The Journal of Physical Chemistry A

© Copyright 1999 by the American Chemical Society

VOLUME 103, NUMBER 5, FEBRUARY 4, 1999

ARTICLES

Photoinduced Electron Transfer from a Higher Excited State of a Porphyrin in a Zinc Porphyrin−Ruthenium(II) *tris*-Bipyridine Dyad

Denis LeGourriérec,[†] Mikael Andersson,[†] Jan Davidsson,[†] Emad Mukhtar,[†] Licheng Sun,[‡] and Leif Hammarström*,[†]

Department of Physical Chemistry, Uppsala University, P.O. Box 532, S-751 21 Uppsala, Sweden, and
Department of Chemistry, Division of Organic Chemistry, Royal Institute of Technology,
S-100 44 Stockholm, Sweden

Received: October 15, 1998

Pump−probe spectroscopy and steady state emission measurements have been used to demonstrate electron transfer from the excited state populated by excitation in the Soret band (denoted S_2) of a zinc porphyrin to a covalently linked ruthenium(II) *tris*-bipyridine complex (ZnTTP-L-Ru(bpy)$_3$). The lifetime of 1.6 ps measured for the S_2 state of the zinc porphyrin (ZnTTP) was reduced to 0.8 ps in the dyad. On the basis of fluorescence data and transient absorption spectra, energy transfer from the porphyrin to the ruthenium was found to be negligible. Instead, electron transfer from the S_2 state occurred with a rate constant of 6×10^{11} s^{-1}.

1. Introduction

Porphyrin systems have received much attention owing to their great variety and their important role in biology, in particular in photosynthesis.[1] In natural photosynthetic systems, the primary electron transfer step occurs from a porphyrin-based complex.[1] Photophysical properties of porphyrins have been extensively investigated,[1,2] and model compounds have been developed[3] in order to gain a better understanding of natural photosynthetic mechanisms. A number of articles have been published[3] on electron transfer from the first excited state (S_1) of a porphyrin complex covalently linked to an electron acceptor (e.g., a second porphyrin, a quinone, or a ruthenium polypyridine).

A characteristic of porphyrins is the very intense absorption band in the region of 400−430 nm, called the B or Soret band. Although more than one transition is associated with this band,[2] the excited state generated by excitation in this spectral region has been denoted S_2 in the literature.[1,2,4] The S_2 state is separated by a large energy gap from the lowest excited state, denoted S_1. According to literature notation,[1,4] we refer to S_1 as the electronic state populated by excitation in the Q-bands (500−650 nm), although S_1 actually consists of two states that are degenerate in regular metalloporphyrins.[2] This large energy gap means that radiationless deactivation of the S_2 to the S_1 state is slow enough to allow competing processes to occur. For zinc tetraphenylporphyrin (ZnTPP), Gurzadyan et al.[4] measured by fluorescence upconversion a lifetime of 2.35 ps in ethanol for the decay of S_2 which they correlated with the rise of S_1. Fluorescence from S_2 has been reported with a lifetime of 3.5 ps in acetonitrile[5] for ZnTPP and intermolecular electron transfer has been reported from S_2 to dichloromethane.[5] Electron transfer has also been demonstrated by pump−probe spectroscopy from the water-soluble zinc *meso*-tetrasulphonatophenyl porphyrin (ZnTPPS^{4-}) to methyl viologen (MV^{2+}) in a ZnTTPS^{4}−MV^{2+} complex by Andersson et al.[6] In the absence of MV^{2+}, a lifetime of 1.3 ps was measured for the S_2 state, while S_2 decayed within the duration of the pulse ($<$200 fs) in the presence of MV^{2+}.

There is much interest in studying electron transfer from

---

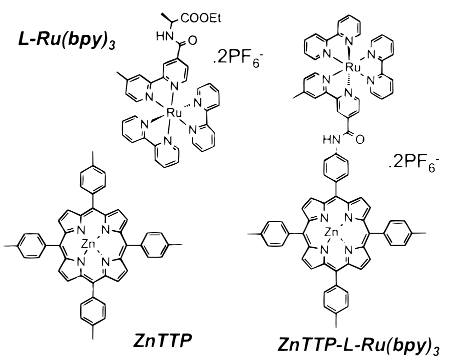
* Corresponding author. Fax: +46-18-508542. E.mail: leifh@fki.uu.se.

[†] Uppsala University.

[‡] Royal Institute of Technology.

10.1021/jp984150w CCC: $18.00

SCHEME 1 : Structures



higher excited states, which have a different energy and a different electronic distribution than the lowest excited state. From a fundamental viewpoint, it opens the possibility for new comparisons of reactivity in porphyrin-acceptor complexes. Also, in compounds used for solar energy conversion, more energy is available for photochemical reactions from higher excited states than from S_1. We have carried out pump−probe and steady state measurements on a zinc tetratolylporphyrin covalently linked to a ruthenium(II) *tris*-bipyridine complex (ZnTTP-L-Ru(bpy)$_3$ see Scheme 1). The two moieties, connected by an amide spacer, are separated by about 17 Å center to center. In this molecule, we have observed electron transfer from the porphyrin S_1 state to the ruthenium moiety on the 100 ps time scale and these results will be published in a forthcoming paper. Interestingly, we also found a much faster electron transfer from the second excited state (S_2), which we report in this paper. This is the first time that electron transfer from the S_2 state is reported in a well defined molecular structure and where the product formation is time resolved.

2. Experimental Section

The structure of the compounds studied in this work is provided in Scheme 1 and their synthesis will be described in a later publication. The pump−probe measurements were carried out on the femtosecond laser system at the Department of Physical Chemistry, University of Uppsala. The instrument has recently been described elsewhere.[6] The pump light (414 nm) was obtained by second harmonic generation of the fundamental laser light in a BBO crystal (1 mm thick). A white light continuum, generated in a rotating quartz plate was used for probing. The pulses had a temporal width of about 150 fs. A 1 mm thick rotating sample cell was used. In the kinetic measurements, a blue filter (Schott BG13) was positioned in the probe beam in front of the cell in order to reduce the intensity of the white light above 500 nm. In the spectral measurements, the first half of the spectrum (up to 500 nm) was measured with a blue filter (Schott BG13) positioned in the probe beam at the entrance of the spectrograph (MS257, Oriel Instrument) equipped with a CCD detector. This helped to improve the signal to noise ratio by reducing the most intense part of the white light. Above 500 nm, no filter was used.

Absorption spectra were recorded on a Hewlett Packard HP 8453 and fluorescence spectra were measured on a SPEX-Fluorolog fluorimeter. The solvent used was spectroscopic grade dimethyl formamide (DMF) (Uvasol, Merk). Concentrations for pump-probe measurements were adjusted to obtain an absorbance of ca. 0.25 at the excitation wavelength. For relative quantum yield measurements, the absorbance was ca. 0.05 at the excitation wavelength in order to minimise the inner filter effect. Aerated solutions were used for all measurements.

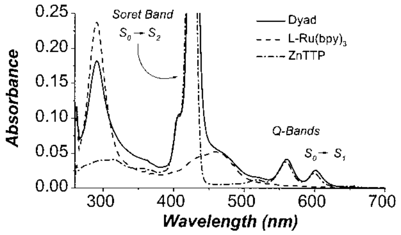


Figure 1. . Absorption spectra in DMF for the ZnTTP-L-Ru(bpy)$_3$ dyad, ZnTTP, and L-Ru(bpy)$_3$.

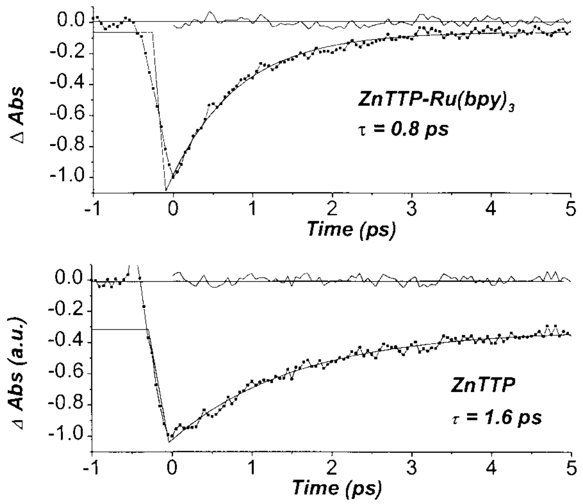


Figure 2. Decay profiles for ZnTTP-L-Ru(bpy)$_3$ and ZnTTP, single exponential fit and residuals. Pump 414 nm, probe 435 nm.

3. Results

The absorption spectra of the ZnTTP-L-Ru(bpy)$_3$ dyad and its individual components ZnTTP and L-Ru(bpy)$_3$ are shown in Figure 1. No significant spectral shift of the peaks characteristic of the porphyrin and ruthenium moieties is observed in the spectrum of the dyad, indicating that the electronic interaction between the two moieties is weak. It should be noted that the spectrum of the dyad does not exactly match the sum of the spectra of the individual components in the UV region. This is in agreement with previous observations on similar systems[7] in which the reactants are in close proximity.

Fluorescence quantum yields for the porphyrin moiety of the dyad were determined relative to ZnTTP in DMF. When exciting in the porphyrin Q-bands, the fluorescence of the dyad is reduced to 13% of its intensity in ZnTTP due to quenching by electron transfer to the appended ruthenium complex as demonstrated in the literature for several similar compounds.[7,8] When exciting the dyad in the Soret band, only 7% of the ZnTTP fluorescence is observed, suggesting that only half of the S_2 population converts to S_1 and the other half instead reacts via a different process.

The depopulation of the S_2 state was also investigated by femtosecond pump−probe spectroscopy. The sample was pumped at 414 nm (blue edge of the Soret band) and probed at 435 nm. At this probe wavelength, a bleaching is observed due to the relatively low extinction coefficient of the S_2 state,[6] while the S_1 and ground state absorptions are similar. As shown in Figure 2, the lifetime of S_2 in the dyad (0.8 ps) is shorter by a factor of two compared to ZnTTP (1.6 ps). This suggests, in agreement with the quantum yield results, the presence of an additional deactivation channel for S_2 in the dyad.

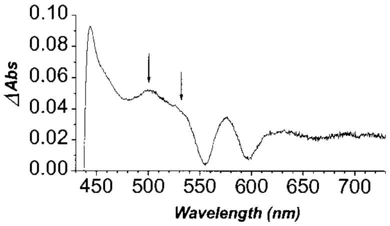


Figure 3. Transient absorption spectrum from ZnTTP-L-Ru(bpy)$_3$ after 10 ps exciting at 414 nm. The spectrum corresponds to a mixture of S$_1$ and charge transferred states (see text).

4. Discussion

For ZnTTP, the S$_2$ to S$_1$ conversion is quantitative. Thus, the 1:2 ratio of the porphyrin fluorescence yield for excitation in the Soret band versus the Q-band shows that one-half of the S$_2$ population in the dyad decays via a different reaction path. This is in agreement with the 50% reduction of the S$_2$ lifetime of the dyad compared to ZnTTP. Two conceivable pathways may be operating besides internal conversion to S$_1$: electron transfer and energy transfer to the ruthenium moiety, the former leading to a charge separated state. On the basis of the steady state fluorescence measurements and transient absorption spectra, we were able to discriminate between these two mechanisms.

The fluorescence spectra obtained by exciting in the Q-band (560 nm, no ruthenium absorption) and in the Soret band (427 nm, <5% ruthenium absorption) match exactly and no contribution from the ruthenium complex could be seen. However, when exciting in the ruthenium band (450 nm), an easily detectable ruthenium emission is observed (although it is quenched by ca. 95% by energy transfer to the porphyrin triplet). Thus, the Soret band excitation does not generate any sensitized ruthenium emission and energy transfer from the porphyrin S$_2$ state can therefore not be significant.

The transient absorption spectrum recorded 10 ps after the excitation pulse exhibits a shoulder near a sharp peak at 440 nm which may be assigned to the S$_1$ state,[5,6,9] another maximum at 500 nm and a shoulder near 530 nm (see arrows, Figure 3). This spectrum cannot be explained only by porphyrin states. The absorption spectra of pure porphyrin S$_1$ states[5,6,9] and T$_1$ states[9] available in the literature do not possess the feature we observed near 500 nm after 10 ps. However, one spectral feature characteristic of the reduced ruthenium complex, which is expected in the charge separated species, is a band near 500 nm.[10] Thus, we assign the transient spectrum after 10 ps to a combination of 50% of the porphyrin S$_1$ state and 50% of the charge separated state (porphyrin cation[11] and reduced ruthenium complex).

These observations suggest that energy transfer to the ruthenium moiety does not play a major role in the depopulation of the S$_2$ state. Electron transfer to the ruthenium and internal conversion to S$_1$ therefore appear as the two main competing mechanisms contributing to the decay of S$_2$, each accounting for 50% of its decay. From the measured lifetime values for the dyad and ZnTTP, the rate constant for electron transfer $k_{ET} = 6 \times 10^{11}\ s^{-1}$ was calculated.

Redox data available on related compounds may be used to estimate the energy position of the charge separated state. Thus, a fair estimation may be obtained using values of 0.81 V[12] for the oxidation potential of the porphyrin and −1.17 V for the reduction potential of a ruthenium tris-bipyridine possessing the same amide substituent in acetonitrile.[13] On this basis, the charge separated state is thought to lie at an energy of 1.96 eV relative to the ground state, which means a driving force of about 0.94 eV for electron transfer from S$_2$. The rather fast electron transfer we observe suggests that the reaction is nearly activationless ($-\Delta G° \approx \lambda$). A reorganization energy $\lambda \approx 1.0$ eV is indeed typical in polar solvents.[14]

5. Conclusion

We have shown that intramolecular electron transfer is taking place from the higher excited state S$_2$ of a zinc porphyrin to a covalently linked ruthenium complex ($k_{ET} = 6 \times 10^{11}\ s^{-1}$), while electron transfer from the lowest excited state S$_1$ is a 100 times slower. The difference in reactivity could be utilised in a molecular device[15] where different electronic outputs are generated depending on the wavelength of the incident light. Work on electron transfer from S$_1$ and subsequent reactions is being carried out and will be published in a forthcoming paper. We hope that the present paper will inspire further work on electron transfer from the S$_2$ state of porphyrins, so far a nearly unexplored area.

Acknowledgment. This work was supported by grants from the Knut and Alice Wallenberg Foundation, the Swedish Research Council for Engineering Sciences, the Swedish Natural Science Research Council, the European TMR Program (TMR Network Grant CT96-0031), and the Nordic Energy Research Program.

References and Notes

(1) Kalyanasundaram, K. *Photochemistry of Polypyridines and Porphyrin Complexes*; Academic Press: London, 1992.

(2) Gouterman, M. In *The Porphyrins*; Academic Press: New York, 1978; Vol. III.

(3) Gust, D.; Moore, T. A. *Photoinduced Electron Transfer III; Topics in Current Chemistry 159*; Springer-Verlag: Berlin, 1991; Vol. 159, 103. Wasielewski, M.R. *Chem. Rev.* **1992**, *92*, 435. Kurreck, H.; Huber, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 849. Harriman, A.; Sauvage, J-P. *Chem. Soc. Rev.* **1996**, 41.

(4) Gurzadyan, G. G.; Tran-Thi, T.-H.; Gustavsson, T. *J. Chem. Phys.* **1998**, *108*, 385. DeGraziano, J. M.; Liddell, P. A.; Leggett, L.; Moore, A. L.; Moore, T. A.; Gust D. *J. Phys. Chem.* **1994**, *98*, 1758.

(5) Chosrowjan, H.; Tanigichi, S.; Okada, T.; Takagi, S.; Arai, T.; Tokumaru, K. *Chem. Phys. Lett.* **1995**, *242*, 644.

(6) Andersson, M.; Davidsson, J.; Korppi-Tommola, J.; Peltola, T.; Hammarström, L. *J. Phys. Chem.* **1998**. Submitted for publication.

(7) Flamigni, L.; Armaroli, N.; Barigelletti, F.; Balzani, V.; Collin, J-P.; Dalbavie, J-O.; Heitz, V.; Sauvage, J-P. *J. Chem. Phys. B* **1997**, *101*, 5936.

(8) Collin, J-P.; Dalbavie, J-O.; Heitz, V.; Sauvage, J-P.; Flamigni, L.; Armaroli, N.; Balzani, V.; Barigelletti, F.; Montanari, I. *Bull. Soc. Chim. Fr.* **1996**, *133*, 749.

(9) Rodriguez, J.; Kirmaier, C.; Holten, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 6500.

(10) Mulazzani, Q. G.; Emmi, S.; Fuochi, P. G.; Hoffman, M. Z.; Venturi, M. *J. Am. Chem. Soc.* **1978**, *100*, 981.

(11) Neta, P. *J. Phys. Chem.* **1981**, *85*, 3678. Brun, A. M.; Harriman, A.; Heitz, V.; Sauvage, J-P. *J. Am. Chem. Soc.* **1991**, *113*, 8657.

(12) Gust, D.; Moore, T. A.; Moore, A. L.; Gao, F.; Luttrull, D.; DeGraziano, J. M.; Ma, X. C.; Makings, L. R.; Lee, S.-J.; Trier, T. T.; Bittersmann, E.; Seely, G. R.; Woodward, S.; Bensasson, R. V.; Rougée, M.; De Schryver, F. C.; Van der Auweraer, M. *J. Am. Chem. Soc.* **1991**, *113*, 3638.

(13) Abrahamsson, M.; Hammarström, L. Unpublished results.

(14) Marcus, R. A.; Sutin, M. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(15) Balzani, V.; Scandola, F. In *Comprehensive Supramolecular Chemistry*, Reinhout, D. N., Ed.; Pergamon: Oxford, **1996**; Vol. 10, Chapter 23.