# Kinetics of Charge Transfer from Zinc Tetraphenylporphyrin to an axially Co-ordinated Pyridine

**Andrew M. Crouch, Devendra K. Sharma, and Cooper H. Langford***

*Canadian Centre for Picosecond Laser Spectroscopy, Department of Chemistry, Concordia University, 1455 deMaisonneuve Boulevard W., Montreal, Quebec H3G 1M8, Canada*

The aromatic radical anion charge transfer state of a pyridine–zinc tetraphenylporphyrin complex is formed in good yield with a time constant of 3 ns following generation of the porphyrin triplet.

Charge transfer processes involving porphyrin excited state donors and linked acceptor molecules have attracted a great deal of interest for their relevance to construction of models of photosynthesis. In the course of a study of systems which can develop vectorial photoinduced charge transport across a film along a concentration gradient, we have been led to investigate the charge transfer state which arises following irradiation of zinc tetraphenylporphyrin [Zn(TPP)] which is axially co-ordinated by pyridine. This state proves to be accessible from the π–π* triplet state of Zn(TPP) with a time constant of *ca.* 3 ns.

The experiments were conducted using 355 nm excitation from the third harmonic of a mode-locked Nd/YAG laser system in the Canadian Centre for picosecond laser spectroscopy. The pulse width was *ca.* 30 ps and the pulse energy was 2.5 mJ (or less if a filter was employed to study intensity dependence). A continuum pulse from 425 to 675 nm with the same temporal characteristics provided a probe which could be delayed from 0 ps to 10 ns.

Figure 1 shows the spectra of Zn(TPP) (0.8 nM) in $CH_2Cl_2$. The excited state absorptions of the singlet and triplet π–π* states are expected to overlap strongly[1] but the triplet absorbs slightly more to the red.[1] Only small changes are seen in Figure 1 between 0 ps and 10 ns despite the fact that the 645 nm fluorescence decay lifetime measured on the same apparatus with the aid of a Hammamatsu Streak Camera with 20 ps resolution was 1.9 ns (in agreement with ref. 2). This indicates that: (a) the singlet and triplet overlap, and/or (b) the 1.9 ns singlet decay time represents a minimum rate of formation of the triplet. (There may be routes to the triplet from the 355 nm Franck–Condon state that do not pass through the lowest singlet.) Also, photoelectron transfer to solvent from the singlet, as suggested for the Cd and Hg analogues,[1] may contribute to the small absorbance growth in the red.

On repeating the experiment in the co-ordinating solvent methanol, changes in the spectra over 10 ns were slightly larger but still too small to allow assignment. (It is probable that singlet–triplet intersystem crossing is responsible for the changes.) The experiment in pyridine where Zn(TPP) exhibits the spectrum of the six-co-ordinate bis-pyridine species[3] is more revealing.

Figure 2 shows the spectra of Zn(TPP)–(pyridine)$_2$ from 0 ps to 10 ns. In the first 50 ps there is some growth associated with the passage of the pulse. Subsequently, there is growth of the peak at 470 nm, growth of broad absorbance in the red above 600 nm, an isosbestic point at about 506 nm, and no indication of ground state recovery. (See bleaching at 564 nm.) The peak at 470 nm and the broad absorbance in the red are the signature of the pyridine co-ordinated radical cation.[4] The growth of absorbance in the blue corresponds to the changes that were reported for reaction of a water soluble Zn(TPP) derivative with nitrobenzene.[5] Thus, we assign the 10 ns spectrum to the charge transfer state Zn(TPP)$^{\cdot+}$pyridine$^{\cdot-}$.

The time constant for development of this state from the Zn(TPP) triplet is 3 ± 1 ns. The yield for this charge transfer

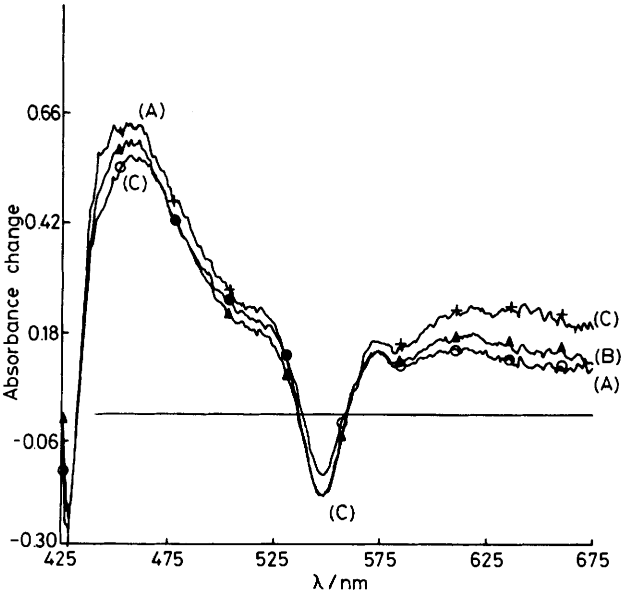

**Figure 1.** The difference spectra of Zn(TPP) in $CH_2Cl_2$ at representative delay times after excitation at 355 nm. (A), 20 ps; (B), 1 ns; (C), 10 ns.

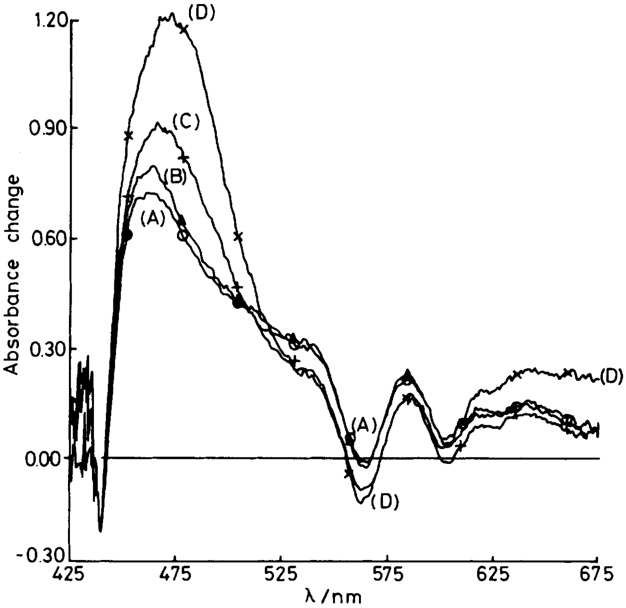

**Figure 2.** The difference spectra of Zn(TPP)–(pyridine)$_2$ in pyridine at representative delay times after excitation at 355 nm. (A), 20 ps; (B), 50 ps; (C), 1 ns; (D), 10 ns.

state was estimated from the ground state bleaching after 10 ns. It appears to be *ca.* 0.5.

Similar spectra are obtained when Zn(TPP) is dissolved in MeOH in the presence of an excess of the polymer used in formation of the photoelectrochemically active film. This polymer consists of a blend of polyvinylpyridine and a polystyrene substituted at two of three ring sites with quaternary cations.[6]

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## References

1 M. P. Irvine, R. J. Harrison, M. A. Strahand, and G. S. Beddard, *Ber. Bunsenges. Phys. Chem.*, 1985, **89**, 226.

2 K. Kalyanasundaram and M. Neumann-Spallart, *J. Phys. Chem.*, 1982, **86**, 5163.

3 K. M. Kadish and R. K. Rhodes, *Inorg. Chem.*, 1981, **20**, 2961.

4 K. M. Kadish, L. R. Shiue, R. K. Rhodes, and L. A. Bottomley, *Inorg. Chem.*, 1981, **20**, 1274.

5 G. S. Nahor and J. Rabani, *J. Phys. Chem.*, 1985, **89**, 2468.

6 C. H. Langford, I. Ordonnez, D. A. Biro, A. M. Crouch, D. Guay, and J-P. Dodelet, 171st Meeting, The Electrochemical Society, Philadelphia, May, 1987, Abstract 361.