Efficient Energy Transfer in Supramolecular, Hydrogen-Bonded Polypyridylruthenium-Osmium Complexes

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Hydrogen bond association between ruthenium bibenzimidazole and carboxylated polypyridylosmium complexes results in stable supramolecular aggregates. The determined stability constant of $\log K \approx 6 \pm 0.3$ allows efficient energy transfer from the ruthenium to the osmium moiety.

Introduction

Primary processes in natural photosynthesis consist of photon absorption and fast, directional and highly efficient energy transfer along chains of chlorophyll molecules. The efficiency and directionality of the energy-transfer processes are determined by the spatial orientation of the individual chromophores, which is defined by supramolecular forces such as hydrogen bonding and by minute variations of their chemical environment.[1] Artificial systems are most often based on polypyridylruthenium and -osmium complexes, which, due to their photophysical and electrochemical properties, are ideal models. The vast majority of investigations in this area have been generated with covalently linked systems, which are based on highly complicated ligand synthesis.[2] This distinct contrast between natural building principles employing relatively simple components and artificial model components has, to the best of our knowledge, only been overcome in one principle example where hydrogen-bonded ruthenium and osmium complexes have been investigated.[3] The association between both components was accomplished by exploiting the complementary base-pairing of cytosine and guanine, however the complicated ligand synthesis together with relatively low stability constants are serious disadvantages which leave room for considerable improvement. Recently, we have found that the cis diamine moiety of cationic bibenzimidazole ruthenium complexes is an ideal hydrogen bond donor, especially for carboxylate groups.[4] On the basis of this observation it is our intention to develop stable, supramolecular hydrogen-bonded systems where we can study the dependence of the efficiency and directionality of energy-transfer processes on the type of supramolecular association and the modification of the chemical composition of the components. Here we describe the investigation of the first example of these systems based on a novel dicationic ruthenium bibenzimidazole complex as hydrogen-bond donor and a monocationic osmium bipyridine carboxylate[5] as hydrogen-bond acceptor.

Results and Discussion

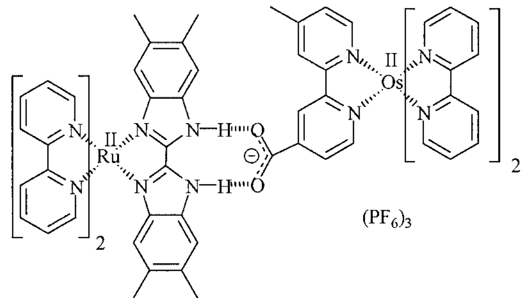

Figure 1. Supramolecular aggregate consisting of bis(2,2′-bipyridine)(4,4′,5,5′-tetramethyl-2,2′-bibenzimidazole)ruthenium(II), Ru(biH$_2$), and bis(2,2′-bipyridine)(4-carboxy-4′-methyl-2,2′-bipyridine)osmium(II), Os(mcbpy)

The investigation was conducted using a bis(2,2′-bipyridine)(4,4′,5,5′-tetramethyl-2,2′-

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bibenzimidazole)ruthenium(II) complex, Ru(biH$_2$), as donor and a bis(2,2′-bipyridine)(4-carboxy-4′-methyl-2,2′-bipyridine)osmium(II) complex, Os(mcbpy), as acceptor (Figure 1). It is known that the biimidazole complex is fully protonated in solution and the carboxylate function fully deprotonated,[4,5] which should facilitate the hydrogen bond formation. The synthetic accessibility of the mononuclear components is relatively straightforward and has been described previously.[4,6−9]

In order to investigate the potential of this approach the emission intensity of Ru(biH$_2$) was investigated in the presence of different polypyridylosmium compounds. As reference [Os(bpy)$_3$]$^{2+}$, containing no carboxylate function, was used. It did not significantly alter the observed emission spectrum of Ru(biH$_2$), as depicted in Figure 2a. In contrast the carboxylated derivative Os(mcbpy) induced a significant decrease in emission intensity of Ru(biH$_2$), which suggested that an intermolecular energy transfer took place, Figure 2b.

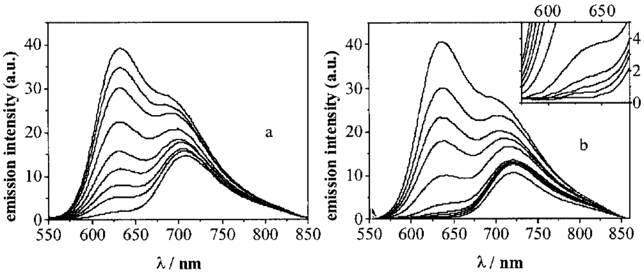

Figure 2. a) Emission spectra of the mixtures of Ru(biH$_2$) and Os(bpy)$_3$ in dichloromethane at various concentrations of Ru(biH$_2$); b) emission spectra of the mixtures of Ru(biH$_2$) and Os(mcbpy) in dichloromethane at various concentrations of Ru(biH$_2$); inset: zoom of region between 575 and 675 nm showing the changes for x between 0.1 and 1 [c(Os complex) = 0.95×10^{-6} mol/L, c[Ru(biH$_2$)] = x * c(Os complex), x = 0.1, 0.33, 0.5. 0.67, 1, 1.5, 2, 2.5, 3, 4]

A more detailed analysis of the obtained data clearly shows that the emission intensities of Ru(biH$_2$) and Os(bpy)$_3$$^{2+}$ are independent of their respective ratio, whereas the Ru(biH$_2$)-based emission is quiet effectively quenched in the presence of Os(mcbpy). The titration of the luminescence intensities of Ru(biH$_2$) in the presence of Os(mcbpy) yields valuable information about the supramolecular association in solution. The quantity of ruthenium donor was varied, beginning with one-tenth of the Os(mcbpy) concentration to reach, in regular steps, a one to one ratio of donor and acceptor. The concentration of Ru(biH$_2$) was further increased until the final concentration of Ru(biH$_2$) in the last solution was four times higher than the Os(mcbpy) concentration. The results are depicted in Figure 3, all emission spectra consist of the sum of the Ru(biH$_2$)- and Os(mcbpy)-based emissions because a selective excitation of the two fragments is not possible. It is evident from Figure 3 that Os(mcbpy) efficiently quenches the Ru(biH$_2$)-based emission until the concentration of Ru(biH$_2$) exceeds the one to one ratio with respect to Os(mcbpy), whereas Os(bpy)$_3$$^{2+}$ does not influence the emission of Ru(biH$_2$).

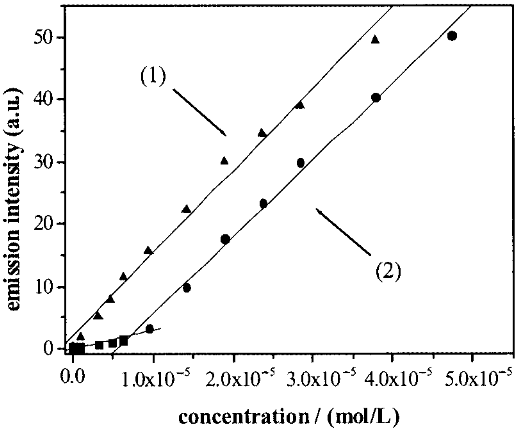

Figure 3. Emission intensity vs. concentration of Ru(biH$_2$) spectra with Os(bpy)$_3$ (1) and Os(mcbpy) (2) in dichloromethane [c(Os complex) = 0.95×10^{-6} mol/L, c[Ru(biH$_2$)] = x * c(Os complex), x = 0.1, 0.33, 0.5. 0.67, 1, 1.5, 2, 2.5, 3, 4]

These results suggest that the ruthenium bibenzimidazole complex interacts with the monocarboxylated osmium complex in such a way that intermolecular energy transfer may occur and that the carboxylate function is essential for this interaction, as depicted in Figure 1.

A careful examination of the obtained data shows that the ruthenium-based phosphorescence in the H-bonded dimer is not completely quenched. One possibility to explain this is a thermodynamic equilibrium between the two free complexes — Ru(biH$_2$) and Os(mcbpy) — and the supramolecular dimer [Ru(biH$_2$)Os(mcbpy)].

On the other hand, it has to be considered that the quenching of the ruthenium-based emission is perhaps not fast enough and, consequently, an emission of a very low intensity level is detected. In order to obtain more detailed information on this process, time-resolved photophysical investigations were performed. Ru(biH$_2$) has an absorption maximum at 482 nm and an emission maximum at 630 nm. Os(mcbpy) has an absorption maximum at 487 nm and an emission maximum at 717 nm. Due to the large separation of nearly 90 nm between both emission maxima it is therefore possible to monitor the emission intensities or lifetimes of the excited states of both complexes independently in the same solution without interference. To gain more insight into this problem luminescence lifetime measurements of the titrated solution were carried out. Figure 4a shows the decay of a one to two mixture of Ru(biH$_2$) and Os(mcbpy) in dichloromethane monitored close to the emission maximum of Ru(biH$_2$) to avoid any Os(mcbpy) signal.

If we compare the decay of the mixture with the decay of the pure donor solution, it is obvious that in the mixture a shorter lived component causes biexponential decay. The lifetime of the short component lies under 10 ns and the unbound Ru(biH$_2$) donor has the same lifetime as in the solution containing no Os(mcbpy) acceptor. Figure 4b depicts the data monitored at the Ru(biH$_2$)-based emission

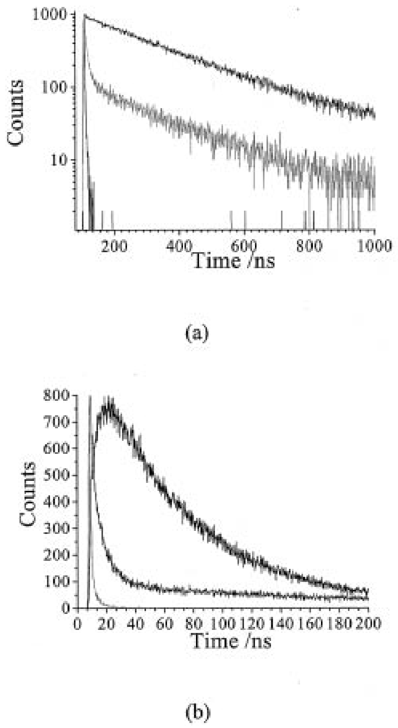

Figure 4. a) Overlay of Ru(biH_2) (top), Ru(biH_2)/Os(mcbpy) (ratio 1:2; middle) and IRF (Instrument Response Function; bottom) monitored at 620 nm; b) overlay of Ru(biH_2) (top, monitored at 620 nm) and Os(mcbpy) (middle, monitored at 750 nm) in a 1:2 ratio, IRF (Instrument Response Function; bottom, monitored at 620 nm)

wavelength and at the Os(mcbpy)-based emission. The shape of the Os(mcbpy)-based decay monitored at 750 nm, where Ru(biH_2) does not emit, leads to the conclusion that as long as the short component of Ru(biH_2) dominates its decay for approximately 30 ns the counted number of photons emitted by Os(mcbpy) increases to reach a maximum. After the maximum is passed, the exhibited decay is similar to that observed for free Os(mcbpy). A possible explanation for this behaviour is that the population of the emitting ^{3}MLCT state of Os(mcbpy) is rising. It is evident that the increase of counted photons has to be due to an additional population of these states. A plausible source of this extra population is energy transfer from the Ru(biH_2) ^{3}MLCT state

The obtained results show that a hydrogen-bonded heterodinuclear associate is formed, that efficient energy transfer occurs and that the supramolecular associate is in equilibrium with its unbound components, according to Ru(biH_2) [A] and Os(mcbpy) [B] in equilibrium with Ru(biH_2)Os(mcbpy) [A-B] [Equation (1) and (2)].

$$[A] = ([A_0]\cdot I_Q)/I_{NQ} \qquad (1)$$

$$K = ([A_0] - [A])/[A]([B_0] - [A_0] + [A]) \qquad (2)$$

Within all these assumptions it is possible to determine the equilibrium constant as $\log K \approx 6 \pm 0.3$ using Equation (2).

Conclusion

The results of the initial investigations presented here clearly show that the perfectly tailored geometrical parameters of the hydrogen-bond interaction groups together with the reduced coulombic repulsion between a monocationic Os(mcbpy) and a dicationic Ru(biH_2) lead to stable supramolecular model compounds for photosynthetic light harvesting complexes. Barigelletti and Ward reported a log(K) ≤ 3.7 for the formation of a mixed cytosine-modified ruthenium and guanine-substituted osmium complex exhibiting a detectable change of luminescence properties indicative of Ru → Os energy transfer.[3] The difference in the association constants of the system described in this work compared to the one reported by Barigelletti et al. is extraordinarily high. The equilibrium constant is about two to three orders of magnitude higher although there is only a double instead of a triple chelating effect of H-bonding interactions involved within the biimidazole carboxylate system. Furthermore, the structure of the moieties connected by H-bonding in this study appears almost simple in contrast to the synthetic effort made to yield the nucleobase-modified polypyridyl complexes. The application of these construction principles should lead to more advanced compounds which might be used to gain more detailed insight into processes occurring in natural photosynthesis.

Experimental Section

Materials

All solvents used for spectroscopic measurements were of Uvasol (Merck) grade. All other reagents were HPLC grade. *cis*-[$RuCl_2(bpy)_2$]·$2H_2O$,[10] *cis*-[$OsCl_2(bpy)_2$]·$2H_2O$,[11] and [Os(mcbpy)$(bpy)_2$](PF_6)[6] were prepared by standard procedures. All reagents for synthesis, $RuCl_3\cdot 3H_2O$ (ABCR), 2,2′-bipyridine, trichloroacetic acid, 4,5-dimethyl-1,2-phenylenediamine, and 4,′4-dimethyl-2,2′-bipyridine (Aldrich) were used as received without further purification.

The synthesis of 5,5′,6,6′-tetramethyl-2,2′-bisbenzimidazole was a modification of the method of Reedijk et al.[12] 4-Carboxy-4′-methyl-2,2′-bipyridine was prepared according to literature procedures.[13]

UV/Visible spectra were obtained using a Shimadzu UV 3100 UV/Vis-NIR spectrophotometer. Emission spectra were obtained using a Perkin−Elmer LS50 luminescence spectrometer; at room temperature the measurements were taken using an excitation slide of 10 nm and emission slit of 10 nm. The NMR spectra were recorded on a Bruker 400 MHz spectrophotometer. The mass spectrometry was carried out on a SSQ 170, Finnigan Mat. The Electrospray mass spectrometry was performed on a Finnigan MAT 95 XL double focussing sector field instrument (Thermo Finnigan GmbH, Bremen, Germany) adjusted to a mass resolution of about 2000. The two complexes were first dissolved in a small amount of acetonitrile and then diluted with dichloromethane to a final concentration of 3×10^{-6} M respectively. This solution was introduced into the ion source at a flow rate of 40μL/min. The spray voltage was 4.5 kV and nitrogen was used as sheath gas.

Luminescence lifetime measurements were obtained using an Edinburgh Analytical Instruments (EAI) time-correlated single-photon counting apparatus (TCSPC) comprised of two model J-yA monochromators (emission and excitation), a single photon photomultiplier detection system model 5300, and a F900 nanosecond flashlamp (N2 filled at 1.1 atm pressure, 40 kHz) interfaced with a personal computer via a Norland MCA card. A 500 nm cut-off filter was used in emission to attenuate scatter of the excitation light (337 nm); luminescence was monitored at 640 nm. Data correlation and manipulation was carried out using EAI F900 software version 5.1.3.

Emission lifetimes were calculated using a single-exponential fitting function, Levenberg−Marquardt algorithm with iterative deconvolution (Edinburgh instruments F900 software). The reduced χ^2 and residual plots were used to judge the quality of the fits. Samples were of low concentration (2×10^{-5} M) dissolved in a small amount of dichloromethane at room temperature. The lifetimes of the complexes in equilibrium was measured in aerated dichloromethane. The lifetime errors are estimated to be less than 8%.

The following assumptions were made for the determination of the stability constant *K*. [A_0] [initial concentration of Ru(biH$_2$)] and [B_0] [initial concentration of Os(mcbpy)] of the solutions are determined from the weighted masses of donor and acceptor. The ratio of [A] to [A_0] might be expressed by the quotient of the intensities of I_{NQ} to I_Q ($I_{NQ/Q}$ emission intensity for different concentration for not quenched and quenched case) at the maximum of the ruthenium donor (λ_{max} = 630 nm). In order to determine the I_{NQ} correctly the emission intensity of Ru(biH$_2$) was determined in the presence of non-binding [Os(bpy)$_3$]$^{2+}$. At the monitored emission wavelength of 630 nm the absorption of the two osmium complexes, the binding Os(mcbpy) and [Os(bpy)$_3$]$^{2+}$, is different. Therefore we have to consider a correcting factor x for I_{NQ}, the concentration [A] may therefore be determined using Equation (1) and the corrected I_{NQ}.

Synthesis of [Ru(tmbbiH$_2$)(bpy)$_2$](PF$_6$)$_2$, Ru(biH$_2$): [RuCl$_2$(bpy)$_2$]·2H$_2$O (0.19 mmol) and 5,5′,6,6′-tetramethyl-2,2′-bisbenzimidazole (0.19 mmol) were suspended in a mixture of EtOH/H$_2$O (1:1 v/v, 30 mL) and stirred and refluxed overnight. The reaction mixture was allowed to cool to room temperature and filtered. The volume of the solution was reduced (to ca. 10 mL) by rotary evaporation, and the product was precipitated as the PF$_6$ salt. The crude product was washed with water and diethyl ether, and chromatographed on silica with an eluent formed of THF, CH$_3$CN, KNO$_3$ (saturated aqueous solution) (12:4:0.5, v/v/v). The first peak (main band) contained the desired compound, which was finally obtained by recrystallisation from acetone and water. [C$_{38}$H$_{34}$F$_{12}$N$_8$P$_2$Ru]$^{2+}$ (993.7): calcd. C 45.93, H 3.45, N 11.28; found C 46.44, H 3.41, N 10.98. ESI-MS: *m*/*z* = 704.0 [C$_{38}$H$_{34}$N$_8$Ru], 352.3 [C$_{38}$H$_{34}$N$_8$Ru]$^{2+}$. ^{1}H NMR (CD$_3$CN): δ = 8.54 (d, 2 H), 8.44 (d, 2 H), 8.16 (dd, 2 H), 8.05 (d, 2 H), 7.97 (dd, 2 H), 7.93 (d, 2 H), 7.49 (dd, 2 H), 7.47 (s, 2 H), 7.34 (dd, 2 H), 5.39 (s, 2 H), 2.65 (s, 6 H), 2.15 (s, 6 H) ppm. ^{13}C NMR (CD$_3$CN): δ = 20.37, 20.55, 114.66, 116.07, 124.61, 125.01, 128.08, 128.47, 134.53, 135.46, 137.16, 137.85, 138.34, 141.31, 144.44, 153.70, 154.16, 158.36, 160.07 ppm. UV/Vis (CH$_2$Cl$_2$): λ_{max} = 482 nm (ε = 9200 M^{-1}cm^{-1}). Emission (CH$_2$Cl$_2$): λ_{max} = 630 nm. Lifetime of excited state (CH$_2$Cl$_2$): τ = 238 ns.

Acknowledgments

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