

Supramolecular assemblies for light-induced electron-transfer reactions

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Abstract

In this paper, we present a summary of our work on highly photostable supramolecular ruthenium complexes, which may be incorporated into more complex systems for artificial solar energy conversion. We have used supramolecular chemistry and photochemistry to synthesize highly photostable ruthenium bipyridine coronates and a bipyridazine podate complex and to enhance photoelectron-transfer reactions in physical model systems for artificial photosynthesis. The recent progress of covalent and non-covalent sensitizer-relay assemblies for highly efficient photoelectron transfer is described.

A detailed mechanistic investigation of the binding behavior of cationic species to crown-ether-modified bipyridine derivatives is presented as an example of supramolecular binding in systems for photoelectron transfer. The host properties of the free ligands and the derived bis-heteroleptic ruthenium complexes are compared using UV-visible, luminescence quenching and proton nuclear magnetic resonance titrations. The combination of these three methods confirms that supramolecular binding of cations and the electron relay methylviologen (MV^{2+}) to the complexes can be observed. The binding constants determined are of the order of $(1-6) \times 10^4 \text{ l mol}^{-1}$ for the crown-ether ruthenium complexes and $1 \times 10^2-4 \times 10^3 \text{ l mol}^{-1}$ for the crown-ether ligands. Single-photon-counting (SPC) investigations give strong indications for the coexistence of different binding mechanisms. The kinetic scheme of Yekta *et al.* has been adapted to interpret the binding mechanism.

1. Introduction

Supramolecular photochemistry, as a means of controlling individual subunits in defined spatial assemblies, has become an interesting field of research [1]. However, the potential application to solar energy conversion [2] is still in the developmental stage. For this reason, research is being carried out into the design of artificial photosynthetic systems mimicking the reactions of natural photosynthesis without employing its reaction center (RC) subunits [3].

The process in nature's tetrapyrrolic macrocyclic RC involves a photoinduced long-range electron transfer (ET) and, consequently, long-range charge separation with a quantum yield of almost unity [4]. A number of model studies have been performed to enhance the understanding of the second process [5]. During the last 5 years, we have been interested in supramolecular assemblies containing ruthenium complexes for the production of artificial photosynthesis. The main aim is to find new ru-

thenium sensitizers of sufficient photostability and photoelectron-transfer properties which can be integrated into appropriate supramolecular assemblies.

In this paper, we describe the successful application of supramolecular chemistry and photochemistry for the design and determination of the photophysical properties of the following: (1) high-stability crown-ether-linked ruthenium coronates; (2) oligoethyleneglycol-substituted ruthenium complexes and ruthenium podate; (3) a covalently linked sensitizer-relay assembly for very efficient ET. The binding constants of cations and the electron relay methylviologen (MV^{2+}) to crown-ether ligands and crown-ether ruthenium complexes are determined.

2. Experimental details

The syntheses of the crown ether coronates **1** [6], the tris-homoleptic ruthenium bipyridazine complexes **2** [7], the ruthenium podate **3** [7], the sensitizer-relay assembly **4** [8], the crown-ether-

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modified ruthenium complexes **5** [9, 10] and the ester-linked crown ether bipyridines **6** [9] have been described in detail in the literature.

The purification of the crown ether ruthenium complexes was performed by high performance liquid chromatography (HPLC) on an RP-C18 column. The separation was started with an aqueous buffer (0.10 mol l⁻¹ triethylamine, 0.10 mol l⁻¹ glacial acetic acid, pH 6.0 in bidistilled water) to which acetonitrile was added (up to 60%) in an optimized gradient.

For the UV titrations, a Uvikon 860 (Kontron) UV-visible spectrometer was used. The concentration of the host was held at approximately 1 × 10⁻⁴ mol l⁻¹ and the concentration of the guest in the system was varied. A high density of data was recorded in the region between 20% and 80% complexation [11]. Typical conditions and the experimental apparatus for the luminescence quenching titrations are discussed in ref. 12.

The single-photon-counting (SPC) apparatus and the experimental conditions are described in ref. 13. The computer program KPLTXITR for the calculation of the binding constants from proton nuclear magnetic resonance (¹H-NMR) shifts was originally developed by Kramer [14].

3. Highly photostable ruthenium coronates

Sensitizers for solar energy conversion should possess the following properties: good absorption at the maximum wavelength of the solar spectrum, an excited state lifetime in the microsecond range, suitable redox potentials for ET, high thermal and photostability and the ability to undergo fast ET reactions.

3.1. Ruthenium coronates

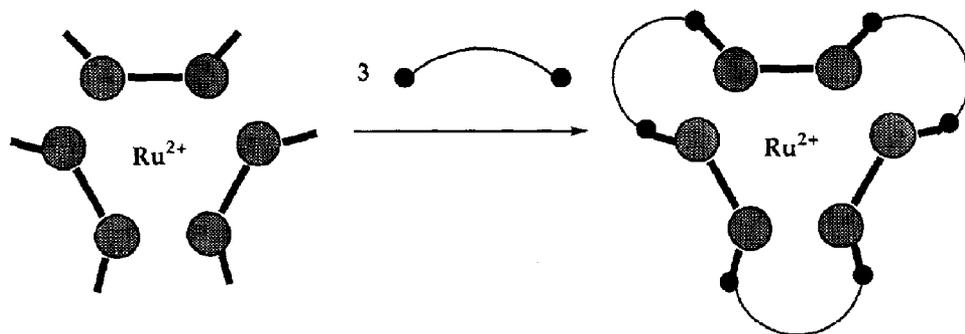
A very efficient method for the synthesis of highly stable ruthenium complexes is the direct linking of the three ligands of a preformed ruthenium complex in a one-step reaction. Scheme 1 outlines the reaction principles. Suitable ruthenium complexes are prepared and the linking reaction (employing oligoethyleneglycol units) is performed by application of the dilution principle. The linking reaction involves a modification of the cesium-carbonate method for the highly efficient preparation of esters [6, 15]. The advantages of supramolecular ruthenium coronates, especially in comparison with known ruthenium cryptates [16], is the enhanced water solubility due to the crown-ether moieties attached to the molecules and the smaller size of the supramolecular unit. No spacers

are needed and thus the accessibility to electron relays is increased. Since the distance between photoexcited ruthenium complexes and possible electron acceptors, such as methylviologen, is very important in controlling the efficiency of charge transfer, small supramolecular units are much more promising for practical applications. Nevertheless, the use of oligoethyleneglycol units for linking of the ligands leads to an efficient internal quenching of the ruthenium metal-to-ligand charge transfer (³MLCT) state. As shown in Table 1, the lifetimes of the excited states of the supramolecular coronates **1a–1c** (Fig. 1) are decreased dramatically. Therefore a reduced ability to undergo photoredox reactions may be predicted for the ruthenium coronates.

In order to test the limitations of these sensitizers for sacrificial water reduction, photolysis experiments were carried out using polychromatic visible irradiation, employing the three ruthenium coronates **1a–1c** as sensitizers, methylviologen as electron relay, a supramolecular TiO₂-Pt catalyst [3] and triethanolamine (TEOA) as sacrificial donor [6]. The amount of hydrogen produced is about one-fifth that obtained with the standard system using [Ru(bpy)₃]Cl₂ (bpy, 2,2'-bipyridine) as sensitizer (see Fig. 2). In contrast with the standard sensitizer, which is destroyed by light-induced photoanation (PA) [17], the coronates show almost total photoinertness ($\Phi_{PA} \ll 10^{-4}$). With regard to possible applications, this improved photostability permits higher amounts of long-term hydrogen production in spite of the lower quantum yields and luminescence lifetimes (see Table 1). Redox potentials, which are similar to those of [Ru(bpy)₃]Cl₂, are also provided in Table 1 to permit a better comparison of the coronates **1a–1c** and [Ru(bpy)₃]Cl₂.

3.2. Oligoethyleneglycol-substituted bipyridazine complexes

The design of a ruthenium podate possessing very high photostability, a long excited state lifetime and good water solubility was achieved by combining photostable ruthenium bipyridazine complexes with supramolecular podate synthesis. Unbridged ruthenium bipyridazine complexes display relatively good stability against PA (photoanation from at least one of the excited states). Their photostability cannot be attributed to the lowering of the ³MLCT state [2] (see Table 2), but the dissociative metal-centered (³MC) state is expected to increase in energy due to a dramatic change in the π -electron density in the aromatic ligand



Scheme 1. Principles of synthesis of crown-ether-linked ruthenium coronates.

TABLE 1. Photophysical properties of the coronates 1a–1c

Complex	E_{ox} (V)		E_{red} (V)	τ_{F} (in water) (ns)
	$\text{Ru}^{2+\beta+}$	$\text{Ru}^{2+\gamma\beta+}$	$\text{Ru}^{2+\gamma\text{I}+}$	
1a	1.09	-1.51	1.18	2.81
1b	1.02	-1.58	0.95	32.1
1c	0.84	-1.76	1.27	3.45

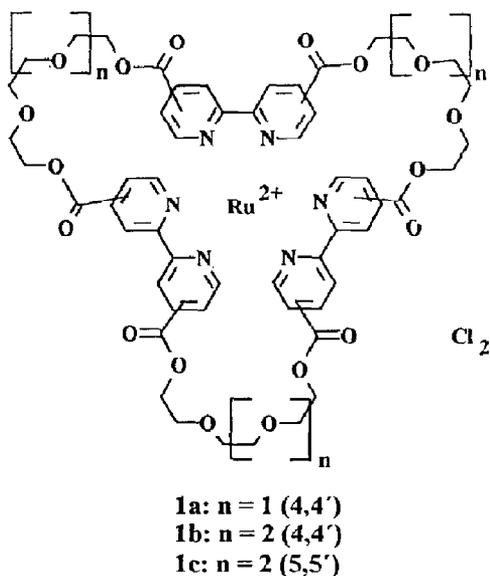
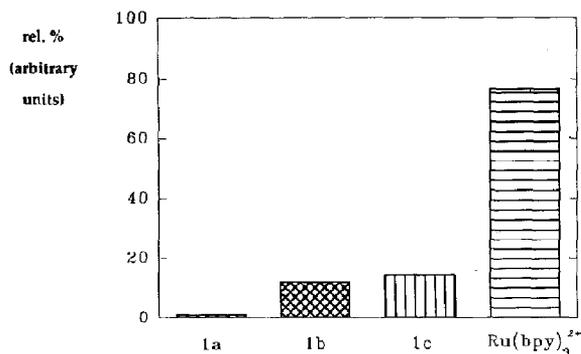


Fig. 1. Crown-ether-linked ruthenium coronates 1a–1c.

compared with 2,2'-bipyridine [10]. Thus the unbridged complexes **2a–2d** shown in Fig. 3 possess a quantum yield of PA at about the limit of detection, $\Phi_{\text{PA}} = 1 \times 10^{-3}$.

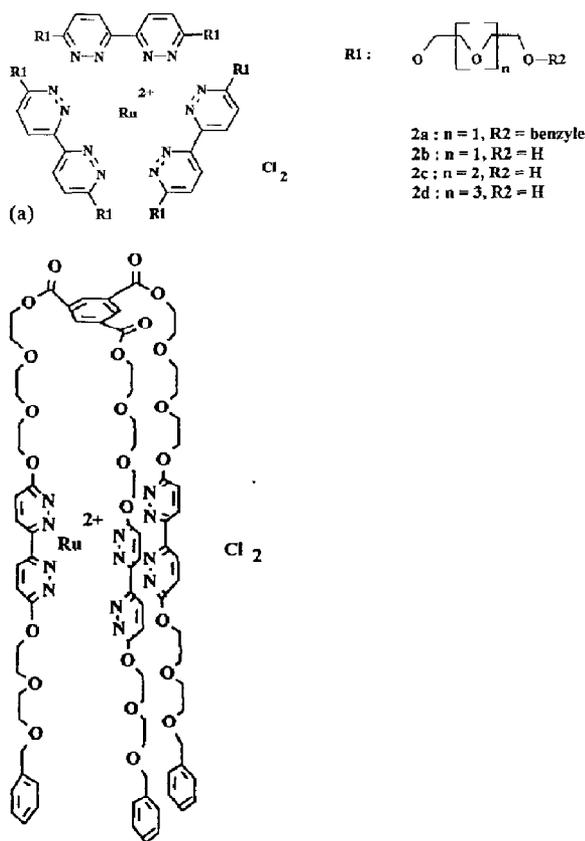
This relatively high photostability of ruthenium bipyridazine complexes has been combined with podate synthesis [1]. In this case we used oligoethyleneglycol chains as bridging units to ensure good water solubility of the resulting podate. The

Fig. 2. Amount of H_2 (μl) generated after 120 min of irradiation using the coronates 1a–1c and $[\text{Ru}(\text{bpy})_3]^{2+}$ as sensitizers. Donor, triethanolamine; catalyst, microheterogeneous $\text{TiO}_2\text{-Pt}$; electron relay, methylviologen (MV^{2+}).

photostability of the ruthenium podate **3** exceeds the measurable order of magnitude of the PA reaction using our experimental apparatus. It has been estimated to be $\Phi_{\text{PA}} \ll 10^{-4}$. It should be noted that the attached oligoethyleneglycol moieties of the ruthenium podate complexes not only permit high photostability, but also allow supramolecular interaction with cations and electron relays. The photophysical properties of these supramolecular ruthenium complexes can be changed by complexation to alkali and alkaline earth ions [18]. The quenching of **2c** with methylviologen yields a non-linearity in the Stern–Volmer plot, which we attribute to supramolecular interaction between the ethyleneglycol chains and the positively charged electron relay methylviologen (Fig. 4). From the linear regression, a quenching constant of the order of $k_{\text{q}} = 0.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ can be calculated. This value must be regarded as a first-order approximation.

TABLE 2. Excitation and emission maxima, luminescence quantum yield, lifetimes and redox potentials of 2a–2d and 3

Complex	λ_{ex} (nm)	λ_{em} (nm)	Φ_{L}	τ_{L} (in water) (ns)	E_{OX} (V) (Ru ²⁺ → ³⁺)	E_{red} (V) (Ru ²⁺ → ¹⁺)
2a	421, 457	631	0.045	1463 ± 54	−0.71	1.34
2b	420, 458	630	0.046	1571 ± 64	−0.66	1.35
2c	420, 459	627	0.055	1943 ± 87	−0.57	1.37
2d	422, 469	616	0.13	3345 ± 95	−0.77	1.09
3	421, 462	620	0.052	1986 + 309	−0.72	1.11



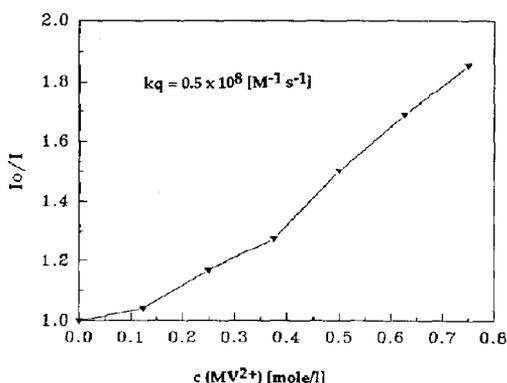
(b) 3

Fig. 3. Oligoethyleneglycol-substituted ruthenium bipyridazine complexes 2a–2d and 3.

4. Supramolecular sensitizer–relay dyads

4.1. Covalently linked assemblies

Since ET reactions in solution are limited, in principle, by the rate of diffusion of the medium itself, the supramolecular interaction between donor and acceptor involves the crossing of this diffusion barrier. The simple equation [3]

Fig. 4. Quenching of 2c with MV²⁺.

$$L = (D \times \tau)^{1/2} \quad (1)$$

where L is the average diffusion distance of the excited sensitizer during its luminescence lifetime, D is the diffusion constant of the medium employed and τ is the luminescence lifetime of the excited sensitizer, demonstrates that the enhancement of the ³MLCT lifetime of ruthenium complexes does not lead to an increase in photoelectron-transfer reactions in solution in an efficient manner [2].

The structure of the covalent sensitizer–relay assembly **4** is shown in Fig. 5. Details of the synthesis and photophysical properties are given in ref. 8. The covalently linked sensitizer–relay assembly illustrates the advantages of well-designed supramolecular systems for artificial photosynthesis (sacrificial hydrogen production as well as reduction of carbon dioxide to methane). Both processes, the reduction of water to hydrogen and methane formation, require more than one electron, and therefore the redox catalyst must act in both the photochemical one-electron reactions and the thermal two- and multi-electron reactions. In the experiments shown here, a ruthenium sol was employed.

The reduction of water to hydrogen requires only two electrons



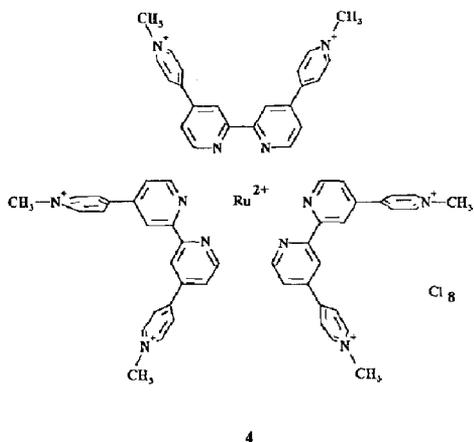
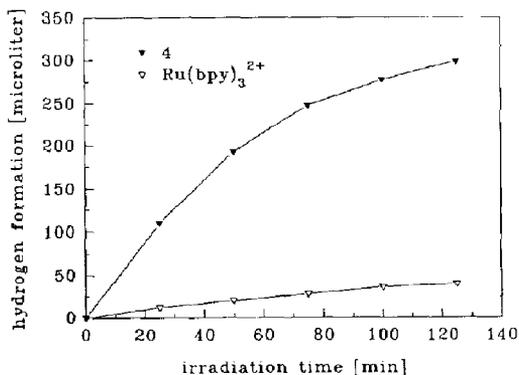


Fig. 5. Sensitizer-relay assembly 4.

Fig. 6. Hydrogen evolution: ▼, 4; ▽, [Ru(bpy)₃]²⁺ and MPVS; catalyst, platinum sol.

Eight electrons are required for the transformation of carbon dioxide into methane



Nevertheless, the main advantage of the latter process is its much lower redox potential compared with the reduction of water [9, 19].

From Fig. 6, it can be seen that hydrogen production by the sensitizer-relay assembly 4 is six times higher than that achieved by the standard sensitizer [Ru(bpy)₃]²⁺ and electron relay MPVS (3,3'-dimethyl-propyl-viologen-sulfonate) [19]. Figure 7 shows that methane formation from carbon dioxide is enhanced even more (tenfold larger). Another advantage of this simple supramolecular system is the absence of an electron relay in the photolysis system.

To our knowledge, this supramolecular sensitizer-relay assembly provides one of the most efficient photoredox systems for artificial photosynthesis. However, the long-term stability of the

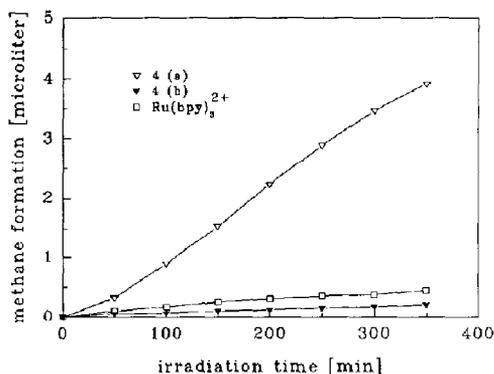


Fig. 7. CH₄ evolution: ▽, 4 using a CO₂-NaHCO₃ buffer; ▼, 4 in the absence of CO₂ and NaHCO₃; □, [Ru(bpy)₃]²⁺ as sensitizer with PVS (propyl-viologen-sulfonate) as electron relay. In all experiments, TEOA was used as sacrificial electron donor and a ruthenium sol as catalyst.

system is not fully satisfactory and must be increased in future.

4.2. Non-covalently linked assemblies

Despite the excellent photophysical and photochemical properties of covalently attached sensitizer-relay assemblies (e.g. ruthenium complex 4), there are serious disadvantages of covalently attached photoredox systems: their preparation involves multistep synthesis and the overall reaction yields are small; the flexibility of covalently linked systems is small due to synthesis constraints (the chemical substructures of the supramolecular system cannot be changed easily).

In our approach to non-covalently linked sensitizer-relay assemblies, we designed ruthenium complexes containing an ester-linked crown-ether moiety capable of binding cations and positively charged electron relays. ET quenching of photoexcited ruthenium complexes by a supramolecularly bound electron acceptor can occur rapidly due to the preformation of sensitizer-relay associates. The diffusion properties of the system are not the determining features [1]. In this case, covalent and non-covalent supramolecular systems are similar.

One of the most important differences between covalently and non-covalently linked supramolecular assemblies for photoelectron transfer is that non-covalently linked systems generally possess greater dynamic flexibility. This is important to enable ET out of the supramolecular sensitizer-relay unit. Otherwise back electron transfer may dominate, and no electrons for thermal re-

action processes (such as the formation of dihydrogen or methane) will be produced.

Possible ET reaction pathways include: exchange reactions between reduced electron relays inside the crown-ether cavity and non-reduced species from outside; electron exchange reactions between bound and unbound relays. The second reaction pathway seems to be favored for two reasons: (1) force-field calculations indicate an upshift of the actual potential of the bound electron relay; (2) there is an enlargement of the dihedral angle between the two aromatic subunits of, for example, methylviologen in the crown-ether-bound state. Consequently, thermal ET could occur from bound crown ether to free diffusing viologens [10].

This thermal ET reaction is analogous to that in the photochemical RC of *Rhodospseudomonas viridis* (and other bacteria and green plants), where ET occurs from the bound to the unbound quinone acceptor [4].

4.3. Binding constants

The binding constants of cations and the electron relay methylviologen to the supramolecular sensitizers **5a–5f** [9] and the corresponding crown-ether ligand **6** (as reference system) (Fig. 8) [9] are presented to provide more detailed information on the binding behavior in these non-covalently linked supramolecular sensitizer–relay assemblies.

The binding behavior of the free ligand was investigated to determine the presence of cooperative allosteric effects, as proposed by Rebek and coworkers [20] for crown-ether bipyridines of a similar structure. These allosteric effects can be very important in tuning the binding properties of the crown ethers attached to ruthenium complexes. Predictions from molecular modeling [10] indicate that the binding properties of the ester-linked crown-ether bipyridines should increase, when their nitrogen centers are chelated to ruthenium(II) in a metal complex, because the dihedral angle between the aromatic rings should decrease and thus the volume of the crown-ether cavity increases.

Complexation of a guest by a host species is often associated with a change in photophysical and other properties, such as NMR shifts or electron spin resonance (ESR) parameters [21]. Several (photo)physical parameters can be monitored to determine whether positively charged species are included in the 21C5 or 24C6 cavity of a crown-ether-modified bipyridine ligand. We compare results from UV, luminescence quenching and ¹H-NMR titrations. There is one serious complication.

These methods are not indicative of one specific binding mode. Therefore a fast equilibrium between the binding of a cation or viologen inside the crown-ether cavity and its attraction to the oligoethyleneglycol chain outside the cavity cannot be distinguished in our experiments. Therefore the calculated binding constants permit only an overall description of the process, but no final structural information can be derived.

4.3.1. UV titrations

Changes in the absorption spectra of the host system on addition of salt solutions were analyzed using the equations of Bourson and Valeur [21]. Characteristic changes in the absorption properties were detected in the spectral range 220–350 nm.

$$A_0(A_0 - A) = \epsilon_L / (\epsilon_L - \epsilon_{ML}) \times \{1 / (K_S[S] + 1)\} \quad (4)$$

where A is the absorption at a given wavelength, ϵ is the molar absorption coefficient, K_S is the binding constant, $[S]$ is the substrate concentration and subscripts ML and L refer to the complex and ligand respectively.

A double reciprocal plot of $(A_0/A_0 - A)$ vs. $[S]^{-1}$ yields a straight line and the binding constant is given by the intercept to slope ratio. Measurements on **5a–5f** and **6** were carried out in water, acetonitrile and H₂O–CH₃CN (1:1 mixture v/v). The added guest species differ in size and cationic charge (Table 3). The measured binding constants K_S for the free ligand **6** increase with the charge of the complexed cation (1+ to 3+) and with the polarity of the medium (10^2 – 3×10^3 l mol⁻¹) due to conformational changes of the crown-ether unit (Table 3). Interestingly, the constant derived for the ruthenium complex **5f** is about tenfold higher than that of the free ligand **6**. In our opinion, this result confirms molecular modeling observations, which indicate that the coordination of the ferrous nitrogens to the metal center results in a coplanar bipyridine system, and so a larger crown-ether cavity is created. The increase in the effective size of the cavity and the lack of the competitive effect [22] of the aromatic nitrogens in **5f** lead to a higher binding constant.

4.3.2. Luminescence quenching experiments

The determination of the binding constants from luminescence quenching titrations was derived in analogy with eqn. (4) of Bourson and Valeur [21]

$$I_{F0} / (I_{F0} - I_F) = (\epsilon_L \Phi_L - \epsilon_{ML} \Phi_{ML}) \{1 / (K_S[S] + 1)\} \quad (5)$$

where I_{F0} is the initial luminescence intensity, I_F is the luminescence intensity after the addition of a quencher, ϵ_L is the molar absorption coefficient of the ligand, ϵ_{ML} is the molar absorption coefficient

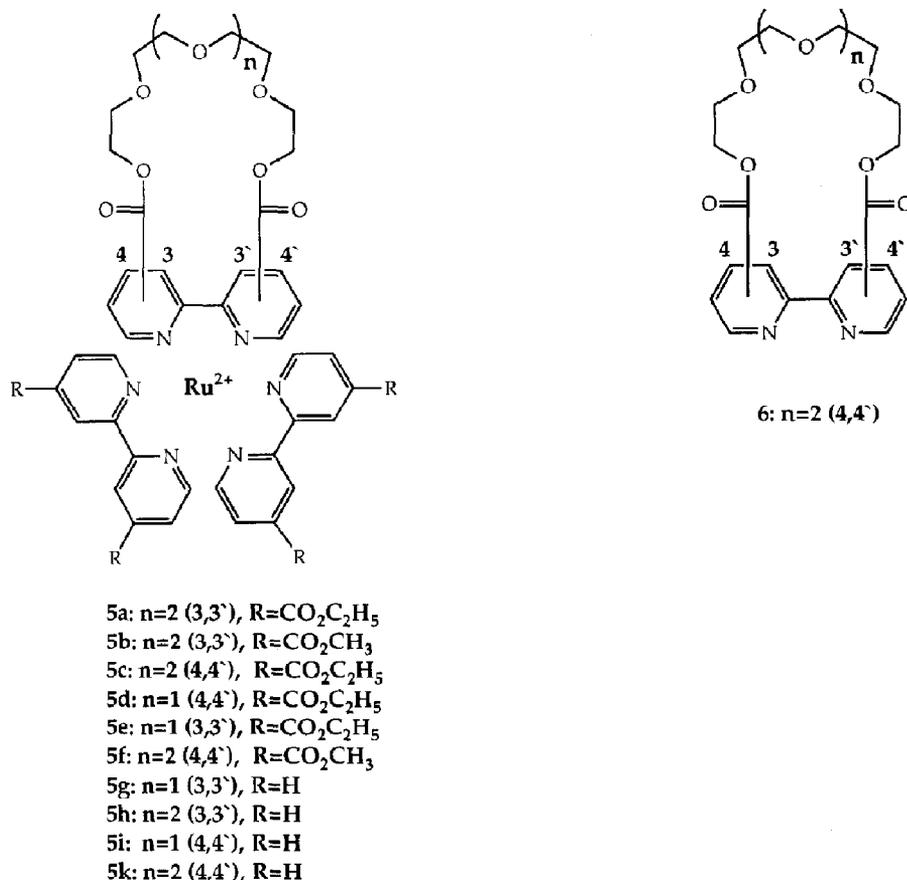


Fig. 8. Bis-heteroleptic crown-ether ruthenium complexes 5a–5k and ligand 6.

TABLE 3. Binding constants of 5f and 6 in H₂O–CH₃CN (1:1, v/v) (A), acetonitrile (B) and water (C)

Host	Substrate	Solvent	$K_S \times 10^2$ (l mol ⁻¹)	Correlation coefficient
6	N(CH ₃) ₄ ⁺	A	1	0.999
6	Eu ³⁺	A	34	0.982
6	MV ²⁺	A	28	0.969
6	MV ²⁺	B	6	0.984
5f	MV ²⁺	C	260	0.998

of the complex formed and Φ_{ML} is the luminescence quantum yield of the complex.

The broad ³MLCT luminescence band of the crown ether ruthenium complexes was integrated in the spectral range 550–800 nm. This experiment provides another indication of complex formation: non-linear Stern–Volmer plots are observed in the luminescence quenching experiments [12] for the crown-ether-modified ruthenium complexes with viologens. Analyzing the quenching data according to eqn. (5) yields binding constants of the same

order of magnitude as those derived from UV titrations (Table 4).

4.3.3. ¹H-NMR titrations

¹H-NMR was used as a third method to determine the binding constants. Binding of guest molecules in the crown ether moiety of the bi-pyridine derivative 6 should lead to predictable chemical shifts. The measurements were performed in deuterioacetonitrile. From the measured chemical shifts at different salt concentrations, the

TABLE 4. Binding constants of 5a–5e, calculated from methylviologen quenching data

Complex	Substrate	c (mol l ⁻¹)	$K_S \times 10^4$ (l mol ⁻¹)
5a	MV ²⁺	10 ⁻⁴	1.40
5b	MV ²⁺	10 ⁻⁴	4.80
5c	MV ²⁺	10 ⁻⁴	4.14
5d	MV ²⁺	10 ⁻⁴	5.73
5e	MV ²⁺	10 ⁻⁴	3.90

binding constants were calculated using a computer program originally developed by Kramer [14]; this program can fit curves for multistep equilibria by numerical integration using Newton zero search in several dimensions. The binding constants are in good agreement with those obtained by UV titration within measurement error (Table 5).

4.4. Single-photon-counting (SPC) experiments

An SPC experiment was carried out to obtain additional information on the binding mechanism of methylviologen to complex **5k**, which possesses two bipyridine units as basic ligands and a 24C6 crown-ether-modified bipyridine as a third ligand. As shown in Fig. 9, the Stern–Volmer plots derived from the luminescence intensity and lifetime quenching data do not overlap. From the deviation of the plots at higher concentration (above 400 μM MV^{2+}), a large contribution of static quenching to the quenching mechanism can be concluded. At the maximum viologen concentration in this experimental sequence, about 50% of the quenching arises from a static quenching mechanism. Due to experimental constraints, all quenching processes which occur faster than approximately 1 ns

TABLE 5. Comparison of the binding constants from $^1\text{H-NMR}$ and UV titration

Ligand	Substrate	K_s (1 mol^{-1}) (UV)	K_s (1 mol^{-1}) ($^1\text{H-NMR}$)
6	$\text{MV}(\text{PF}_6)_2$	600	805
6	$\text{N}(\text{CH}_3)_4\text{PF}_6$	100	52

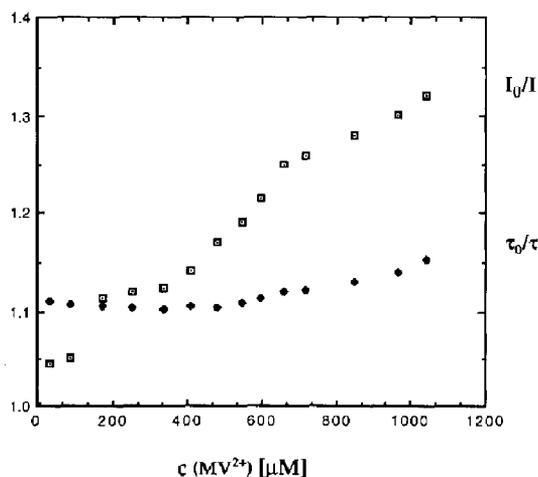
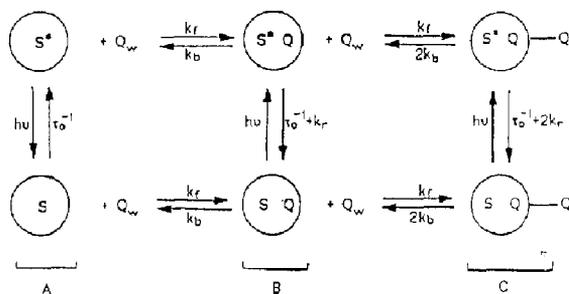


Fig. 9. Comparison between luminescence intensity (\square) and lifetime (\blacklozenge) quenching of **5k** by MV^{2+} in water. $C_{st} = 2.0 \times 10^{-6} \text{ mol l}^{-1}$.



Scheme 2. Interpretation of the quenching reactions according to Yekta *et al.* [22]: region A, the sensitizer displays luminescence (luminescence lifetime τ_0); region B, a quencher is bound as guest inside the host function of the crown-ether-modified sensitizer (k_r , reaction constant between bound sensitizer and quencher; k_b , reaction constant for the binding reaction (f, forward); k_b , reaction constant for the back reaction); region C, in addition to the quenching in region B, additional quenching from outside the supramolecular sensitizer-relay assembly can take place.

must be denoted as “static” using this particular apparatus.

Another very interesting region can be found at methylviologen concentrations between 10 and 200 μM . In this region, lifetime quenching is found to be stronger than luminescence intensity quenching. It should be noted that these experiments were carried out without a salt buffer, because supramolecular binding would be too weak to be detected in the presence of higher salt concentrations in the solution.

Changes in the ionic strength of the solution can cause a significant increase or decrease in the luminescence intensity [2]. However, the faster increase in lifetime quenching compared with luminescence intensity quenching indicates the presence of at least a second binding mode in the crown-ether complex plus methylviologen system. It should also be noted that the specific conditions required by the SPC experiment [13] do not allow a direct comparison of the binding behavior by the three methods described above.

According to our experimental results, the kinetic scheme developed by Yekta *et al.* [22] (Scheme 2) best describes the “real binding behavior”. It describes not only the 1:1 quenching process, but also the quenching from additional viologens outside the crown-ether cavity. This seems to be of special importance, because there is more than an equal amount of viologen in the system during steady state and time-resolved quenching experiments [12]. Further investigations, such as picosecond laser studies or the observation of spin-labeled viologens by ESR, could provide more insight into the mechanistic details.

5. Discussion

In this section, we focus on the non-covalently linked sensitizer–relay assemblies. To obtain a better understanding of the interaction between our crown-ether-modified ruthenium sensitizers and the cationic relays methylviologen and octylviologen (OV^{2+}), a Rehm–Weller plot of the quenching results from 12 different crown-ether ruthenium complexes is given in Fig. 10. According to the semiempirical free-enthalpy relationship of Rehm and Weller [23]

$$\Delta G^\ddagger = \frac{1}{2}\Delta G + \{(\frac{1}{2}\Delta G)^2 + (\Delta G^\ddagger(0))^{2}\}^{1/2} \quad (6)$$

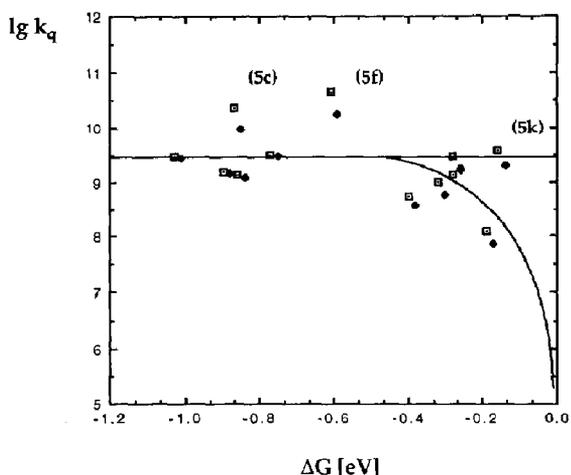


Fig. 10. Rehm–Weller plot of 12 crown-ether-modified ruthenium sensitizers and MV^{2+} and OV^{2+} as electron relays (see text for further explanation).

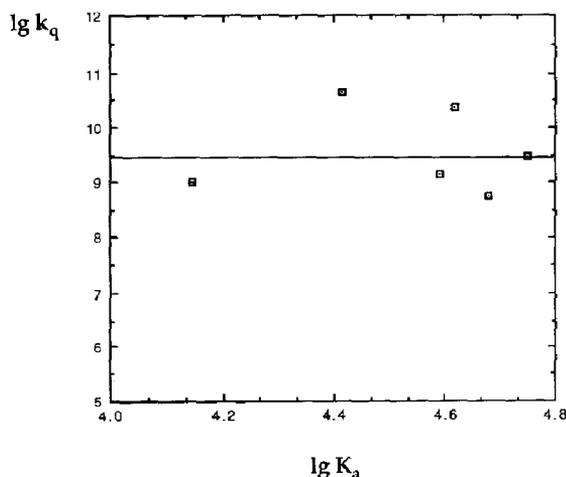


Fig. 11. Plot of the logarithmic quenching constants vs. the binding constants calculated from the same quenching experiments (data from Table 4 and Fig. 10).

the quenching constant between a photodonor and an electron relay is predicted to reach the limit of diffusion in the system if the free energy of the process is sufficient. As shown in Fig. 10, the crown-ether-modified ruthenium complexes follow the prediction by Rehm and Weller in good approximation, except for complexes **5c**, **5f** and **5k**. These complexes possess a 24C6 crown ether moiety in the 4,4' position (compound **6** in this report) of the bipyridine ligand and greatly exceed the diffusion barrier. From molecular modeling, we have concluded [10] that the crown-ether ligand **6** should be especially favorable for the binding of methylviologen and other viologens inside the crown-ether cavity. Contrary to these calculations, the binding constants obtained by UV and 1H -NMR titration are higher for other crown ether-modified ruthenium complexes with methylviologen.

As can be seen from Fig. 11, there is no clear correlation between the measured Stern–Volmer quenching constants and the calculated binding constants. This provides experimental support for the assumption of more than one simple binding mode of the viologens to the crown ether ruthenium complexes. The binding constants derived from UV titration and luminescence quenching can be regarded as non-specific information about the supramolecular interactions of the two species. However, for ligand **6** 1H -NMR clearly demonstrates the binding of methylviologen inside the cavity. Special binding modes with very efficient ET properties may exist, whereas other binding modes may lead to only weak interactions between the photodonor and acceptor pair.

6. Conclusions

In this paper, we have described the successful application of supramolecular photochemistry for the synthesis of highly stable ruthenium coronates **1a–1c** and ruthenium bipyridazine complexes **2a–2d** and **3**, as well as for the generation of systems for enhanced photoelectron transfer. The supramolecular species **4** and **5**, incorporated into artificial photosynthesis systems, may accelerate from the sensitizer to the relay due to the tight contact between the reacting species. In these systems, enhanced ET can be attained using covalently or non-covalently linked assemblies.

The non-covalent binding of **5f** or **6** and positively charged species was demonstrated by

the determination of the corresponding binding constants by three independent methods. Rehm-Weller behavior was observed during quenching of the ruthenium complexes **5a**–**5k** with methylviologen and octylviologen, except for **5c**, **5f** and **5k**. These complexes possess a 24C6 crown-ether moiety in the 4,4' position of the bipyridine ligand and greatly exceed the diffusion barrier. SPC experiments indicated that the binding mechanism may be much more complicated than simply the entering of the crown-ether cavity by the cation or electron relay. The best interpretation of all the observed effects was achieved using the kinetic scheme of Yekta *et al.* [22] originally developed for quenching processes in micelles.

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