avoid this problem a fast electron transfer (bimolecular) is necessary. Looking for the optimal system thus means that both unimolecular and bimolecular light-induced processes should have high values. The main task of modern research in the field of artificial photosynthesis is to find a cyclic system for water cleavage. It should possess:

- (1) a fast forward reaction of the radical pair ($S^+ R^-$) with a negligible back reaction.
- (2) an efficient system to allow the one-electron sensitizers to carry out multielectron redox processes as nature does.

Until today no reproducible cyclic system for artificial photosynthesis has been found (not regarding semiconductors however, Serpone *et al* 1985). Therefore, studies of sacrificial systems are good models for photoredox processes to generate oxygen (Henglein 1984; Harriman *et al* 1988; Mills *et al* 1988; Heppe 1994), hydrogen (Creutz and Sutin 1975; Balzani *et al* 1978; Kiwi *et al* 1982; Dürr *et al* 1983, 1985; Seddon and Seddon 1984; Kalyanasundaram 1992) or methane (Willner *et al* 1987) from water or carbon dioxide. Typical parameters to be optimized in such systems are collected in scheme 1.

Scheme 1. Tailor made compounds.

Figure 2. Reaction scheme for the photochemical water cleavage.

Scheme 2. Synthesis of Ru(II)-coronates using the cesiumcarbonate method.

1.1 Sensitizers

From the different possible sensitizers, we have mainly focussed our interest on Ru-polypyridine complexes (Dürr *et al* 1983, 1985). Good results in this field have been obtained by various groups (Creutz and Sutin 1975; Balzani *et al* 1978; Kiwi *et al* 1982; Seddon and Seddon 1984; Balzani 1987; Balzani and Scandola 1990; Dürr and Schneider 1991) as well as by us (Dürr *et al* 1983, 1985) regarding the parameters mentioned in scheme 1.

One value however – high *photostability* – is still a major challenge.

A very efficient way of stabilization is the change of the MLCT versus the MC-levels in Ru-polypyridine complexes (Balzani 1987; Balzani and Scandola 1990). Another approach is linking the different bipyridine units in such complexes by intramolecular bridges. This concept was advanced for the first time by Sargeson (1984). We have used this approach to generate two types of new molecules, the Ru-coronates **1** (Boßmann and Dürr 1992) and the Ru-podates (Dürr and Schwarz 1993) **2**. The synthetic scheme for **1** and the formula for **2** is shown in schemes 2 and 3. These two classes of bridged Ru-polypyridine complexes possess the photophysical properties as shown in tables 1 and 2. All parameters of this new class of molecules are suitable for artificial photosynthetic systems. One parameter, is however, especially remarkable, i.e. photostability or the inverse, called photoanation of the bridged Ru complexes.

Table 3 shows that Ru-coronates **1** are among the most photostable Ru-polypyridines. Ru-podate **2f** seems to exceed even this photostability and is amongst

Scheme 3. Ru-podate (Pod) **2**.

Table 1. Photophysical properties of Ru-(bpdz)₃-polyethers and Ru-podate.

Complex	λ_{ex} (nm)	λ_{em} (nm)	ϕ_F
<u>2a</u>	421	457	631
<u>2b</u>	420	458	630
<u>2c</u>	420	459	627
<u>2d</u>	422	469	616

Table 2. Photophysical data of Ru(bpdz)₃-polyethers 2a–2d and Ru-podate 2f.

Complex	$\tau_L(\text{H}_2\text{O})$ [ns]	$\tau_L(\text{MeOH})$ [ns]	$\tau_L(\text{CH}_3\text{CN})$
<u>2a</u>	1463 + 54	2295 + 87	3154
<u>2b</u>	1571 + 64	2275 + 86	3136
<u>2c</u>	1943 + 87	2480 + 114	
<u>2d</u>	3345 + 95	3246 + 97	3448
<u>2f</u>	1986 + 309		

Table 3. Photoanation quantum yields and rates of Ru-coronates 1c and -podates 2. Photoanation of RyL_3^{2+} -compounds (at 298 K).

	τ [ns]	$\phi_r \times 10^2$	ϕ_p
Ru(coronate) <u>1</u>	3.45 ^b	6.0	$< 10^{-6a}$
Ru(podate) <u>2f</u>	1986c	5.3	$\ll 10^{-6a}$

^aNo change after 10 d irradiation; ^bpropio-/butyronitrile; ^cH₂O

the best Ru-polypyridines (Rodriguez-Ubis *et al* 1984; Grammenudi and Vögtle 1986; Alpha *et al* 1987; Dürr *et al* 1988, 1991) with respect to photoanation.

3. Covalently and non-covalently linked sensitizer-relay-assemblies—Supramolecular effects

Balzani (Balzani 1987; Balzani and Scandola 1990) has shown that nature employs, in principle, a molecular photochemical device which is used for vectorial transport of electric charge. Thus light is converted to chemical or electrical energy (figure 3).

In principle two approaches to realize nature's functions are possible. The components of an artificial photosynthetic unit can be based on a supramolecular

Function Photoinduced vectorial transport of electric charge
Utilization Conversion of light into chemical or electrical energy

Molecular photochemical device

Role of light Thermodynamic

Necessary functions Light absorption; electron transfer

Components:

Interface towards light Pel

Interface towards use Pel and/or Rel

Other components C, (Rel)

Supramolecular structure Appropriate sequential assembly of the components; one-dimensional (rigid) structure

Requirements Those of Pel, Rel, C. thermodynamic and kinetic requirements of the electron transfer acts to make the charge separation efficient

Example Artificial photosynthesis

Figure 3. Supramolecular photochemistry – photoinduced vectorial transport of electrical charge (adapted from Balzani 1987).

Figure 4. Model (charm calculation) of octylviologen/bpy-crown interaction.

Scheme 4.

Scheme 5.

assembly which is linked: (a) by strong (covalent) bonds, or (b) by weaker (non-covalent) bonds.

In these supramolecular structures energy dissipation should be fast and back transfer – the energy wasting step – should be negligible. Triads paralleling the natural photosynthetic unit were studied by Maruyama (Osuka *et al* 1988, 1990), Wasielewski (1992) and others. Lehn and coworkers (Rodriguez-Ubis *et al* 1984; Grammenudi and Vögtle 1986; Alpha *et al* 1987; Dürr *et al* 1988, 1991) published an absorption-energy transmission diad.

Meyer (1990) prepared with his group the first Ru-polypyridine-containing triad. A similar one was made by Sauvage *et al* (1989).

(a) We synthesized a Ru-polypyridine diad (Dürr *et al* 1989) **3**. This diad contains the sensitizer and the relay in the same molecule (scheme 4).

(b) A second approach was tested in our group by including crown-ether units at suitable positions in the Ru-polypyridine complex **4** (Dürr and Schneider 1991). The structure of these complexes is shown in scheme 5 and figure 4 (showing the interaction of ligand and OV^{2+}). These molecules were studied by typical Stern–Volmer techniques. MV^{2+} and the more lipophilic octylviologen were employed as quenchers. As figure 5 demonstrates typical nonlinear Stern–Volmer plots for quenching are obtained. The kinetic scheme 6 shows that a complex situation prevails. MV^{2+} and OV^{2+} may act in the quenching modes shown in scheme 6 (Boßmann *et al* 1992).

4. Oxidation of water to oxygen

The cleavage of water as has been demonstrated (*vide supra*) needs good light harvesting molecules having suitable parameters in the excited state. However, to

Figure 5. Stern–Volmer plot of statical quenching of Ru-crown ether **4** with relay (MV^{2+} and OV^{2+}) (a) and (b) $\underline{4b'}/MV^{2+}$ or $\underline{4b'}/OV^{2+}$; (c) and (d) $\underline{4c}/MV^{2+}$ or $\underline{4c}/OV^{2+}$.

Scheme 6. Kinetic scheme for quenching of sensitizers 1–4 with viologens (MV^{2+} , OV^{2+}). S = sensitizers 4; Q = boundquencher in the crown ether unit (MV^{2+} , OV^{2+}); τ_0 = luminescence lifetime in the absence of Q; k_f and k_b = forward and backward rate of binding of Q, respectively; k_r = unimolecular reactive rate constant of quenching in the crown ether unit; Q_w = water solubilized quencher (MV^{2+} , OV^{2+}).

reduce or oxidize water the excited state species must also have the appropriate redox potentials.

Table 4 summarizes the redox potentials required for water cleavage. The redox potentials for CO_2 reduction (*vide infra*) are included as well. To study the different reactions involved separately, many groups have investigated so called sacrificial systems to simplify the very complex processes.

For oxygen generation nature uses the catalytic system shown in scheme 7. We have worked with a sacrificial system for oxygen generation represented in scheme 8.

The main problem here is to exclude atmospheric oxygen rigorously, a task many groups have struggled with (Harriman *et al* 1988; Mills *et al* 1988; Heppe 1994).

Scheme 7. Hypothetical scheme for water oxidation.

Table 4. Redox potentials for H₂O and CO₂ reduction and H₂O oxidation.

Reaction	Potential, E^0 (V)
$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	-0.41
$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.52
$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HCOOH}$	-0.62
$\text{CO}_2 + 6\text{H}^+ + 6e^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.38
$\text{CO}_2 + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-0.24
$\text{O}_2 + 2\text{H}^+ + 4e^- \rightarrow 2\text{OH}^- - 2e^-$	+0.82

Scheme 8. Photoinduced sacrificial water oxidation.**Table 5.** O₂-production in the sacrificial system Ru-polypyridine/Co(NH₃)₅Cl₃/RuO₂.Acceptor: Co(NH₃)₅Cl₃ in acetate buffer (pH 4.75)Catalyst: RuO₂-suspension

Sensitizers (S)	Maximal O ₂ yield [μl]	Slope (μl/min)
Ru(bpy) ₂ (5,5'-dmbpy)Cl ₂	13.0	0.60
Ru(bpy) ₂ (4,4'-dmbpy)Cl ₂	12.0	0.38
Ru(bpy) ₂ (5,6-dmphen)Cl ₂	10.5	0.49
Ru(4,4'-dmbpy) ₃ Cl ₂	10.3	0.27
Ru(4,4'-dmbpy) ₂ (bpy)Cl ₂	10.2	0.44
Ru(5,5'-dmbpy) ₃ Cl ₂	9.0	0.36
Ru(bpy) ₃ Cl ₂	6.9	0.33
Ru(phen) ₂ (4,4'-dmbpy)Cl ₂	6.6	0.22
Ru(bpy) ₂ (Bp4COOTEK)Cl ₂	6.0	0.21
Ru(5,6-dmphen) ₃ Cl ₂	4.2	0.19

We were using a set up developed by Memming, Meissner and coworkers (Memming *et al* 1992).

In the sacrificial system referred to above we have generated O_2 as is shown in table 5. The standard system being based on $Ru(bpy)_3^{2+}$ is exceeded in its O_2 -producing ability by modified Ru-polypyridines. Donating groups in the bipyridine moiety of $Ru(L_3)^{2+}$ have proved to be most efficient.

5. Reduction of water and carbon dioxide

The reduction of water-employing Ru-polypyridines has been studied for quite a while by many groups (Kalyanasundaram *et al* 1969; Creutz and Sutin 1975; Balzani *et al* 1978; Kiwi *et al* 1982; Seddon and Seddon 1984; Kalyanasundaram 1992). The essential problem is to use efficient and selective catalysts. A series of Pt-metals has been employed in these investigations. As typical examples $Ru(bpy)_3^{2+}$ - and $Ru(phen)_3^{2+}$ -derivatives are selected (figure 6) (Dürr *et al* 1985; Trierweiler 1989; Kraus

Figure 6. Hydrogen production depending on sensitizer (sensitizer $Ru(L_3)^{2+}$; relay: MPVS*, catalyst: Ru-Sol, donor: TEOA).

Figure 7. H_2 -generation rates with the coronate sensitizers 1a, 1b and 1c.

Figure 8. (a, b) Hydrogen evolution in the sacrificial system containing A ($\square$), B ($\blacktriangle$) or 3 ($\bullet$) as sensitizer and 2-TMV $^{2+}$ as relay at pH = 7 and 4.7. (c) CH $_4$ -evolution using the sensitizer-relay-assembly 3, TEOA as donor and Ru as catalyst.

Figure 9. H_2 -generation with sensitizer-relay-assembly $\underline{4a}/\text{MV}^{2+}$, $\underline{4b'}/\text{MV}^{2+}$ and $\underline{4c}/\text{MV}^{2+}$, triethanolamine as donor, methylviologen/propylviologen-sulfonate as electron relay and a microheterogeneous TiO_2 -Pt-catalyst compared to $\text{Ru}(\text{bpy})_3^{2+}$. (a) $\text{Ru}(\text{bpy})_2$ PEC($\underline{4a}$), (b) $\text{Ru}(\text{bp}4\text{CO}_2\text{Me})_2$ bp4 (pentaethylene crown) $\underline{4b'}$; (c) $\text{Ru}(\text{bp}4\text{CO}_2\text{Et})_2$ bp4 (pentaethylene crown) $\underline{4c}$, (d) $\text{Ru}(\text{bpy})_3$.

1991). Using Ru and Os catalysts instead of Pt-metals extends the scope of this reaction considerably. In addition to H_2 from H_2O , CH_4 may also be generated by reduction of CO_2 (Rodriguez-Ubis *et al* 1984; Alpha *et al* 1987; Willner *et al* 1987; Dürr *et al* 1988, 1991).

This is an interesting process which – if optimized and used on a large scale – would contribute to the solution of the greenhouse effect.

It has been found by Willner (Willner *et al* 1987), in collaboration with our group, that $\text{Ru}(\text{bpy})_3^{2+}$ yields H_2 and CH_4 . Employing $\text{Ru}(\text{bpz})_3^{2+}$ as sensitizer gives rise to a selective production of CH_4 (Willner *et al* 1987).

In model studies for our supramolecular systems we examined a series of Ru–bipyridine and phenanthroline complexes. One of the best complexes in hydrogen generation is the diester ($\text{Ru}-4,4'\text{-bis-CO}_2\text{Et-bpy})_3^{2+}$ (Willner *et al* 1990) (figure 6). This is also one of the most efficient complexes producing CH_4 from CO_2 . Ru-coronates $\underline{1}$ have been shown to produce H_2 despite the large sterical demand of the sensitizers involved. However, the sterically very large Ru-complexes give about 1/6 of the hydrogen yield compared to $\text{Ru}(\text{bpy})_3^{2+}$ (Boßmann and Dürr 1990) (figure 7). The sensitizer-relay assembly $\underline{3}$ has been employed for H_2 and methane generation. It is much more efficient than the standard system as shown in figures 8a–c. Hydrogen evolution from the supramolecular $\text{Ru}(\text{bpy})_2$ PEK $^{2+}$ ($\underline{4}$)/ MV^{2+} assembly is clearly superior to the standard $\text{Ru}(\text{bpy})_3^{2+}$ (see figure 9). In figure 10 a schematic representation of the mechanism of this system is given.

6. Conclusions

It has been shown that Ru–polypyridine complexes can

- (i) be stabilized with respect to photoanation by intramolecular links as in coronates $\underline{1}$ or podates $\underline{2}$;

Figure 10. Quenching model of the bis-heteroleptic-crown ether-ruthenium sensitizers 4. (A) The quenching mechanism is diffusion controlled; the binding of MV²⁺ in the crown ether receptor is not observed because of its low concentration ([Q] rel = 0–0.2). (B) The binding MV²⁺ in the crown ether unit is the dominant process; the quenching constants are higher than the diffusion-controlled rate of diffusion ([Q] rel = 0.2–0.8). (C) The quenching constants decrease; further quenching is diffusion controlled. (D) At relatively high total concentrations electron transfer from the bound MV²⁺ to the free MV²⁺ occurs, leading to a rapid increase in the quenching constants.

- (ii) undergo efficient bimolecular electron transfer in covalently or non-covalently (supramolecular) linked sensitizer-relay-aggregates, such as 3 and 4;
- (iii) be used efficiently in oxygen formation involving electron-donating groups;
- (iv) be employed in hydrogen generation in classical and supramolecular systems;
- (v) efficiently produce CH₄ from CO₂.

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