Highly Photostable Sensitizers for Artificial Photosynthesis. Ru(II)-3,3′-Bis(diazine)-6,6′-oligo(ethylene glycol) Complexes and a New Class of Podates

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Abstract: Absorption spectra, emission spectra (90 and 298 K), luminescence lifetimes, luminescence quantum yields, and photochemical behavior of a semicage bipyridazine (bpdz) Ru(II) complex K6 and related open-chain bpdz model complexes K1–4 have been studied and compared with those of $Ru(bpy)_3^{2+}$ K5. The absorption bands in the visible spectra of K1–4 and Ru–podate K6 are close in energy to the corresponding bands of $Ru(bpy)_3^{2+}$, whereas the emission bands are slightly red shifted. The luminescence lifetimes of K1–4/K6 (1500–3400 ns) are longer than that of K5 (600 ns). The open-chain bpdz model complexes K1–4 and especially K6 are highly photoinert ($\phi_p \leq 10^{-5}$) relative to the photodissociation of $Ru(bpy)_3^{2+}$ ($\phi_p = 0.068$). These excellent photophysical properties and stabilities of the complexes K1–4 and the Ru–podate K6 allow their effective use as photosensitizers in electron-transfer processes.

Artificial photosynthesis is an important research subject in recent years.[1] It is of basic interest since artificial photosynthetic systems mimic the functions of the natural process and are of practical value for solar energy conversion and storage.[2] One essential part of such systems is the light-harvesting unit that induces the electron transfer upon excitation. Ru–poly(pyridines),[3] metal–porphyrins,[4,5] phthalocyanines,[6,7] organic dyes,[8] and semiconductors[9–11] have been used for this purpose.

Ru(II)–poly(pyridine) complexes have been widely applied as photosensitizers in artificial photosystems[3] because of their superior photophysical properties and available synthetic routes for the preparation of mixed hexacoordinated complexes. A major drawback for most of these Ru complexes or sensitizers is their light-induced ligand photodissociation.[12] This reaction degrades the photosensitizer and competes with the light-induced electron transfer. It is generally agreed that this photodissociation, e.g. for $Ru(bpy)_3^{2+}$, proceeds via a thermally activated radiationless transition from a luminescent triplet metal-to-ligand charge transfer (^{3}MLCT) to a triplet metal-centered (^{3}MC) level with subsequent cleavage of one Ru–N bond.[13] Two strategies were advanced to overcome the degradation of the photosensitizers. One approach is to increase the energy gap between ^{3}MC and ^{3}MLCT and thereby decrease the population of the former state. This leads to complexes exhibiting higher stability but results in low luminescence lifetimes and quantum yields.[14–16] A second approach is to link the ligands by chemical bonds in a cage structure.[17] By this method, the first coordination sphere around the central ion is not affected, and therefore the photophysical properties as well as the temperature independent decay processes of the complexes are almost unchanged as compared to $Ru(bpy)_3^{2+}$.

We have chosen the cage approach to eliminate photodissociation of the Ru complexes and therefore designed an appropriate synthetic concept. The ligand should allow enough space for the central ion and adopt a spheric configuration. Such steric restrictions are the key point leading to unaffected photophysical properties.[18] Also, spacer and bridgehead groups, which are unable to react as intramolecular electron donors, should be selected. Such intramolecular electron transfer could create a radical state from which photodissociation occurs. In addition, a second coordination sphere which allows high water solubility is needed to generate photosensitizers that operate in aqueous media.

Employing this strategy, we have previously prepared a Ru–bipyridine cryptand.[19] This ligand was synthesized by Lehn et al.[20] and by us independently. The Ru–bipyridine cryptand possesses a distorted coordination sphere due to the short spacer groups. As a result, the energy gap of the ^{3}MLCT relative to the ^{3}MC changed and resulted in a fast radiationless decay of the

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excited state, due to the donor groups associated with the ligand. An improved sensitizer following the same ideas was tested in the cage and semicage complexes by Balzani, Vögtle, et al.[21] We have designed a class of new ligands that includes bis(diazines) (bpdz) as coordination sites and prepared a capped Ru(II) complex with bpdz ligands. It is anticipated that Ru(II)–diazine complexes will exhibit higher stabilities toward photoinduced dissociation as compared to the Ru(II)–bipyridine analogues. Bpdz possesses good π-acceptor and σ-donor capacity.[22] Both of these parameters interact synergistically in the stabilization of Ru-L_3 complexes via "back-bonding". Ernst and Kaim[23] have determined the energies for the LUMO and SLUMO for the isomeric bis(diazine) ligands: 3,3′-bipyridazine (bpdz), 4,4′-bipyrimidine (bpym), 2,2′-bipyrazine (bpz), and 2,2′-bipyrimidine (bpym) as well as for 2,2′-bipyridine (bpy). Combining these data with experimental pK_a values, we expected that the bpdz system will exhibit a strong back-bonding toward π-electron-rich metal fragments and with the smallest LUMO/SLUMO difference among the ligands. These two facts should improve the stability of Ru–bpdz complexes against dissociation. We chose oligoethylene glycols as spacer groups since these residues would enhance water solubility and additionally would allow supramolecular interactions with positively charged ions, e.g. organic electron acceptors or inorganic ions.[24] The flexible ligand should also easily adopt the octahedral coordination sphere.

Using this approach we have synthesized and characterized recently a hemicage Ru(II)–oligo(ethylene glycol)–bpdz complex (Ru–podate) K6 and open-chain Ru(II)–oligo(ethylene glycol)–bpdz complexes K1–4 (Chart I) and revealed that their photophysical properties can be tuned by association of ions at the ethylene glycol chains.[14] In this paper we report on the photophysical properties of the new Ru complexes K1–4 and K6 and confirm the photostability of these complexes against photodissociation. We demonstrate that K6 is among the most stable Ru complexes compared to the six complexes known so far (vide supra).

Experimental Section

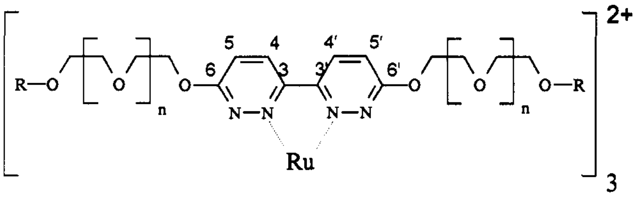
Physical Measurements. UV/vis spectra were recorded on an Uvikon 680 or Kontron spectrophotometer. Corrected emission spectra were obtained with a Hitachi F-3000 spectrofluorometer. The photochemical experiments were carried out at room temperature in MeCN solutions containing 0.01 M/L Cl^- as benzyltriethylammonium chloride. A diluted solution (OD= 0.8) of each complex was sealed under vacuum in a 3-mL cell after four freeze–pump–thaw cycles. Excitation was performed with a XBO lamp (450 W, Osram) using a cutoff filter KV 410 and an IR filter (12-cm water cell).

The photoreactions were followed by UV/vis spectroscopy (^{3}MLCT). The emission lifetimes were measured by an Edinburgh Instruments Model Fl-900 single-photon counter.

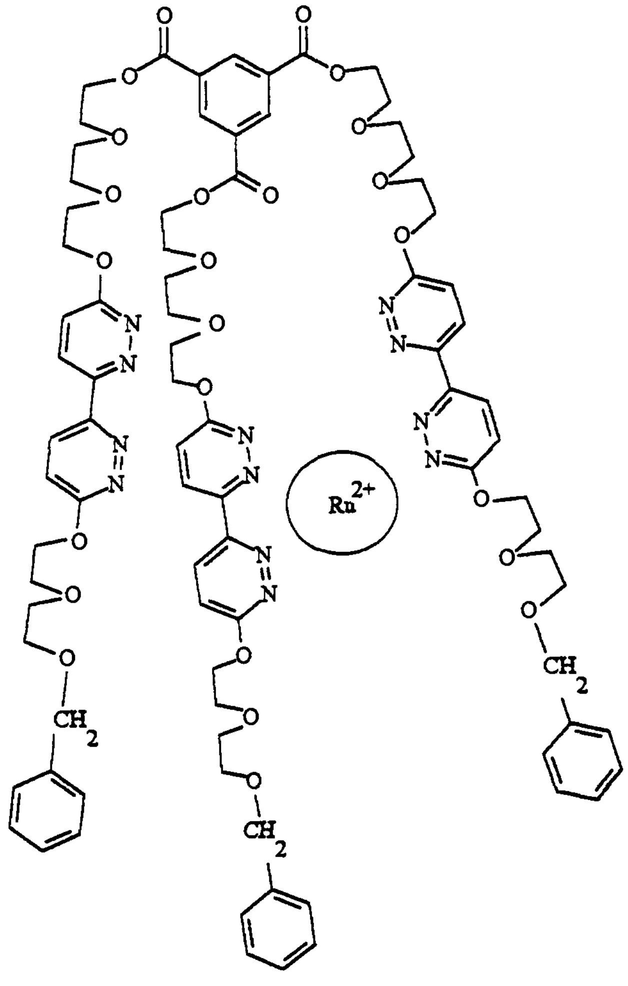
Preparation of K1–4 and K6. All solvents were of the best commercially available grade. The complexes K1–6 were prepared by heating Ru($DMSO)_4Cl_2$ and the ligands in EtOH/H_2O (v/v 3:1) at 80 °C for 8 h. All the complexes gave satisfactory elementary analysis. Detailed synthesis will be described elsewhere.

The quality of the single-exponential analysis was assessed by the χ^2 values being close to unity and the Durbin–Watson parameter (DW) being above 1.6.

Chart I



Complex	n	-R
K1	1	-H
K2	2	-H
K3	3	-H
K4	1	-benzyl
K5	$Ru(bpy)_3^{2+}$	
K6	see below	



K6

Emission quantum yields in water at 25 °C were determined in deoxygenated solutions (Ar bubbling for 30 min) by comparing the emission yield to that of $Ru(bpy)_3^{2+}$ ($\phi_1 = 0.042$).[25,26] The quantum yield for photodissociation of $Ru(bpy)_3^{2+}$ was measured by following the bleaching of the ^{3}MLCT band upon illumination and corresponds to $\phi = 0.062$. The value obtained is in excellent agreement with the reported value.[30] The photodissociation quantum yields of K1–4 and K6 are based on the assumption that photodissociation of the complexes leads to bleaching of the MLCT band or the appearance of new absorption bands.

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Table I. Absorption Maxima and Luminescence Data of Ru Complexes K1–6

Ru complex	MLCT[a] absorption (298 K) λ_{max}, nm (log ϵ)		MLCT[b] emission λ_{max}(77 K), nm	MLCT[b] emission λ_{max}(298 K), nm
K1	452 (4.20)	414 (4.24)	594	631
K2	453 (4.19)	414 (4.21)	596	630
K3	453 (4.18)	414 (4.19)	595	627
K4	455 (4.14)	416 (4.14)	595	616
K5	454 (4.17)	422 (4.03)	590	618
K6	462 (4.10)	416 (4.13)	595	620

[a] H_2O solution. [b] In EtOH/H_2O (95:5 v/v).

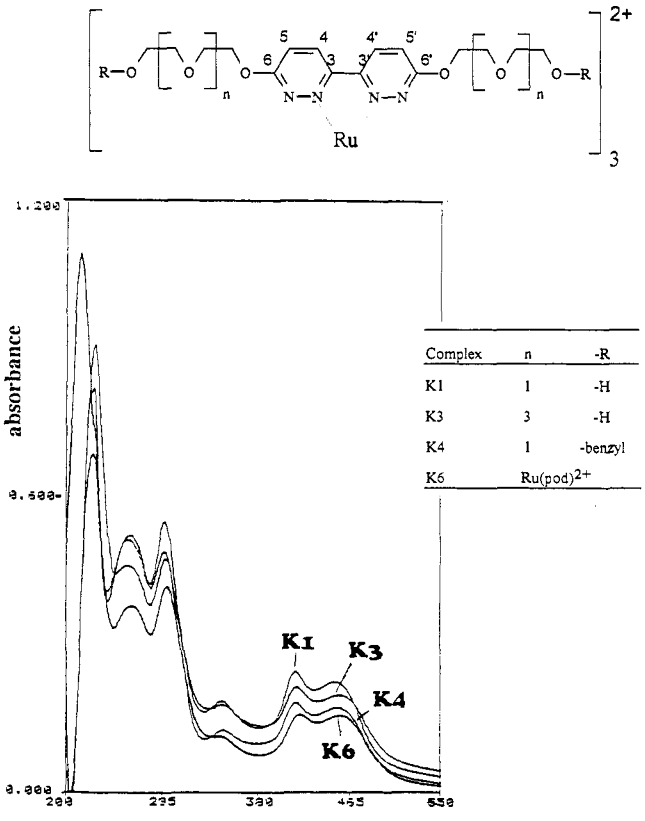

Figure 1. UV/vis overlay of complexes K1, K3, K4, and K6 (10^{-5} in H_2O as solvent).

Results and Discussion

UV/Vis Spectra. The absorption spectrum of $Ru(bpy)_3^{2+}$ K5 has been extensively discussed and analyzed in the last decade.[27-29] The bands at 185 and 289 nm are LC transitions, the band at 455 nm is attributed to a MLCT, and the shoulders between 300 and 350 nm are attributed to MC transitions. The absorption bands of the complexes K1–4 and K6 are summarized in Table I shown in Figure 1, and compared to those of $Ru(bpy)_3^{2+}$ K5. The complexes show absorption maxima similar to $Ru(bpy)_3^{2+}$ K5 and exhibit two clearly separated MLCT maxima, due to charge transfer into both LUMO and SLUMO levels of the bpdz units.[23] The experimental results are supported by Hückel MO perturbation calculations performed by Ernst and Kaim.[23] They found that the bpdz unit gives the smallest LUMO/SLUMO energy gap among bpy and bis(diazine) ligands. This would open up an additional pathway for deactivation and probably prevents the thermal activation to a higher MC level with subsequent photodissociation. From Table I one can identify an MC band at the same wavelength as that for $Ru(bpy)_3^{2+}$ K5 (~350 nm), indicating an MC energy level quite similar for these complexes. In agreement with Balzani and Vögtle[21] the Ru–podate K6 shows a smaller extinction coefficient of the ^{3}MLCT band compared with the unbridged complexes K1–4. This may reflect a slightly different coordination geometry in K6 versus K1–4.

Table II. Luminescence Quantum Yields, Luminescence Lifetimes, and Photodissociation Quantum Yields

	τ, ns[a] H_2O	MeOH	ACN	ϕ_l	photodissociation (298 K) ϕ_p
K1	1460	2290	3150	0.045	$<10^{-5}$
K2	1570	2270	3140	0.046	$<10^{-5}$
K3	1940	2480	3220	0.055	$<10^{-5}$
K4	3340	3250	3450	0.13	$<10^{-5}$
K5	620			0.042	0.068[30]
K6	1990			0.053	$<10^{-6}$

[a] The experiments were carried out at 25 °C.

Emission Spectra. The emission maxima of complexes K1–4 and K6 at 77 and 298 K are given in Table I, and their luminescence lifetimes and quantum yields in different solvents are shown in Table II. The luminescence spectra of the ^{3}MLCT emission for the RuL_3^{2+} complexes K1–4 and K6 in H_2O at 298 K as well as in H_2O/EtOH at 77 K are almost identical. The maximum wavelength ranges from 616 nm (K4) to 631 nm (K1), at 298 K, and from 594 to 598 nm at 77 K depending on the ligand (see Table I). Because of the similarity of absorption and emission energies of the bpdz complexes K1–4 and K6 compared to those of $Ru(bpy)_3^{2+}$ K5, we assume a normal ^{3}MLCT emission of Ru(II)-bis(diazine) complexes.

Emission Lifetimes. The emission lifetimes of the bpdz complexes K1–4 and K6 exceed that of $Ru(bpy)_3^{2+}$ by 1 order of magnitude. Note also that with increasing chain length (K1 → K3) the lifetime increases. This is presumably due to an intramolecular interaction between the oligoethylene glycol chains in 6,6′-position of K1–4 and K6 resulting in a retardation in the deactivation of the excited state by the solvent environment. By decreasing the polarity of the solvent (H_2O → MeOH → MeCN), the interaction between the Ru complexes and the solvent decreases, giving rise to longer lifetimes. This hypothesis is supported by the fact that the complexes K1–4 exhibit a similar lifetime in different solutions, as a result of shielding the complex against interaction with the solvent by the six benzyl substituents linked to the poly(ethylene glycol) chains. The higher lifetime of K6 versus K1–3 can be attributed to the bridged structure of the three remaining benzyl groups, which will diminish radiationless decay pathways (Table II).

Photostability. As known from literature,[30] the irradiation of $Ru(bpy)_3^{2+}$ in the presence of Cl^- anions (^{3}MLCT excitation) causes quite large spectral changes, resulting in the appearance of a new band at 552 nm due to the formation of $Ru(bpy)_2Cl_2$. Temperature dependent lifetime and quantum yield measurements indicated that the CT state undergoes thermal activation due to a d–d state from which photodegradation occurs. The quantum yield for this photosubstitution process depends largely on the nature of the solvent and on the counterion of the complex (e.g. Cl^-).[30] The similarity of the absorption spectra of $Ru(bpy)_3^{2+}$ K5 and K1–4/K6 allows one to compare the photodegradation of the new complexes to that of $Ru(bpy)_3^{2+}$. We thus irradiated the complexes K1–4 and K6 with an XBO-Osram Xe lamp for 10 days, and we could not detect any rise of a new absorption that could indicate the formation of photosubstitution products. Thus, even the unbridged Ru–bpdz complexes K1–4 show this extremely high stability. Table II summarizes the quantum yields for photodegradation of the new series of bis(diazine) Ru(II) complex and compares those values to that of $Ru(bp)_3^{2+}$. The studies on photodegradation of $Ru(bpy)_3^{2+}$ suggest that initial excitation leads to a ^{3}CT state. This state is thermally deactivated to a ^{3}MC state which undergoes further deactivation by loss of a bipyridine group and subsequent photodissociation (Ru–N bond cleavage). The lack of ligand photodissociation for the cage K6 results from linking of bpdz units by the aromatic bridgehead and the oligo(ethylene glycol) spacer groups. Thus, the Ru cation cannot easily escape the complex K6. In addition, the slightly low lying MLCT level of the Ru–bpdz complexes K1–4 and K6, in contrast to that of $Ru(bpy)_3^{2+}$ K5, results in a higher ^3MC–^3MLCT energy gap in the series of new complexes. This decreases the rate of the photodissociation and stabilizes the complexes K1–4 and K6. Nonetheless, it should be noted that there is only a slight increase in the ^3MLCT–^3MC energy gap (8–11 kJ/mol) of K1–4 and K6 as compared to K5 that cannot explain the high stability of the unbridged complexes K1–4. Therefore, we assume that after excitation not only the LUMO but also the SLUMO level is populated, preventing a thermal activation of the ^3MC from the former. Nonetheless, a further factor that could effect the high photostability of K1–4 involves rebinding of the multidentate ligand in the cage even after Ru–N bond cleavage.

We conclude that the unbridged bpdz complexes K1–4 and especially Ru–podate K6 reveal high photostabilities toward metal–ligand photodissociation. The stabilities are among the best values which have been measured for uncaged and caged tris-homoleptic Ru(II) complexes. Further advantages of the bpdz–Ru(II) complexes involve improved luminescence lifetimes (up to 3500 ns) and quantum yields (0.05).

Thus, substitution of the bipyridine ligand by 6,6'-oligo(ethylene glycol)-3,3'-bipyridazine as ligand affords the new open-chain and hemicage series of Ru(II) complexes K1–4 and K6 of excellent photophysical properties. The long luminescence lifetimes and improved quantum yields of these complexes, together with their photostabilities (10^4 higher than $Ru(bpy)_3^{2+}$), provide a series of new photosensitizers that can be applied to initiate electron transfer in artificial photosynthetic systems.

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