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SUPRAMOLECULAR SENSITIZER–RELAY ASSEMBLIES. AN EVALUATION OF BINDING CONSTANTS FROM NON-LINEAR STERN–VOLMER PLOTS*

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A novel technique for determining the binding constants of host–guest complexes, viz. the bis-cationic electron relays methylviologen and octylviologen in the macrocyclic host of novel (bisheteroleptic) crown ether–ruthenium sensitizers, is described. This technique allows the separation of the quenching effects of bound and free electron relays. It can be used to calculate binding constants in non-covalently linked supramolecular systems evaluating the electron transfer process between guest and host. High binding constants comparable to those in many natural enzymes and the photosynthetic reaction centre were found. As an explanation for the behaviour of the sensitizers bound to the bipyridinium cations it is suggested that photoelectron transfer affects the binding between the excited sensitizer and the bound acceptor.

INTRODUCTION

Recently we reported the synthesis[1,2a] and the (photo)physical properties[2b] of novel bis-heteroleptic crown ether–ruthenium sensitizers of the type **1–4** (Scheme 1). These compounds possess the appropriate photophysical properties (e.g. photoredox potentials or lifetimes) for electron transfer compared with bipyridine carboxylate–ruthenium complexes[3] (e.g. **5**) and a macrocyclic host, directly linked to the photoactive metal centre.

As a prerequisite in ruthenium host–guest complexes, being models for artificial photosynthesis, effective electron-transfer is essential.[4] In analogy to the structure of the photosynthetic reaction centre,[5] efficient electron transfer in artificial photosynthetic systems has been accomplished in organized microheterogeneous media[6] and also in sensitizer–relay assemblies[7] possessing a covalent linkage of donor, sensitizer and electron acceptor (relay).

In organized microheterogeneous media the charge-separation step is diffusion controlled,[6] thus the quenching constants cannot exceed this value.[8] On the other hand, a covalently linked sensitizer–relay assembly showing very fast electron transfer rates also favours the back electron-transfer from the photoreduced electron relay to the photo-oxidized sensitizer or donor. Thus the photogenerated electrons and holes cannot be used in subsequent chemical reactions.[7]

In contrast to these studies, binding of bis-cationic electron relays such as methylviologen (MV^{2+}) or octylviologen (OV^{2+}) in the novel bis-heteroleptic crown ether–ruthenium sensitizers **1–4** has been shown to lead to very effective electron transfer and generation of photoreduced electron relays. As a consequence, very efficient sacrificial hydrogen evolution can be observed.[2]

An indication of supramolecular interactions is given by non-linear Stern–Volmer plots (Figures 1–3).[2] An intriguing possibility seemed to be the use of these non-linear Stern–Volmer plots for evaluating the binding constants in supramolecular host–guest complexes. In this paper, we describe an evaluation of the binding constants between guests (MV^{2+}, OV^{2+}) and hosts (supramolecular ruthenium sensitizers **1–4**) using the non-linear Stern–Volmer plots, a careful investigation of the concentration dependence of the quenching effect between ruthenium host complexes **1–4** and MV^{2+} or OV^{2+} and the effects of added ions and β-cyclodextrin and a molecular model for the supramolecular sensitizer–relay assembly explaining the experimental results.

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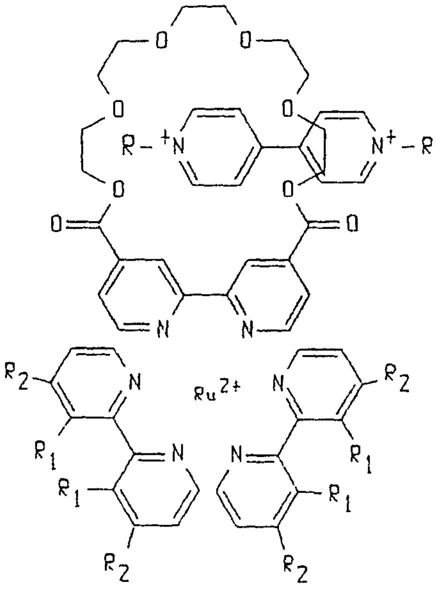
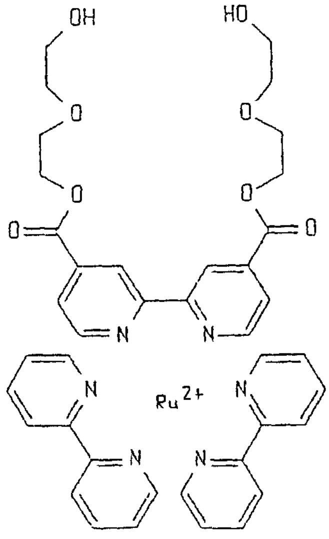


	R_1	R_2
1	H	H
2	$COOCH_3$	H
3	H	$COOCH_3$
4	H	$COOCH_2CH_3$



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Scheme 1. Structures of the novel bis-heteroleptic crown ether–ruthenium sensitizers **1–5** as well as the supramolecular sensitizer/relay complex ($R = -CH_3$, $-C_8H_{17}$)

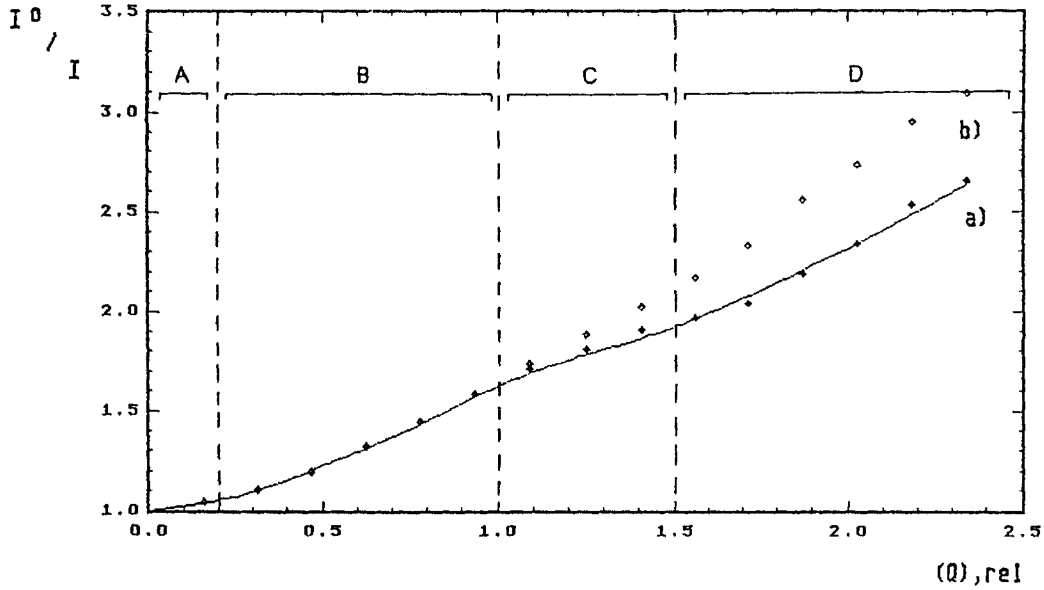


Figure 1. Stern–Volmer plots for the sensitzer **3** and the electron relay MV^{2+} at various total concentrations (all components dissolved in water); sections A–D see Figure. (a) $c_3 = 0{\cdot}70 \times 10^{-4}$ mol l^{-1}; $c_{MV^{2+}} = 0$–$1{\cdot}75 \times 10^{-4}$ mol l^{-1}. (b) $c_3 = 1{\cdot}40 \times 10^{-4}$ mol l^{-1}; $c_{MV^{2+}} = 0$–$3{\cdot}50 \times 10^{-4}$ mol l^{-1}

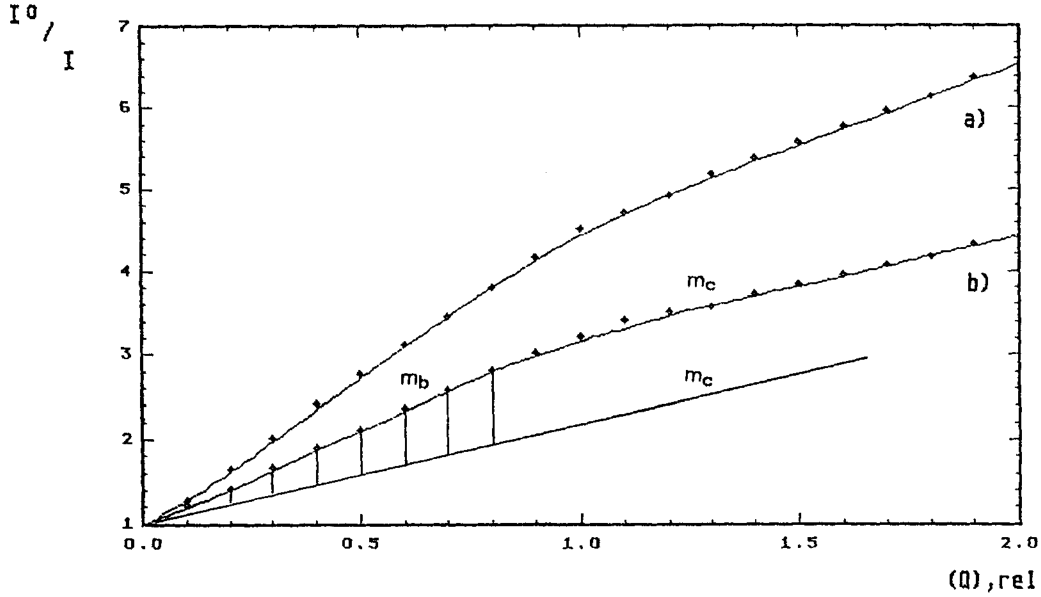


Figure 2. Stern–Volmer plots for the sensitizers **3** and **4** [water–acetonitrile (98 : 2, vv)] and the electron relay MV^{2+} [water–acetonitrile (75 : 25, vv)]. $c_{(3,4)} = 1 \times 10^{-4}$ mol l^{-1}; $c_{MV^{2+}} = 0$–2×10^{-4} mol l^{-1}. (a) **3**–MV^{2+}; (b) **4**–MV^{2+}

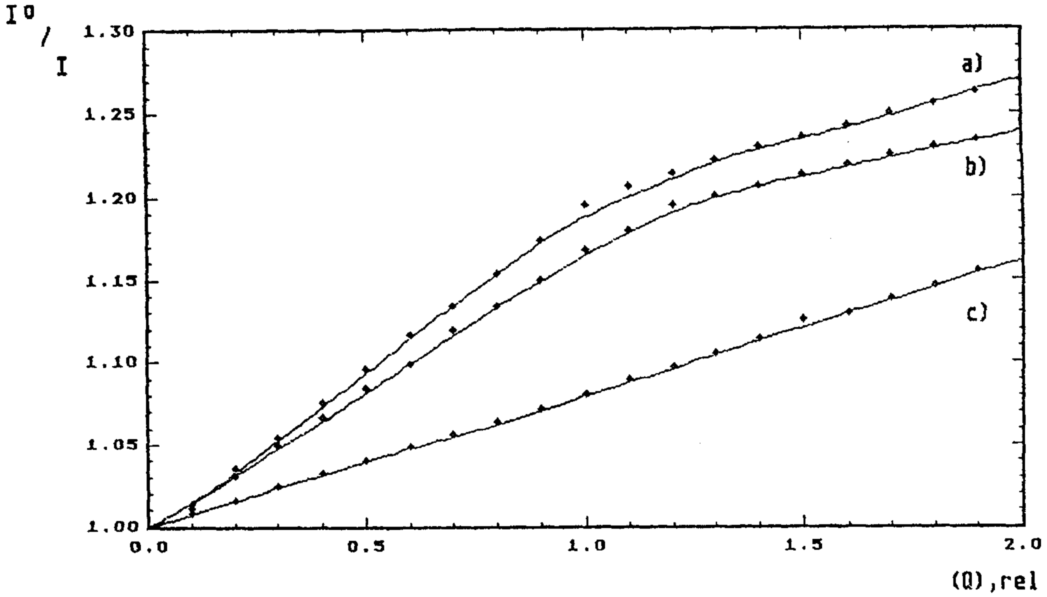
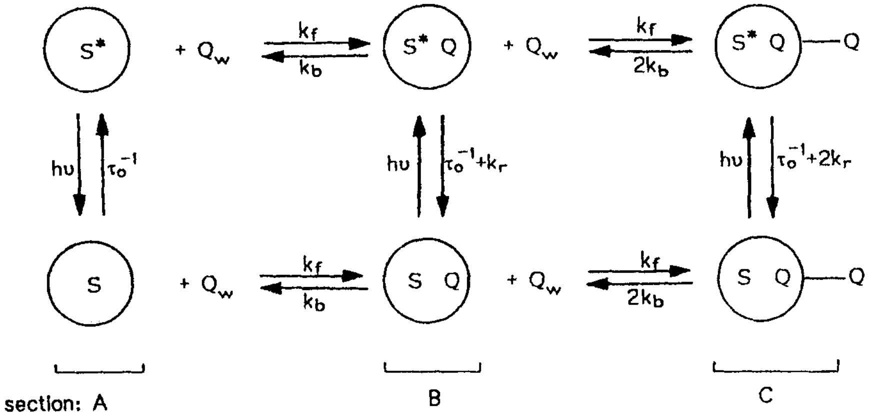


Figure 3. Stern–Volmer plots for the novel sensitizer–relay assemblies **1**–MV^{2+} and **2**–MV^{2+} in comparison with the linear quenching behaviour of the non-complexing bis-tetraethylene glycol–ruthenium–2,2′-bipyridine carboxylate-complex **5** and MV^{2+} (conditions as described in the Experimental section and Figure 2). (a) **1**–MV^{2+}; (b) **2**–MV^{2+} (c) **5** and MV^{2+}

BINDING CONSTANTS

For the determination of binding constants in a supramolecular structure, at least one characteristic property is required which depends monotonously on the formation of the assembly.[9] As is well known, without a supramolecular interaction of the sensitizer and the relay component, ruthenium–polypyridyl sensitizers show electron-transfer quenching.[10a] The kinetic model for the quenching of ruthenium–polypyridyl–crown ethers **1–4** with viologens (MV^{2+}, OV^{2+}) is shown in Scheme 2. This model is adapted from Yekta *et al.*'s paper[10b] referring to quenching processes in micelles.

For the calculating of the binding constant (Figure 4), the 'intramolecular' quenching effect of a bound relay (case B) has to be separated from the 'intermolecular'



Scheme 2. Kinetic scheme for quenching of sensitizers **1–4** with viologens (MV^{2+}, OV^{2+}). S = sensitizeres **1–4**; Q = bound quencher 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+})

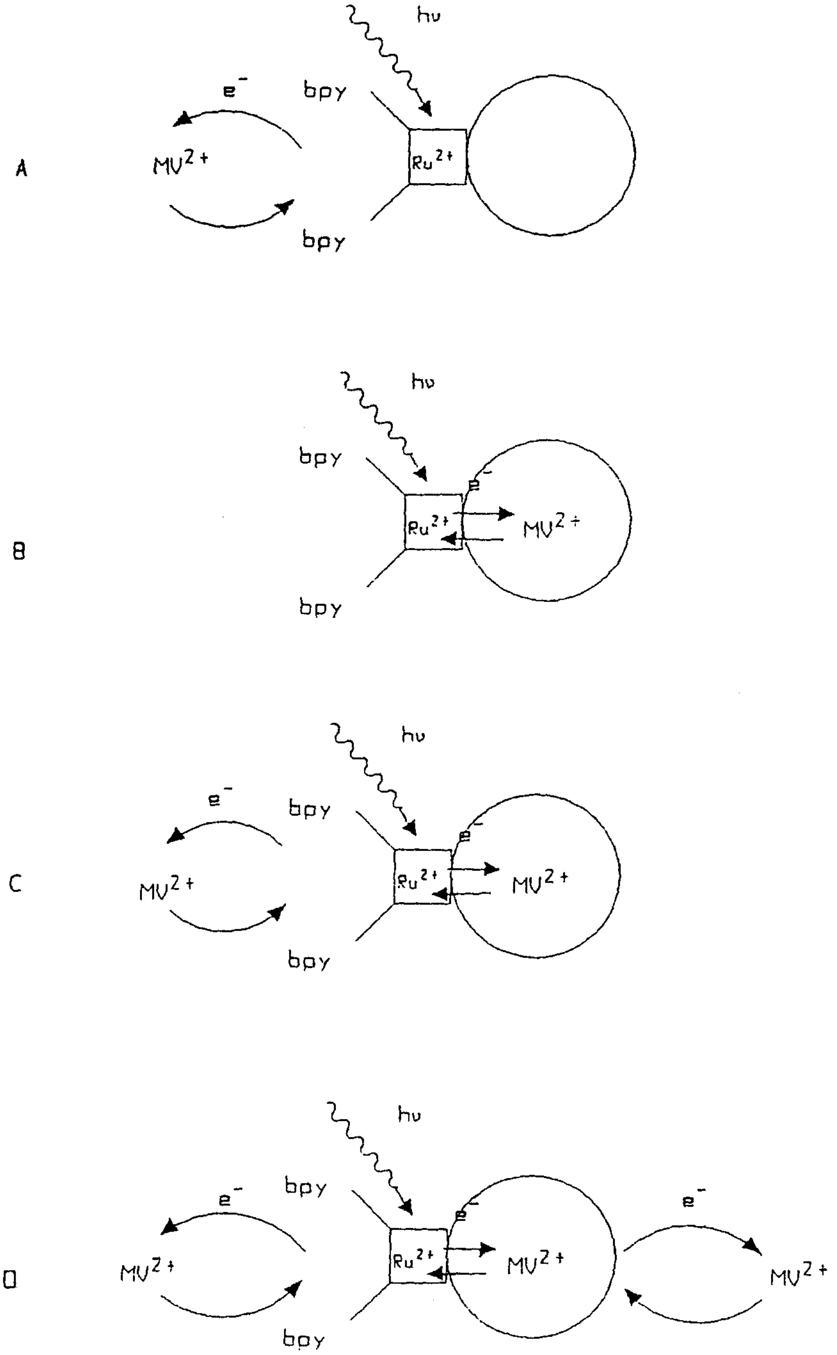


Figure 4. Quenching model of the bis-heteroleptic–crown ether–ruthenium sensitizers **1–4**. (A) The quenching mechanism is diffusion controlled; the binding of MV^{2+} in the crown ether receptor is not observed because of its low concentration ([Q] rel = 0–0·2). (B) The binding MV^{2+} in the crown 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 MV^{2+} to the free MV^{2+} occurs, leading to a rapid increase in the quenching constants

diffusion-controlled quenching process (case C; see below).*

PROCEDURE

The subtraction of the almost linear section C (slope m_c) in the Stern–Volmer diagram (Figure 1) (beginning after 1 : 1 stoichiometry of the viologen guest in the supramolecular host has been reached) from the slope m_b obtained from the quenching experiments in section B (Figures 2 and 3) leads to modified Stern–Volmer plots which are shown in Figures 5 and 6. The slopes m_b' in the range of the guest–host relative concentration from 0·2 to 0·8 are now a monotonous function indicating the formation of the supramolecular sensitizer–relay assemblies.

From the thus modified Stern–Volmer data the binding constants K_b were calculated using ChemSim as a non-linearly fitting program (see Experimental and

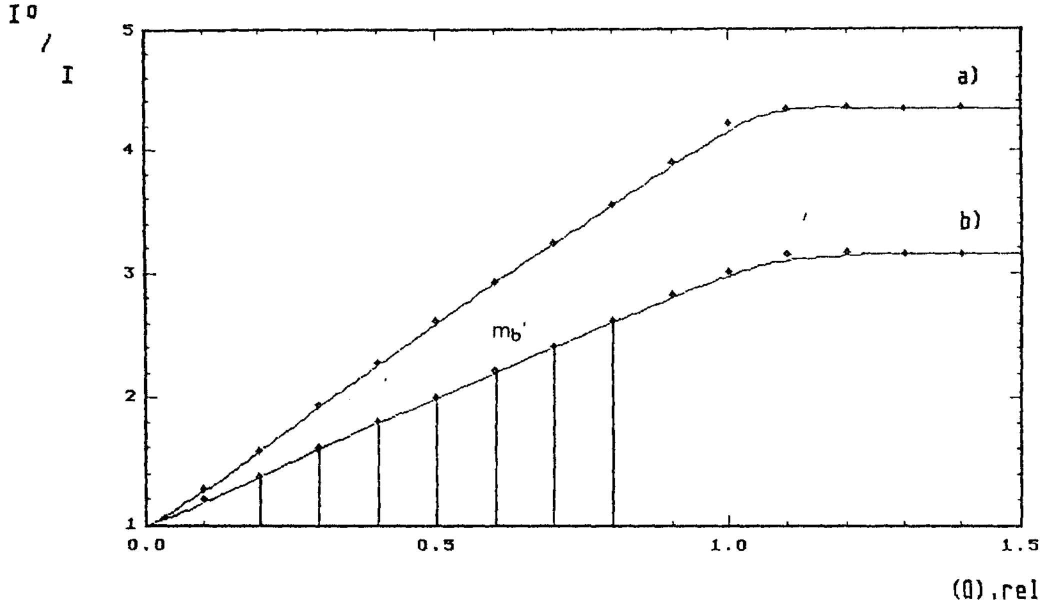


Figure 5. Modified Stern–Volmer plots with slope m_b' after subtraction of the linear part of section C (slope m_c) from the original Stern–Volmer plots ($m_b' = m_b - m_c$). (a) 3–MV^{2+}; (b) 4–MV^{2+}

Table 1. Quenching and binding constants of the novel non-covalently linked sensitizer–relay assemblies (**1**–**4** with MV^{2+} and OV^{2+})

	MV^{2+}		OV^{2+}	
Sensitizer	$k_q \times 10^{-9}$ $(l\ mol^{-1}\ s^{-1})^a$	$K_B \times 10^{-4}$ $(mol^{-1}\ l^{-1})^b$	$k_q \times 10^{-9}$ $(l\ mol^{-1}\ s^{-1})^a$	$K_B \times 10^{-4}$ $(mol^{-1}\ l^{-1})^b$
1	3·86	4·78 ± 0·45	1·96	4·31 ± 0·46
2	4·07	4·33 ± 0·47	4·09	4·06 ± 0·37
3	44·93	4·07 ± 0·39	17·80	3·51 ± 0·31
4	24·16	3·88 ± 0·37	9·66	3·14 ± 0·35
5	1·16	—	0·93	—

[a] Calculated by using the values from 20 to 80% complexation of the non-linear Stern–Volmer plots; c (sensitizer) = 10^{-4} mol l^{-1}; water–acetonitrile (98 : 2, v/v); quencher, methylviologen dichloride, octylviologen dichloride. The diffusion constant of the solvent given is $3{\cdot}0 \times 10^9$ l mol^{-1} s^{-1}.

[b] Calculated by using the corrected Stern–Volmer plots, as shown in Figures 5 and 6; c (sensitizer) = 10^{-4} mol l^{-1}.

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* 'Intramolecular' is defined as intramolecular in the host–guest complex.

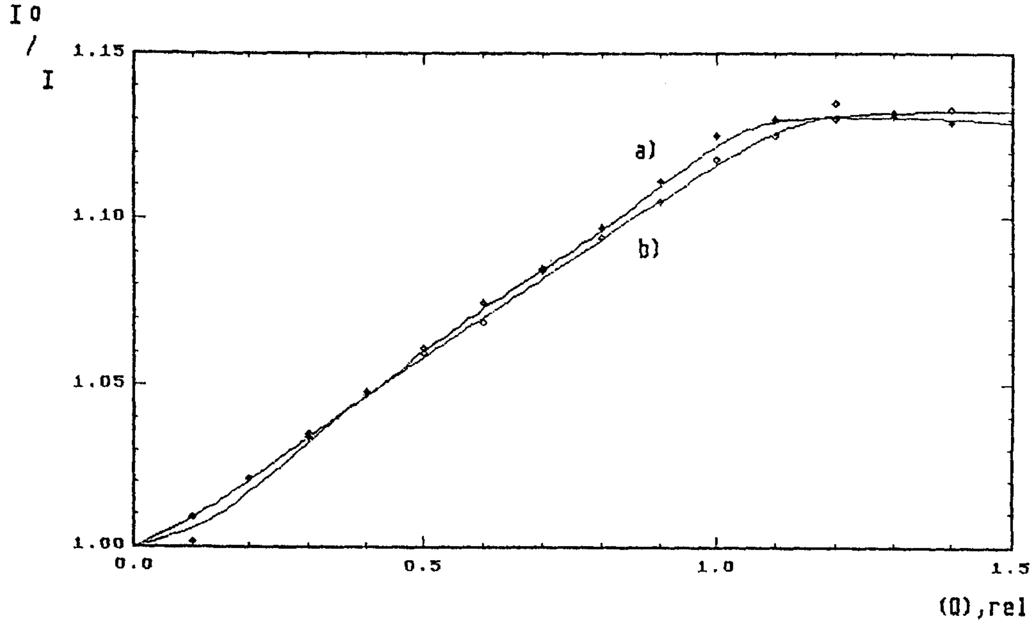

Figure 6. Modified Stern–Volmer plots with slope m_b' after subtraction of the linear part of section C (slope m_c) from the original Stern–Volmer plots ($m_b' = m_b - m_c$). (a) 1–MV^{2+}; (b) 2MV^{2+}

Table 2. Quenching constants of the non-covalently linked sensitizer–relay assembly 3–MV^{2+} for sections B, C and D (see Figure 1) at several sensitizer concentrations (all components dissolved in water)[a]

3 $c \times 10^4$ ($mol\ l^{-1}$)	$k_q \times 10^{-9}$ ($l\ mol^{-1}\ s^{-1}$)		
	B	C	D
1·40	30·28	15·77	27·60
0·70	19·22	9·35	32·20
0·35	25·75	—	30·70

[a] Errors < ±10%; $k_{qA} \approx 0$, $k_{qB} \approx k_{qD} > k_{qC}$.

Computational Details). This is equivalent to employing the equation

$$I_0/I = 1 + K_b[Q] \qquad (1)$$

as taken from Ref. 10c. The results are given in Tables 1 and 2.

A rigorous kinetic treatment following Bourson and Valeur's procedure[10d] based on the equation

$$\frac{I^0}{I^0 - I} = \frac{\varepsilon_S \Phi_S}{\varepsilon_S \Phi_S - \varepsilon_{QS} \Phi_{QS}} \left(\frac{1}{K_b[Q]} + 1 \right) \qquad (2)$$

was carried out for water as solvent (Figure 7). (ε = molar extinction coefficient, Φ = quantum yields and S = sensitizer). A linear relationship is found. The binding constant for 3–MV^{2+} is $K_b = 6 \cdot 62 \times 10^3\ mol^{-1}\ l^{-1}$. This is in fairly good agreement with the value $40 \cdot 70 \times 10^3\ mol^{-1}\ l^{-1}$ obtained in water–acetonitrile (98 : 2, vv).

INDICATION OF HOST–GUEST FORMATION

An indication of the binding of a viologen molecule in the crown ether cavity of **1**–**4** is given by a modified Stern–Volmer experiment in the presence of a competitive ion in the sensitizer–relay assembly. The addition of an equimolecular amount of KSCN and methylviologen to the crown ether sensitizer **1** leads to a less-pronounced non-linearity and thus a decrease in the calculated binding constant of methylviologen in the macrocyclic host **1**. In the presence of $Ba(SCN)_2$, **1** gives a linear Stern–Volmer plot and a very small quenching constant is found. Now the ion is included in the crown ether cavity.

The experimental results thus obtained (Table 3) are in good agreement with the binding constants of alkali metal ions into the 2,2′-bipyridine crown ether receptors determined by Rebek *et al.*[11] [e.g. $(3 \cdot 8–5 \cdot 5) \times 10^4\ mol\ l^{-1}$ for K^+].

A further test of the hypothesis presented is derived from the photoreduction of octylviologen in the presence of triethanolamine as a sacrificial donor and β-cyclodextrin (β-CD) as competitive receptor for the electron relay in its bis- and mono-cationic forms.[12] The binding constant of the bis-cationic octylviologen in the cavity of β-cyclodextrin was determined by

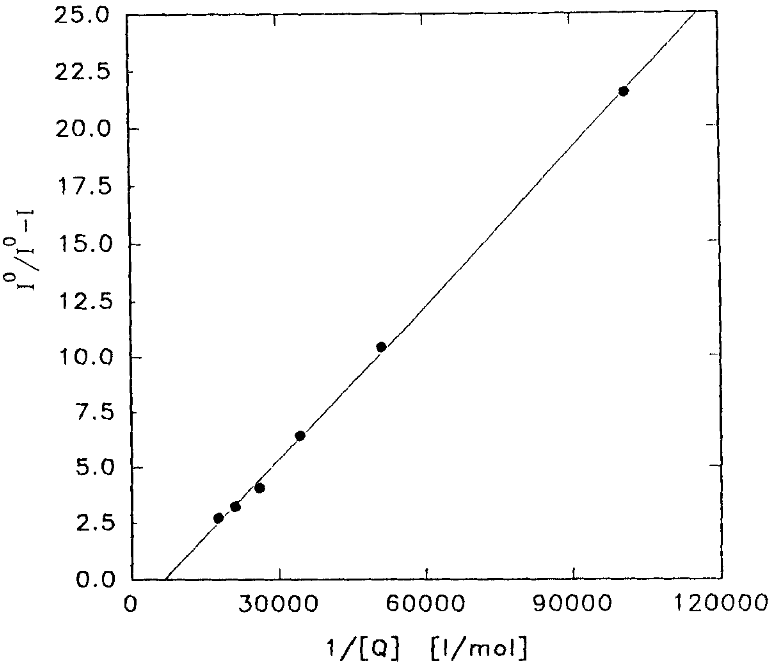

Figure 7. Graphical evaluation of equation (2) for **3**–MV^{2+} in H_2O

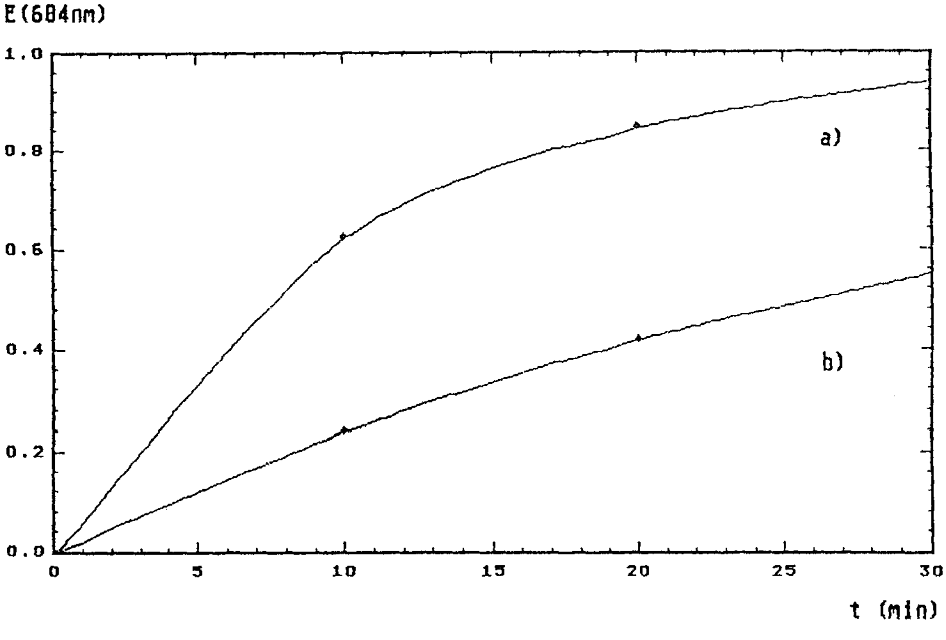

Figure 8. Photogeneration of β-CD–$OV^{+\cdot}$ using the sensitizers **1** and **5** ($c = 1{\cdot}40 \times 10^{-4}$ mol l^{-1}). Octylviologen ($c = 3{\cdot}00 \times 10^{-4}$ mol l^{-1}), β-cyclodextrin as competitive host for the octylviologen ($c = 1{\cdot}00 \times 10^{-3}$ mol l^{-1}) and triethanolamine as sacrificial donor ($c = 7{\cdot}50 \times 10^{-3}$ mol l^{-1}) in water. (a) **1**–OV^{2+}–β-CD; (b) **5** and OV^{2+}–β-CD

Table 3. Quenching and binding constants of MV^{2+} in the macrocyclic host **1** in the presence of the competitive guests K^+ and Ba^{2+}

	$k_q \times 10^{-9}$	$k_B(MV^{2+}) \times 10^{-4}$	$k_B(M^+/M^{2+}) \times 10^{-4}$
1–MV^{2+}–K^+	1·12	4·10–0·55	1·20–0·17
1–MV^{2+}–Ba^{2+}	0·82	—	>10

[a] Calculated using the values from 20 to 80% complexation of the non-linear Stern–Volmer-plots; *c* (sensitizer) = 10^{-4} mol^{-1} l^{-1}; water–acetonitrile (98 : 2, vv); quencher, methylviologen dichloride, octylviologen dichloride. The diffusion constant of the solvent given is $3{\cdot}0 \times 10^9$ l mol^{-1} s^{-1}.

[b] Calculated by using the corrected Stern–Volmer plots as shown in Figures 5 and 6; *c* (sensitizer) = 10^{-4} mol^{-1} l^{-1}.

Willner and co-workers[12] to be $5{\cdot}60 \times 10^3$ mol^{-1} l^{-1}, whereas the biding constant of the mono-reduced octylviologen in β-CD is larger than 1×10^5 mol l^{-1}. The latter should be preferentially bound to β-CD.

A comparison of the photoreaction rates (Figure 8) in the experiments using the sensitizers **1** and **5**–OV^{2+}–β-CD indicates that in the presence of sensitizer **1** there is a significantly higher photoproduction rate of reduced octylviologen, leading to the following conclusions. The binding constant of octylviologen (OV^{2+}) in the crown ether cavity has to be higher than the binding constant of the relay in β-CD. This experimental result is in good agreement with the calculated value of the binding constant. The very large quenching constant in the assembly **1**–OV^{2+}–β-CD leads to an increase in the photoproduction of $OV^{+\bullet}$–β-CD in comparison with **5** (Figure 8).

CALCULATIONS

Force-field calculations[1,2b] (performed using the program CHARMm[13]) of the sensitizer–relay assemblies indicate that only one viologen can be incorporated in the macrocyclic host. The resulting binding constants are high and comparable to those in natural enzymes[14] and the physical bound parts of the photosynthetic reaction centre of *Rhodopseudomonas viridis*.[5]

Force-field calculations also indicate the symmetrical binding of the viologen[1] in the macrocyclic host. The (slightly) lower binding constants which were found for octylviologen can be explained by the steric repulsion between the ester groups of the ligands and the alkyl chains of the octylviologen.

DISCUSSION

The binding constants of the viologens and the macrocyclic hosts **1**–**4** were determined using the modified Stern–Volmer experiment under steady-state irradiation of the absorption maxima. From a series of experiments it is well known that 5–1 kJ mol^{-1} per cationic charge has to be compensated for in these assemblies of a doubly charged metal coplex and a doubly charged viologen.[15] We therefore believe that the energy gain between the sensitizer ether units and the electron relay cationic centres is the reason for the high binding constants. An alternative explanation of the experimental data is based on the fact that the structures of ruthenium–polypyridyl complexes possess 'pockets'.[16] Balzani *et al.*[16] demonstrated the possibility of the selective population of these pockets by polyanionic species. In the same way, the counter ions might fill these 'pockets'. This effect diminishes the positive charge of the ruthenium complex and reduces electrostatic repulsion of the relay.

Force-field calculations (CHARMm, Polygen)[11] and MINDO/3-calculations[17] showed that the ether oxygen atoms, which are strong electron donors, can also fill the 'pockets' if no guest is bound in the macrocyclic host. The cavity of the crown ether receptors **1**–**4** in this state is relatively hydrophilic and hydrogen bonds can exist. The exchange of the water molecules by a biscationic viologen therefore leads to a positive entropy effect.

Steric effects seem to be less important: only a weak correlation of the binding constants and the space demand of the ligands and viologens is found. For the results presented so far, a model on a molecular basis is suggested (Figure 4). The model relates the four sections (A–D) of the non-linear Stern–Volmer plots to four different electron-quenching mechanisms at various relative concentrations for the systems **1**–MV^{2+}, **2**–MV^{2+} and **4**–MV^{2+}. A: minor effects at very low concentrations of the viologen are neglected in the evaluation presented. B: if the relative concentration of the relay increases, the binding of the electron relay in the macrocyclic host dominates and subsequently the quenching constant k_q exceeds the value which is given by the diffusion-controlled rate constant. C: at a molar ratio of 1 : 1 between the sensitizer and viologen the quenching constant is again smaller, and further quenching is diffusion controlled. D: the effects in region D are not fully understood.

An explanation of the experimental results might be as follows. In the case of a high total concentration of the relay, an electron transfer from the bound viologen (lower reduction potential) to a 'free' viologen becomes possible. A very rapid increase in the quencing constant rate results from this concerted process. This step depends very strongly on the solvent.

Changing the sensitizer concentrations (e.g. **3**) in the quenching experiment results in a stronger or weaker non-linearity. At very low and very high concentrations of sensitizer the non-linearity effect is less pronounced. At moderate concentrations the non-linearity can be observed in a very marked way. Here, in section D the quenching constant is even higher than in section B!

The non-linearity and the very high quenching constants derived from Stern–Volmer plots support the binding of the viologens in the macrocyclic host of **1–4**. The much lower quenching constants in the case of the 'open-chain' compound **5** and the blocked crown ether units (using Ba^{2+} as a competitive guest) can be explained by the 'variable-distance model' of Rau *et al.*[18] The electron-transfer quenching rate depends very strongly on the distance between the electron donor and acceptor.

CONCLUSIONS

The formation of sensitizer–relay assemblies from the novel crown ether–ruthenium complexes (**1–4**) and the electron relays methylviologen and octylviologen has been detected. A simple technique for determining the binding constants in these assemblies allows the calculation of binding constants in supramolecular electron transfer systems. In the case of the hosts **1–4** and the bis-cationic electron relays high binding constants were found under continuous irradiation, comparable to those in natural enzymes and the photosynthetic reaction centre.

EXPERIMENTAL AND COMPUTATIONAL DETAILS

The synthesis of the novel bis-heteroleptic crown ether–ruthenium sensitizers has been described recently.[1,2] Octylviologen was prepared as described [16] and dried *in vacuo* at room temperature to give the monohydrate (based on the ^1H NMR spectra in D_2O measured using a Bruker AM400/Aspect 300 system at 25 °C). Methylviologen (monohydrate; Aldrich), triethanolamine (Aldrich) and β-cyclodextrin (Fluka) were commercially available.

Stern–Volmer plots were obtained using a Hitachi F-3000 spectrometer at room temperature at concentrations adjusted to the expected equilibrium constants until a 2 : 1 molar ratio of added viologen to the crown ether sensitizer was reached. All solutions were deoxygenated by purging with nitrogen [deoxygenated using R3-11 catalyst (BASF)] for 20 min before the first measurements and at intervals of 3 min between the following 20 measurements.

In a typical fluorescence titration 500 μl of one of the viologen stock solutions [10^{-3} mol l^{-1} in water–acetonitrile (75 : 25, vv)] were added in 15 steps to 2.50 ml of the bis-heteroleptic crown ether–ruthenium complex [1×10^{-4} mol l^{-1} in water–acetonitrile (98 : 2, vv). The decrease in the fluorescence was detected at the emission maxima.[2]

A change of solvent affected the luminescence lifetimes only in a minor way, so that they were assumed to be constant in a first-order approximation [e.g. τ_L of **1** in water is 507 ns, in water–acetonitrile (98 : 2, vv) it is 522 ns and in water–acetonitrile (96 : 4, vv) it is 542 ns].

The calculations of the complex binding constants, requiring adjustment of the emission quotients to the changes in volume and concentration and for evaluation of more complicated equilibria, were performed using the program CHEMSIM written by R. Kramer for the ATARI 1040 ST. This programme is able to fit curves for multi-step equilibria by numerical integration using a Newton zero search in several dimensions. Owing to the use of both the simplex and the Newton–Raphson[20] algorithm, using fast convergence at the same set of parameters (equilibrium constant and 'intrinsic' fluorescence intensities) independent of the chosen starting values for these variables is obtained.

ACKNOWLEDGEMENTS

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