Photoinduced Electron Transfer between Metal-Coordinated Cyclodextrin Assemblies and Viologens

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Abstract: Two novel tris(bipyridine)ruthenium(II) complexes bearing two and six β-cyclodextrin binding sites on their ligands have been synthesised and characterised. Complex **1**, bearing two cyclodextrins, adopts a conformation in aqueous solution where parts of the aromatic ligands are self-included into the cyclodextrin moieties. This results in a loss of symmetry of the complex and gives rise to a much more complicated ^{1}H NMR spectrum than expected. Photophysical studies indicate that the appended cyclodextrins protect the luminescent ruthenium core from quenching by oxygen, which results in longer excited state lifetimes and higher emission quantum yields compared with the reference compound, the unsubstituted ruthenium tris(bipyridine). Inclusion of suitable guests such as dialkyl-viologens leads to a quenching of the luminescence of the central unit. In these supramolecular donor–acceptor dyads an efficient photoinduced electron transfer from the excited ruthenium moiety (the donor) to the viologen unit (the acceptor) is observed. The alkyl chain length of the acceptor plays an important role on the binding properties; when it exceeds a certain limit the binding becomes strong enough for electron transfer to occur. Interestingly, a viologen with only one long alkyl tail instead of two shows no efficient quenching; this indicates that cooperative interactions between two cyclodextrins binding one viologen are essential to raise the binding constant of the supramolecular dyad.

Keywords: cyclodextrins · electron transfer · inclusion compounds · ruthenium · supramolecular chemistry

Introduction

Green plants and photosynthetic bacteria use sunlight as their source of energy. Through photosynthesis they are able to convert the light into chemical energy, which in turn is used to trigger biological processes. The photosynthetic pathway is characterised by a very high quantum efficiency, which is the result of extremely fast electron transfer over large distances. This proceeds by a complicated cascade of chromophores and a very slow back transfer of the electron.[1] Although much progress has been made in the unravelling of this pivotal process, the explanation of the underlying mechanisms remains one of the biggest challenges for science. Many synthetic models have been prepared to obtain a better understanding of the photophysical properties of simple systems.[2] Most of these are focused on the generation of charge-separated species through photoinduced electron transfer. Covalently linked donor–acceptor (DA) dyads have given us more insight into the processes that influence the transfer of the electron, such as the distance and orientation of both the donor and the acceptor chromophore[3] and the nature of the solvent.[4] The synthesis of such covalently linked dyad systems requires a great deal of effort and therefore noncovalently linked systems which benefit from the supramolecular principles discovered over the last decades have attracted much interest.[5] More recently, better understanding of the photophysical properties has led to the incorporation of function in these systems, as in light-driven molecular machines[6] and chemical sensors.[7] Tris(bipyridine)ruthenium(II) complexes are well known in this field because of their excellent photophysical and excited-state redox properties.[8] Ruthenium(II) is especially interesting since it forms kinetically stable bonds with bipyridines, which makes the synthesis of heteroleptic compounds possible.[8, 9]

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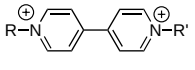
Attaching functional groups to the bipyridine ligands offers a route to bring together several components for a specific function through coordination around the metal.

Recently, the synthesis of bipyridine ligands with two[10, 11] appending cyclodextrins has been reported, as well as the use of these compounds to construct cyclodextrin assemblies through the coordination of metal ions.[12, 13]

In this paper we report the synthesis of two tris(bipyridine)ruthenium(II) complexes bearing two (**1**), and six (**2**) β-cyclodextrin (CD) moieties from the bipyridine-spaced dimer **3**, as shown in Scheme 1. The cyclodextrins are connected to the 4,4′-position of the bipyridine ligand to avoid problems with steric crowding around the metal centre. The ruthenium complex will function as an electron donor while the cyclodextrins act as a binding site for an electron acceptor, that is viologen derivatives such as dinonyl, methyl-nonyl and dipentyl (compounds **4**–**6**, see Scheme 2).



	R	R′	X^-
4	C_9H_{19}	C_9H_{19}	Br^-, Br^-
5	C_5H_{11}	C_5H_{11}	Br^-, Br^-
6	C_9H_{19}	CH_3	Br^-, I^-

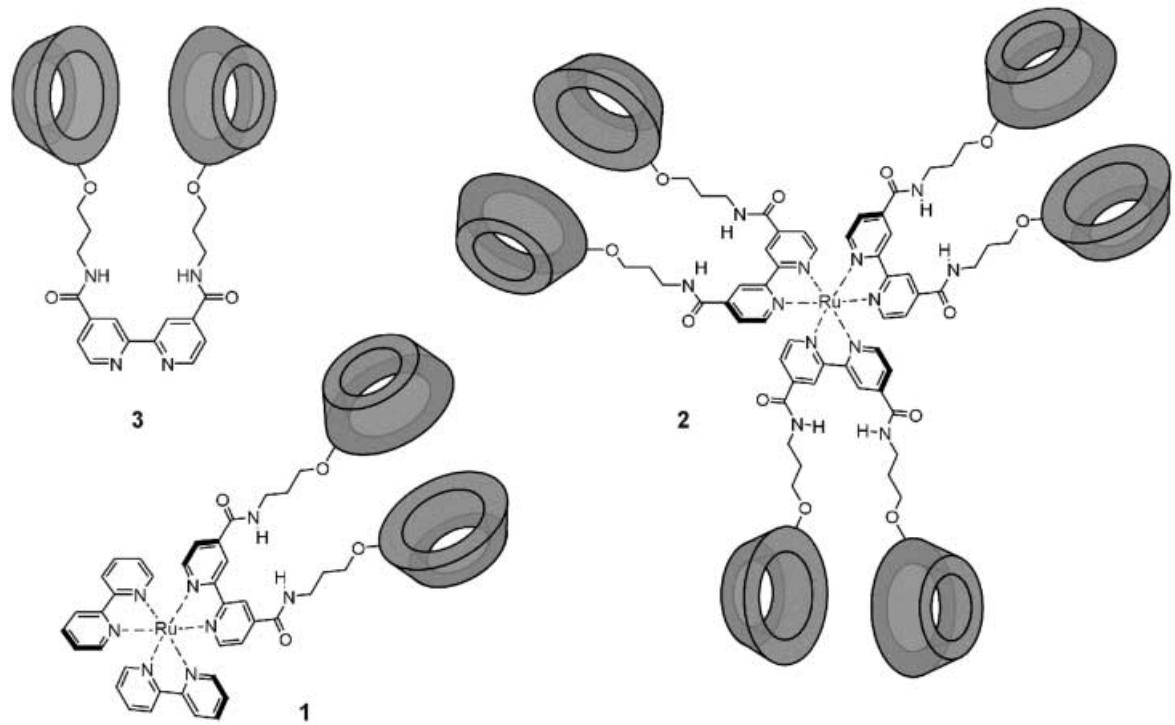
Scheme 2. *N*,*N*′-Dialkyl-4,4′-bipyridine derivatives **4**, **5** and **6** (X^-, counterion).

In ligand **3** two cyclodextrin binding sites are present in one ligand, and they are connected through their secondary sides. For such a compound , cooperative-binding interactions[14] can be expected for the association with ditopic guests, that is guests with two parts that can be bound by a cyclodextrin. Similar cooperative effects between the cyclodextrin binding sites in **1** and **2** for ditopic viologens can lead to higher binding constants and hence the possibility to detect photoinduced electron transfer reactions even at very low host concentrations. In this paper we present an investigation of the photophysical properties of compounds **1** and **2**, including electron-transfer reactions to a bound viologen acceptor as studied by steady-state and time-resolved fluorescence spectroscopy. In addition, we describe the conformational behaviour of these compounds in water (D_2O).

Results and Discussion

Synthesis: The synthesis of the bipyridine-spaced dimer **3** has been described by us before.[10, 12] This ligand was used to construct the two ruthenium(II) complexes **1** and **2**.[15] Compound **2** was synthesised by treating three equivalents of **3** with $RuCl_3$ in mixture of ethanol/water (1:1 *v*/*v*) heated under reflux. The heteroleptic complex **1** was formed by reaction of ligand **3** with $[Ru(bpy)_2Cl_2]$ (1 equiv) in the same solvent system. Complexes **1** and **2** were isolated as their chloride salts by pouring the respective reaction mixtures in acetone and collecting the precipitates. Minor impurities were removed by size-exclusion chromatography. All compounds were fully characterised by ^1H NMR, mass spectrometry and elemental analysis. For all three complexes, two diastereoisomers are formed as a result of the chirality of the octahedral coordination around the ruthenium centre. No efforts were made to separate these isomers.

The viologens **4**–**6** (Scheme 2) were synthesised according to well-established literature procedures[16] by treating 4,4′-



Scheme 1. Ligands and complexes discussed in this paper.

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bipyridine with an excess of the appropriate alkylhalogenide in acetonitrile.

Photophysical properties: An overview of the spectroscopic data is given in Table 1, which also includes the data measured for the reference compound $[Ru(bpy)_3]^{2+}$ The UV/Vis spectra of compounds **1** and **2** in aqueous solution show the characteristic metal to ligand charge transfer bands (MLCT)

Table 1. Spectroscopic and photophysical data for the ruthenium complexes in aqueous solution.

	Abs λ_{max} [nm]	Em λ_{max} [nm]	ε [$M^{-1}cm^{-1}$]	$\tau_{deaerated}$ [ns]	$\tau_{aerated}$ [ns]	$\Phi_{aerated} \times 10^2$	$k_q(O_2)$ [$M^{-1}s^{-1}$]
$[Ru(bpy)_3]^{2+}$	451	605	13000	608	390	2.8[a]	3.2×10^9
1	477	658	14600	480	400	1.8	1.4×10^9
2	464	625	17200	960	811	7.2	0.7×10^9

[a] Taken from ref. [8].

centred at around 450–480 nm and the intense ligand centred (LC) absorptions around 300 nm (Figure 1). The MLCT absorptions of complexes **1** and **2** show a red-shift in comparison with $[Ru(bpy)_3]^{2+}$ due to the presence of the electron withdrawing amide groups on the bipyridines. The red-shift of compound **2** is less pronounced since it is compensated by a blue-shift caused by the reduced σ-donor capacity of the three amide-functionalised bipyridine ligands.[17] The shoulder in the LC band of compound **1** clearly reflects the fact that one of the 2,2′-bipyridine ligands is replaced by a more electron poor bipyridine; this results in a bathochromic shift of almost 20 nm. Also visible is the reduced oscillator strength of the substituted bipyridine, which is reflected in the lower molar extinction coefficient of the LC band for compound **2**.

The emission properties in aqueous solution of compounds **1** and **2**, when excited in their MLCT band, showed the same trends as the absorption spectra (Figure 1, inset). Red-shifts of the emission maxima compared to $[Ru(bpy)_3]^{2+}$ were observed for both complexes. We measured the excited state lifetimes τ of compounds **1** and **2**, which were monoexponential for both complexes. The results (Table 1) reveal a remarkably high value for **2**, which is more than twice as high as that of the model compound $[Ru(bpy)_3]^{2+}$. The same holds for the emission quantum yield Φ for compound **2** (almost threefold increase, see Table 1). Such behaviour can be easily explained by the quenching of dioxygen in aqueous solution for the three complexes. From the experimental lifetimes in solution in the presence (aerated) and absence (deaerated) of oxygen (Table 1), it becomes clear that the quenching is much less effective for **2** in comparison to $[Ru(bpy)_3]^{2+}$. This is due to the structure of complex **2** in which the six cyclodextrins efficiently shield the ruthenium core from the environment. A similar phenomenon has been observed for ruthenium complexes bearing dendritic wedges on their bipyridine ligands.[18] The effect of oxygen quenching can best be quantified by calculating the rate constant (k_q) for this process from the Stern–Volmer equation [Eq. (1)].[8]

$$\frac{\tau_0}{\tau} = 1 + k_q \tau_0 [O_2] \quad (1)$$

τ and τ_0 represent the respective lifetimes in aerated and deaerated solutions, and $[O_2]$ is the saturated concentration of oxygen in water (2.9×10^{-4} M at 298 K).[19] The calculated values (Table 1) reveal that the complexes bearing cyclodextrins indeed have a lower quenching rate than the reference compound $[Ru(bpy)_3]^{2+}$.

NMR experiments: Compound **1** showed interesting conformational behaviour in aqueous solution as seen from its proton NMR spectrum (Figure 2). When recorded in $[D_6]$DMSO the aromatic region of the spectrum showed the expected chemical shift pattern for a heteroleptic complex with general formula $[Ru(bpy)_2L]^{2+}$, where L is the ligand that differs from bipyridine. The spectrum is roughly the sum of the resonances belonging to the cyclodextrin ligand **3**—a singlet at 9.37 ppm (H3), a doublet at 7.81 ppm (H6) and a doublet at 7.74 ppm (H5)—and those of the unsubstituted bipyridine ligands, that is a doublet at 8.87 ppm (H3), a double doublet at 8.22 ppm (H4), a doublet at 7.92 ppm (H6) and another double doublet at 7.57 ppm (H5). The resolution of the spectrum was not high enough to show the small couplings between the *meta*-protons.

When the spectrum was recorded in D_2O (Figure 2b), however, the clear aromatic region was transformed into a multitude of signals. The same phenomenon has been described by us for dimer **3**[10] and other dimers[14]. This effect was ascribed to the formation of a self-inclusion complex in water, in which the aromatic spacer is partly included in one of the two cyclodextrin cavities. For the bipyridine unit, which usually has C_2 symmetry, this in-

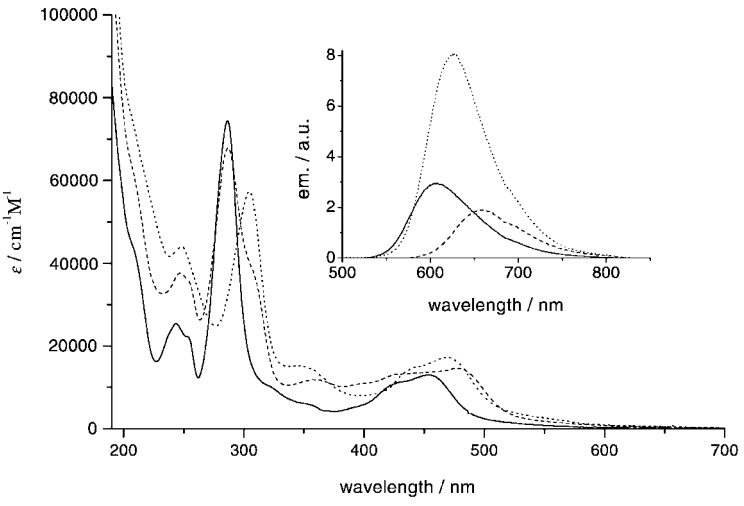

Figure 1. Absorption and emission (inset) spectra of $[Ru(bpy)_3]$ (——), **1** (- - - -), and **2** (••••) in aqueous solution at 25 °C.

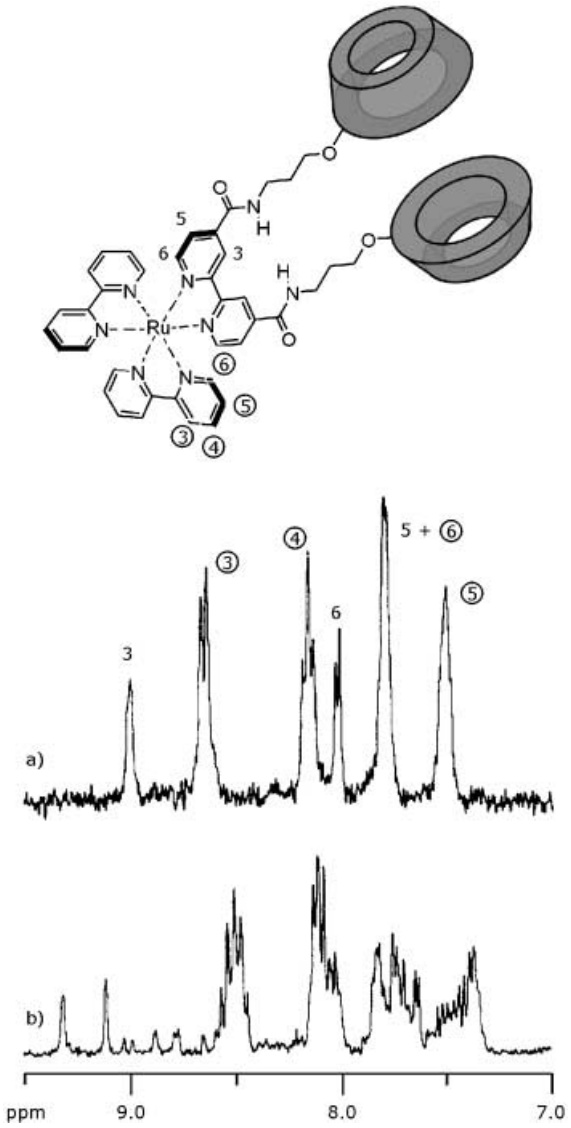

Figure 2. Aromatic region of the 500 MHz proton spectrum of ruthenium complex **1** in a) [D_6]DMSO and b) D_2O.

clusion leads to a loss of symmetry. Every pyridine ring therefore has its individual set of chemical shifts resulting in a doubling of the aromatic signals. In aqueous solution hydrophobic effects provide the driving force for this process, whereas in DMSO these are absent and the symmetric structure is adopted.

Self-inclusion also explains the increase in the number of signals of complex **1**. In this case, however, the process not only leads to a loss of symmetry of the ligand bearing the cyclodextrins, but it also induces asymmetry in the other two bipyridine ligands, since one pyridine ring will be closer to the self-inclusion site than the other. Overall, this will lead to a doubling of aromatic signals in the D_2O spectrum in comparison with the DMSO spectrum. Given the complexity of the spectrum in aqueous solution, however, this alone is not enough to explain the observed pattern. This becomes clearer if we look at the signal at 8.5 ppm, which belongs to the H3 protons of the non-cyclodextrin bipyridines. This peak appeared to be split into four doublets rather than into two. In the 2D COSY spectrum (Figure 3a) the coupling of these H3-protons with the H4 bipyridine protons was visible, which resonate around 8 ppm. Although badly resolved, four cross peaks were present. Subsequently looking at the coupling of the H4 protons with the H5 bipyridine protons, four cross peaks could be identified again. Four peaks also appeared for the coupling between the H5 and H6 protons (Figure 3a). This indicated that also the other bipyridine ligands in the complex, and not only the cyclodextrin-bearing ligand, lost their C_2 symmetry, and therefore have their own set of eight individual peaks. The loss of symmetry of the structure can be explained by assuming that the cyclodextrin that is involved in the inclusion process is closer to one of the bipyridine ligands than to the other. This would make them chemically inequivalent and give them different sets of chemical shifts. In summary, the relatively simple DMSO spectrum of seven resonances is transformed into a complicated spectrum due to the formation of a self-inclusion complex, which removes all symmetry.

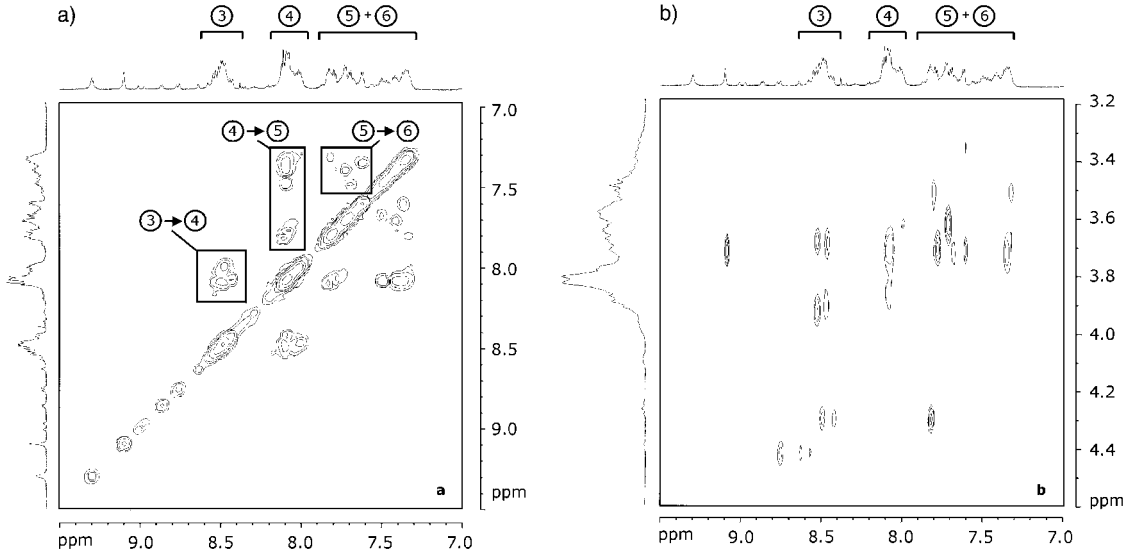

Figure 3. Parts of the 500 MHz a) 2D COSY and b) NOESY spectrum of ruthenium complex **1** in D_2O at 25 °C. For numbering see Figure 2.

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In addition to the aromatic region, the anomeric (4.8–5.2 ppm) and non-anomeric (3.4–3.8 ppm) regions of the spectrum were also affected. Monofunctionalisation of the cyclodextrins results in a loss of their C_7 symmetry, which makes both regions already quite complicated to interpret.[20] In the self-included structure, the cyclodextrins of **1** are no longer equivalent. This leads to a further increase in complexity of the spectrum, which makes it virtually impossible to assign the signals.

The presence of a self-included conformer was further supported by NOESY experiments (Figure 3b), which clearly showed cross peaks between aromatic protons and non-anomeric cyclodextrin protons. Unfortunately the complexity of the cyclodextrin part of spectrum (see above) did not allow us to further analyse the structure of the self-inclusion complex. Since mainly cross peaks appear between protons of the non-cyclodextrin bipyridines, we may tentatively conclude that these are the ligands that are predominantly involved in the self-inclusion process.

The spectrum of compound **2** in D_2O did not show an increase in signals in its aromatic region compared with its spectrum in DMSO. Instead, a slight broadening of the resonances is observed, suggesting some dynamic behaviour. Apparently, steric crowding of the six cyclodextrins around the ruthenium complex blocks the self-inclusion process in this compound.

Photoinduced electron transfer processes: Quenching of the emission of ruthenium complexes by *N*,*N*′-dialkyl-4,4′-bipyridinium ions (viologens) is well documented.[21] This process operates by a photoinduced electron transfer mechanism from the excited ruthenium moiety to the viologen (the acceptor). It can occur both inter- and intramolecularly, for example in dyads, where the ruthenium complex and the viologen are covalently linked.[22] The present systems are supramolecular analogues of these dyads. The β-cyclodextrin hosts can bind the viologen guest, bringing it close to the luminescent metal centre, thereby promoting electron transfer reactions that would otherwise not occur bimolecularly in the diluted conditions used for the supramolecular assembly.

As the viologen guest, we have investigated *N*,*N*′-dinonyl-4,4′-bipyridine (**4**), *N*,*N*′-dipentyl-4,4′-bipyridine (**5**), and *N*-methyl-*N*′-nonyl-4,4′-bipyridine (**6**) (Scheme 2). Long alkyl tails are needed to secure their binding to the cyclodextrins, since the doubly charged bipyridinium unit is too hydrophilic to show a strong interaction with the cyclodextrin cavity.[23] The binding of the viologen **4** to compounds **1** and **2** was studied by fluorimetric and microcalorimetric titrations and the results are summarised in Table 2.

Table 2. Binding constants for the complexes of *N*,*N*′-dinonylviologen **4** to compound **1** and **2**.

	K_b 1:1 [M^{-1}]	K_b 2:1 [M^{-1}]
1	2.4×10^4 [a]	–
2	2.4×10^5 [b]	4.0×10^4 [b]

[a] Obtained from fluorimetric titrations performed at 25 °C in an aqueous 0.1M Tris-HCl buffer of pH 7.0. [b] Microcalorimetric data taken from ref. [12].

Compound **1** can be considered to be a cyclodextrin dimer, in which the two CD cavities can cooperate in the binding of ditopic guest molecules. With its two long alkyl tails, the viologen guest **4** is ditopic in nature and the binding constant of its complex with **1** can be expected to be much higher than the value reported for the complex with monomeric β-cyclodextrin ($K_b = 2 \times 10^2\ M^{-1}$).[23] Table 2 shows that they are indeed higher by at least two orders of magnitude. The surprisingly high binding constants for the complexes of viologen **4** with **1** and **2** are clearly the result of cooperative interactions between multiple β-cyclodextrin cavities. This phenomenon was further investigated with photophysical studies.

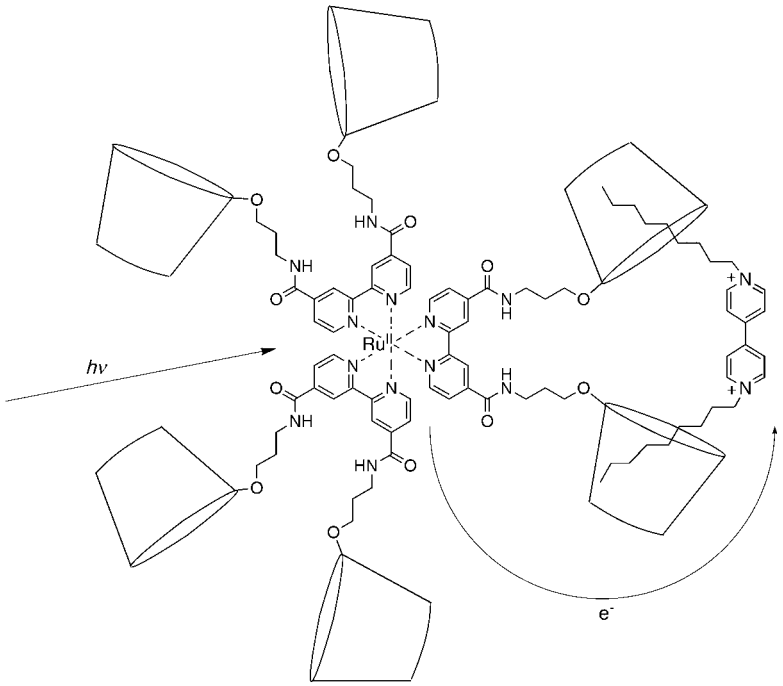
Photoinduced electron transfer within the assembly was investigated in aqueous solution where the concentration of the complexes was maintained constant ($\approx 10^{-5}$ M) and increasing amounts of the viologen were added to the solution to up to 5 molar equivalents. Under these dilute conditions bimolecular processes can be neglected and the observed quenching of the emission of the ruthenium unit can only be ascribed to intercomponent electron transfer between the excited ruthenium moiety (donor) and the bound viologen (electron acceptor), as shown in Scheme 3.

The decrease in emission intensity for complexes **1** and **2** (Figure 4) upon addition of **4** was accompanied by a decrease of the excited state lifetime. Due to the fact that the assembly of the supramolecular dyad is not 100% complete at these dilute conditions, a biexponential decay was observed for both complexes. The decay resolved into a long component, corresponding to the unquenched ruthenium species, and a short component due to the quenching of the excited state because of the electron-transfer reaction. The lifetimes of these short components were determined to be 22 ns and 88 ns for complexes **1** and **2**, respectively.

Transient absorption spectroscopy did not reveal the formation of the mono-reduced viologen species ($V^{+\bullet}$), which has a characteristic absorption at around 600 nm.[24] This is not particularly surprising, since the forward electron transfer is considerably slow (see above), and we would expect a fast back electron transfer due to the larger exoergonicity of the process. Values of $\Delta G = -0.5$ eV for the forward electron transfer and $\Delta G = -1.6$ eV for the back electron transfer have been estimated from the E_{00} value and the redox properties of related components.[25] Furthermore, it is known that the reduced viologen ($V^{+\bullet}$), being less hydrophilic than the fully oxidised state viologen (V^{2+}), binds more strongly to the cyclodextrin cavity.[26] This may lead to a deeper inclusion of the viologen unit into the cavity of the β-cyclodextrin, bringing the viologen and the ruthenium complex even closer. From the lifetime values, the rate constants of the forward electron transfer (k_{et}) can be calculated according to Equation 2.

$$k_{et} = \frac{1}{\tau} - \frac{1}{\tau_0} \qquad (2)$$

τ and τ_0 are the respective lifetimes in the presence and absence of the viologen guest. The calculated values are $k_{et} = 4.3 \times 10^7\ s^{-1}$ and $k_{et} = 1.0 \times 10^7\ s^{-1}$ for the compounds **1** and **2**, respectively. This difference can be explained by considering



Scheme 3. Schematic representation of the photoinduced electron transfer process upon excitation of the ruthenium unit in **2**.

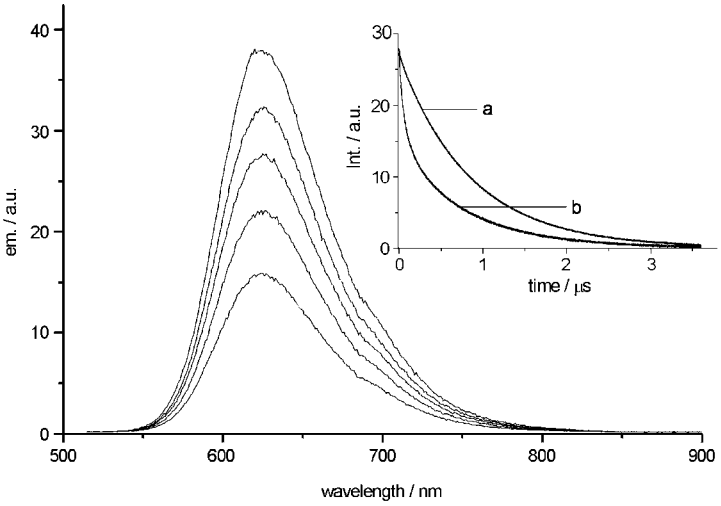


Figure 4. Changes in the emission spectra of **2** upon addition of 0, 0.5, 1, 2, and 5 molar equivalents (top to bottom) of **4** in aerated aqueous solution. Inset: Lifetime decay traces of a) **2** alone and of b) **2** in the presence of two equivalents of **4**.

the difference in structures between **1** and **2**. Contrary to complex **1**, which contains only one cyclodextrin-appended bipyridine ligand, complex **2** has cyclodextrin substituents on all its bipyridine ligands. This leads to a steric hindrance around the ruthenium core and a more extended conformation, resulting in an increase in the distance between the donor–acceptor pair for **2** compared with **1**. For comparison, in a covalently linked dyad where the ruthenium and the viologen are connected by seven methylene groups, with the spacer threaded through a cyclodextrin, the rate for electron transfer was determined to be an order of magnitude slower, that is $2.3 \times 10^6\ s^{-1}$.[27]

A viologen (**5**) with shorter alkyl chains than **4**, namely pentyl chains, was also studied to investigate the dependence of the binding and the electron-transfer rate on the chain length. Experiments carried out under exactly the same conditions as described above for **4** did not lead to a decrease in the emission intensity of the ruthenium complex **2** upon addition of **5**, and no short-lived component was detected in its decay curve. This result is ascribed to the apparent failure of the viologen with pentyl chains **5** to bind sufficiently strongly to complex **2** to give efficient quenching. A similar effect of alkyl chain length has been described in the literature for the binding of alkanoates to β-cyclodextrins in aqueous solution: the binding constants for hexanoate, octanoate, and decanoate increase from $K_b = 67\,M^{-1}$, to $K_b = 1250\,M^{-1}$, and $K_b = 6600\,M^{-1}$, respectively.[28] The same trend has been observed for other guests with hydrophilic head groups and hydrophobic alkyl chains of varying length.[28]

To investigate a possible cooperative effect in the binding of dinonylviologen **4**, we used the asymmetrically substituted viologen **6**, which has one methyl and one nonyl substituent. The methyl group of **6** is obviously shorter than the critical chain length needed for an efficient binding into the cavity of the cyclodextrin, and this compound, therefore, should be considered as a monotopic guest. The emission experiments show that, in order to observe quenching, the concentration of **6** should be increased at least 10 times compared with that of **4**. We also performed a microcalorimetric titration to determine the binding constant of the complex between **2** and **6**. The results are summarised in Table 3. A comparison of the data in Tables 2 and 3 shows that mononnonylviologen **6** displays a much weaker binding to complex **2** than the dinonylviologen **4**, with an association constant lower by an order of magnitude. This is not surprising as **6** was expected to behave as a monotopic guest. These results establish that the strong cooperative binding of viologen **4** to complex **2** is essential to ascertain a sufficiently high concentration of the self-assembled donor–acceptor pair in solution for the electron transfer to be observed by spectroscopic investigations.

Table 3. Binding constants for the complex of *N*-methyl-*N*′-nonylviologen **6** to ruthenium complex **2**.[a]

	K_b [M^{-1}]	ΔH [kcal mol^{-1}]	$T\Delta S$ [kcal mol^{-1}]
1:1	1.2×10^4	−0.97	4.59
1:2	3.5×10^3	−1.29	2.18

[a] Obtained from microcalorimetric titrations performed at 25 °C in an aqueous 0.1 M Tris-HCl buffer of pH 7.0.

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Conclusion

We have prepared and spectroscopically investigated ruthenium complexes bearing β-cyclodextrin hosts and their interaction with viologen derivatives as guests. For the supramolecular host–guest complexes the combination of results of steady-state binding studies of *N*,*N*′-dinonylviologen to the ruthenium complexes **1** and **2** and time-resolved spectroscopy prove that the presence of multiple cyclodextrin binding sites in one molecule not only enhances the binding of ditopic guest molecules such as the viologen, but also shields the ruthenium complex from quenching by oxygen. The resulting high quantum yield and emission lifetime, in particular of complex **2**, make this compound very interesting for use in sensor devices, as we have already briefly communicated.[12] Through a comparison of the time resolved luminescence studies of viologen **4** and **6**, together with the determination of the binding constants for these compounds to the complexes **1** and **2** via calorimetric titration, we have established that cooperative effects of two β-cyclodextrins in the binding of the viologen guests are present.

NMR spectroscopy has provided valuable insights into the conformational behaviour of compounds **1** and **2** in aqueous solutions. A detailed knowledge of the adopted conformations in water is essential for understanding the binding behaviour of these compounds. It was shown that hydrophobic effects force complex **1** to adopt a conformation in water where parts of the aromatic ligands are included in a cyclodextrin cavity. In complex **2** a similar process could occur in principle, but this is not observed, probably because it is prevented by steric crowding of the six cyclodextrins.

Experimental Section

General: Acetonitrile was distilled from CaH_2 prior to use. $RuCl_3 \cdot 3H_2O$ and $[Ru(bpy)_2Cl_2]$ were purchased from Aldrich and used as received. NMR spectra were recorded on a Bruker AC300 and a Bruker AMX500. Chemical shifts are reported relative to the solvent reference ($[D_6]$DMSO: 2.54 ppm, D_2O: 4.72 ppm). Mass spectra were taken on a VG 7070E (FAB) or a Finnigan MAT 900S (ESI) instrument. Luminescence spectra were measured on a Perkin Elmer LS-50B and a SPEX Fluorolog I instrument. UV-Vis spectra were recorded on a Varian Cary 50 or a diode-array HP8453 instrument. Microcalorimetric titrations were performed on a Microcal VP-ITC titration microcalorimeter.

Size-exclusion chromatography was performed on a Sephadex G75 column with a bed volume of 100 mL and an elution speed of 25 mL h^{-1}. Compounds were detected by their UV/Vis absorption at 254 nm.

Fluorimetric titrations were performed at a constant concentration of fluorophore by making a stock solution of the respective ruthenium complex (1.0×10^{-5} M) and using this solution to make a stock solution of the appropriate *N*,*N*′-dialkylbipyridinium salt (typically 2.0×10^{-4} M). All measurements were carried out in a 1.00 cm quartz cuvette (4 mL) at 25 °C in an aqueous 0.1M Tris-HCl buffer of pH 7.0. The excitation wavelength was 458 nm for **1** with excitation slits of 5 nm and emission slits of 10 nm. Small aliquots of the bipyridinium solution were added to a cuvette filled with 2.00 mL of the ruthenium solution. After every addition an emission spectrum was taken and the intensity at a fixed wavelength was determined. These intensities were plotted as a function of the bipyridinium concentration and the data points were analysed assuming a 1:1 equilibrium using a non-linear least-squares curve fitting procedure.

Microcalorimetric titrations: Titrations were performed by adding aliquots of a sample solution of the guest to the host solution (cell volume = 1.415 mL). All measurements were carried out at 25 °C in an aqueous 0.1M Tris-HCl buffer of pH 7.0. Since viologens are known to aggregate in aqueous solution a control experiment was performed by diluting the same guest solution, showing a constant heat flow per injection. This proved that no aggregation occurred at the concentrations used. The final titration curves were corrected for the heat of dilution of the guest and the host in the buffer and analysed using a nonlinear least-square minimisation method with an appropriate model (either 1:1 or 1:2, host:guest).

Time-resolved photophysics: The electron-transfer experiments with the viologens were carried out using freshly prepared solutions of ruthenium complex **2** (1×10^{-5} M^{-1}) in distilled water. The viologen was added in aliquots from a stock solution. The observed curve was fitted to a biexponential decay assuming a constant value of 811 ns for the unquenched lifetime of **2**. The sample was excited with a Coherent Infinity ND/YAG-XPO laser (1 ns pulses FWHM). For detection a Hamamatsu C5680-21 streak camera with a Hamamatsu M5677 Low-Speed Single-Sweep Unit was used. Where necessary single wavelength emission decay traces were recorded with a Tektronix Oscilloscope (TDS468) coupled to a photomultiplier. A photodiode was employed for triggering. The emission was observed through an Oriel 77250 monochromator at an angle of 90 degrees with respect to the excitation, with a 500 nm cut-off filter.

The quantum yields were determined by comparison of the emission intensity of isoabsorbing aerated aqueous solutions of **1** and **2** with $[Ru(bpy)_3]$.[29]

Ruthenium complex 1: This compound was synthesised analogous to complex **2** by mixing equimolar quantities of **3** (50.4 mg) and $[Ru(bpy)_2Cl_2]$ (9.3 mg). Yield: 56 mg (94%); ^{1}H NMR (500 MHz, $[D_6]$DMSO, 298 K): $\delta = 9.37$ (s, 2H), 8.87 (d, 4H), 8.22 (dd, 4H), 7.92 (d, 4H), 7.81 (d, 2H), 7.74 (d, 2H), 7.57 (dd, 4H), 5.04 (s, 2H), 4.87 (s, 12H), 3.80–3.38 (m, 84H), 1.86 (brs, 4H); MS (ESI$^+$, H_2O): *m*/*z*: 1502 $[M-2Cl]^{2+}$; elemental analysis calcd (%) for $C_{122}H_{174}N_{82}O_{72}RuCl_2 \cdot 24H_2O$: C 41.73, H 7.01, N 3.19; found: C 41.53, H 6.88, N 3.02.

Ruthenium complex 2: Cyclodextrin dimer **3** (60 mg) and $RuCl_3 \cdot 3H_2O$ (2.0 mg, 0.33 equiv) were mixed and refluxed in a 1:1 *v*/*v* mixture of ethanol and water for 36 h. The dark orange solution was poured into acetone and the precipitate was isolated by centrifugation. The crude product was purified by size-exclusion chromatography (Sephadex G75, eluent water). After lyophilisation the yield was 55.8 mg (90%). ^{1}H NMR (300 MHz, $[D_6]$DMSO, 298 K): $\delta = 9.25$ (brs, 6H), 7.94 (brs, 6H), 7.85 (brs, 6H), 5.04 (brs, 6H), 4.86 (brs, 36H), 3.75–3.08 (m, 252H), 1.84 (brs, 12H); MS (Maldi-TOF): *m*/*z*: calcd for: 7949.1; found: 7950.6 $[M]^+$; elemental analysis calcd (%) for $C_{306}H_{474}N_{12}O_{216}RuCl_2 \cdot 65H_2O$: C 40.28, H 6.68, N 1.84; found: C 39.61, H 6.01, N 1.83.

General procedure for symmetrically substituted viologens: One equivalent of 4,4′-bipyridine was mixed with an excess of the appropriate 1-alkylbromide in acetonitrile and refluxed for 18 h. The precipitate was isolated by filtration and washed several times with acetonitrile and diethyl ether.

***N*,*N*′-Dinonyl-4,4′-bipyridinium dibromide (4)**: ^{1}H NMR (300 MHz, D_2O, 298 K): $\delta = 9.08$ (d, $^3J = 6.7$ Hz, 4H), 8.51 (d, $^3J = 6.7$ Hz, 4H), 4.69 (t, $^3J = 7.3$ Hz, 4H), 1.32 (brs, 4H), 1.22 (brs, 20H), 0.80 (t, $^3J = 6.9$ Hz, 6H); MS (FAB, glycerol): *m*/*z*: 410 $[M-2Br]^+$.

***N*,*N*′-Dipentyl-4,4′-bipyridinium dibromide (5)**: ^{1}H NMR (300 MHz, D_2O): $\delta = 8.96$ (d, $^3J = 6.7$ Hz, 4H), 8.38 (d, $^3J = 6.7$ Hz, 4H), 4.56 (t, $^3J = 7.0$ Hz, 4H), 1.93 (t, $^3J = 6.7$ Hz, 4H), 1.20 (m, 8H), 0.73 (m, 6H); MS (FAB, glycerol): *m*/*z*: 148.9 $[M]^{2+}$.

***N*-Methyl-*N*′-nonyl-4,4′-bipyridinium bromide iodide (6)**: *N*-Methyl-4,4′-bipyridinium iodide[30] (1.0 g, 3.35 mmol) and 1-nonylbromide (3.5 mL, 15.58 mmol) were refluxed in acetonitrile (100 mL) for 18 h. The orange precipitate was filtered and washed two times with acetonitrile and three times with diethyl ether (20 mL), yielding **6** (890 mg, 52.5%). ^{1}H NMR (300 MHz, D_2O, 298 K): $\delta = 8.98$ (d, $^3J = 6.6$ Hz, 2H), 8.91 (d, $^3J = 6.6$ Hz, 4H), 8.40 (dd, $^3J = 6.6$ Hz, $^3J = 6.6$ Hz, 4H), 4.59 (m, 2H), 4.37 (m, 3H), 1.96 (brm, 2H), 1.17 (brm, 12H), 0.69 (t, $^3J = 6.7$ Hz, 3H); MS (FAB, glycerol): *m*/*z* (%): 298.0 (100) $[M]^+$, 148.8 (90) $[M]^{2+}$.

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