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Ultrafast dynamics of alkyl-substituted porphycenes in solution

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Received 16 December 2005; in final form 13 February 2006
Available online 10 March 2006

Abstract

Dynamics of relaxation from higher electronic excited states was studied for $9, 10, 19, 20$-tetraalkylporphycenes with methyl and propyl substitutents. Depopulation of S_3/S_4 Soret states leading into S_2/S_1 Q levels occurs in about 50 fs. This time is similar, or even shorter than that recently determined for porphyrin, even though the Q-Soret energy separation in the latter is about twice smaller than in porphycenes. The time constant for H or D transfers are shorter than 50 fs indicating very low energy barriers to their transfer. The non-radiative rate constants of both derivatives are related to the motion of the alkyl chain.
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1. Introduction

Porphycenes, the first among constitutional isomers of porphyrin synthesized so-far, captivate attention of researchers for almost 20 years [1]. The interest is motivated by biological importance of such compounds, potential applications in material sciences and in medicine as phototherapeutic agents. Special attention was paid to the problem of tautomerism involving the inner hydrogen atoms [2]. Detailed studies of electronic and vibrational relaxations are available mostly for porphyrins and their metal complexes. For example, ultrafast techniques observed three relaxation time scales for free base tetraphenyl porphyrin excited into the Soret, Q_y and Q_x bands [3]. The three higher singlet states undergo internal conversion to Q_x within a time shorter than 100 fs. Contrary to the free base compound, relaxation in the zinc complex of porphyrin is much slower [4]. Internal conversion from the higher electronic states to S_1 takes place in 200 fs to 1.45 ps, and cooling/vibrational relaxation of S_1 takes tens of picoseconds [4].

Alkyl-substituted porphycenes show interesting dependence of spectral properties on the position of substitutent [5–8]. They can undergo a double H-transfer (DHT) reaction as it happens in 7-azaindole dimer, a widely studied prototype of DNA base pairs [9]. Here, we report on studies of fs-dynamics in *meso*-alkylated porphycenes in solution (Fig. 1). The results show times spanning from 50 fs to ∼5 ps, assigned respectively to S_3, S_4 and S_2, S_1 relaxation involving IVR, cooling and crossing to dark states.

2. Experimental

$9, 10, 19, 20$-Tetrapropylporphycene (TPPC) and $9, 10, 19, 20$-tetramethylporphycene (TMPC) were synthesized and purified according to Ref. [10]. THF (Sigma–Aldrich, spectroscopy grade) was purified by distillation. Picosecond emission decays at magic angle were measured using a time-correlated single-photon counting spectrophotometer (FluoTime 200, Picoquant) [11]. Samples were excited at $371, 393$ or at 635 nm. The instrument response function (IRF) of the system is about 65 ps.

Femtosecond emission transients were collected using fluorescence up-conversion technique. The system consists of a femtosecond Ti:sapphire oscillator (Tissa 100, CDP) pumped with a 5 W diode laser (Verdi 5, Coherent). The
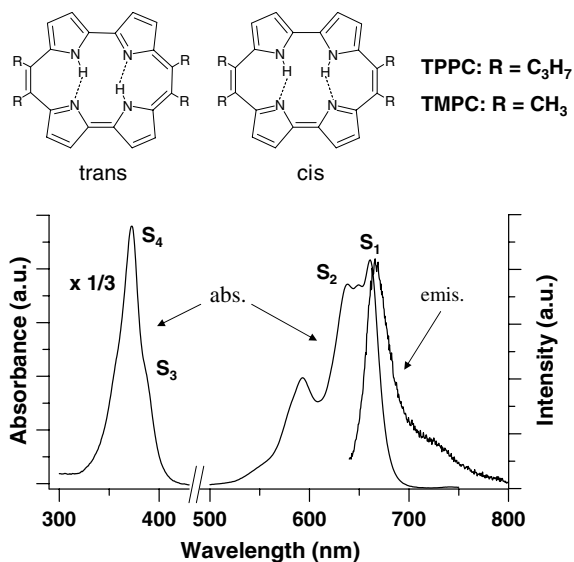

Fig. 1. Top: Molecular structure of *trans* and *cis* tautomers of 9,10,19,20-tetra-*n*-propylporphycene (TPPC) and 9,10,19,20-tetramethylporphycene (TMPC). Bottom: UV–Vis absorption (abs.) and emission (emis.) spectra of TPPC in tetrahydrofuran (THF) at 293 K. For the emission spectrum, the excitation was at 390 nm.

pulses (70 fs, 400 mW) were centered at 780 nm, with 86 MHz repetition rate and doubled in a 1-mm BBO crystal to have the pumping beam (390 nm). The cross correlation of the apparatus measured as a Raman signal from solvent was ∼185 fs. Details can be found in [11]. Both ps and fs decays were deconvoluted and fitted using the Fluofit package (PicoQuant). The quality of the fits was characterized in terms of residuals distribution and the reduced χ^2 value. All experiments were done at 293 K.

3. Results and discussion

Fig. 1 shows the electronic absorption and fluorescence spectra of TPPC in tetrahydrofurane (THF). The corresponding spectra (not shown) of TMPC are very similar in shape and intensity to those of TPPC. The figure also shows the molecular structure of TPPC and TMPC in *trans* and *cis* tautomeric forms. Experiments in matrices [8,12] and molecular beam [13] showed that a double hydrogen-transfer or, in isolated molecules, delocalization of the inner H-atoms over all four nitrogen sites occurs both in S_0 and S_1 states. For absorption (Fig. 1), both compounds exhibit a pattern of the first four excited electronic states (S_1, S_2, S_3 and S_4) characteristic of free base porphyrinoids [8]. The positions of maxima are practically not sensitive to the polarity of solvent, reflecting the larger population of *trans* tautomer at S_0, and in which, due to location of the hydrogen atoms (of N–H bonds) on the opposite side of the inner cavity, there is no dipole moment. The intensity of the emission spectrum is week and has its maximum at 670 nm and a shoulder at ∼ 730 nm. In THF, the fluorescence lifetime is 31 ps upon excitation at 390 nm or at 635 nm.

Fig. 2 shows fs-resolved fluorescence transients of TPPC in THF at selected wavelengths of observation, upon excitation at 390 nm. The transients were fitted using a multi-exponential function, and Table 1 shows the data. For a clear comparison, Fig. 3A shows the transients of TPPC at the shortest and longest wavelengths of observation, and to witness the behavior of TPPC and TMPC in THF, Fig. 3B exhibits their transients at 670 nm. Analysis of the data allows dividing the transients into four regions. For region I (500 nm, Fig. 1) in which the emission should be from S_3 or S_4 states, we observed a monoexponential decay with a time constant of ∼50 fs. For region II (610–630 nm), three components were necessary to fit the transients. The first one is very short (50 ± 30 fs) and its large amplitude decreases at longer wavelengths in this region. The second component has a time of 0.6–1 ps, and its contribution does not significantly change. The third component becomes longer with the wavelength, growing from 4.7 ps at 610 nm to 16 ps at 630 nm. Its amplitude is the smallest one at 610 and increases at longer wavelengths. For region III (640–650 nm), the transients were also fitted using a 3-exponential function. While the times of the fast component are about 60 fs and 1.2 ps, the third component becomes longer (31 ps). It was accurately obtained from the ps-experiment and from the transients recorded at a larger window of observation (Fig. 3B). Finally, for region IV, and which contains the maximum of the CW-emission band, the fs-decaying component is absent, and the transients could be fitted to a two-exponential function having times of 4–5.4 and 31 ps.
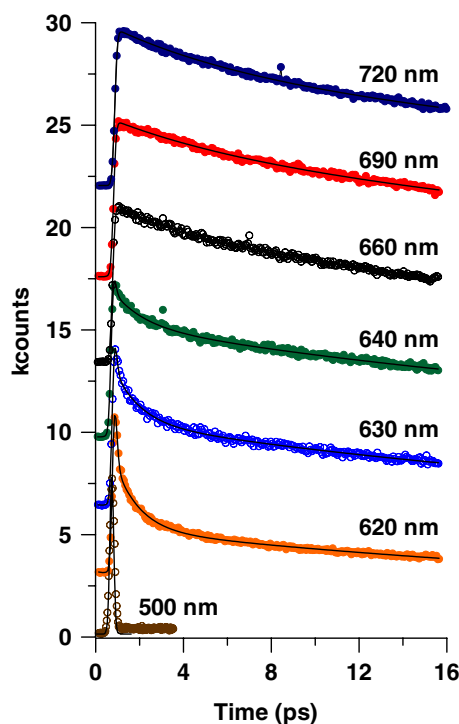

Fig. 2. Femtosecond emission transients of TPPC in THF at different observation wavelengths, upon excitation at 390 nm.

Table 1
Values of time constants and normalized (to 100%) amplitudes upon fitting of the fs emission transients of TPPC in THF at different wavelengths of observation

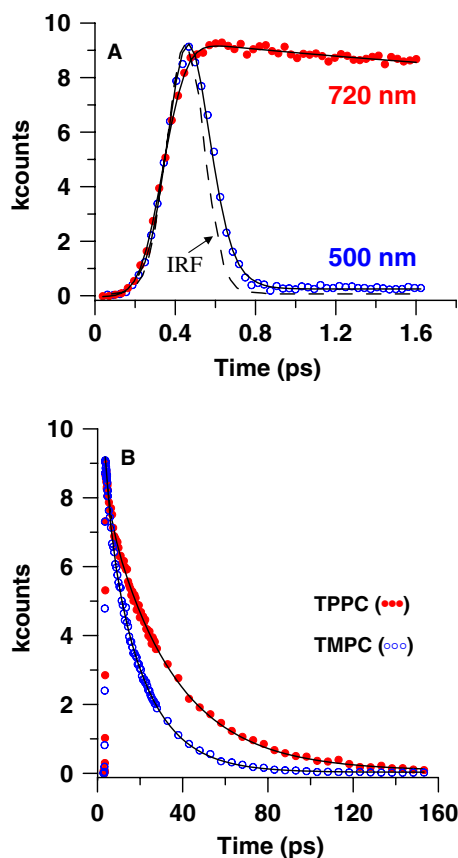| λ / nm	500	610	620	630	640	650	660	670	680	690	720
a_1/%	100	80	70	61	62	58					
τ_1/fs	50	50	60	60	50	50					
a_2/%		14	17	15	10	13	11	13	14	13	22
τ_2/ps		0.6	0.8	1.0	1.3	1.2	2	4.2	5.1	5.2	5.4
a_3/%		6	13	24	28	29	89	87	86	87	78
τ_3/ps		4.7	8.3	16	31	31	31	31	31	31	31

Fig. 3. (A) fs-transient emission of TPPC at 720 (●●●) and 500 nm (○○○), upon excitation at 390 nm. The dashed curve is the cross correlation function from the Raman signal. (B) Transient emission signals of TPPC (●●●) and TMPC (○○○) in THF at 670 nm. The solid lines in A and B are from multiexponential fits of the transients.
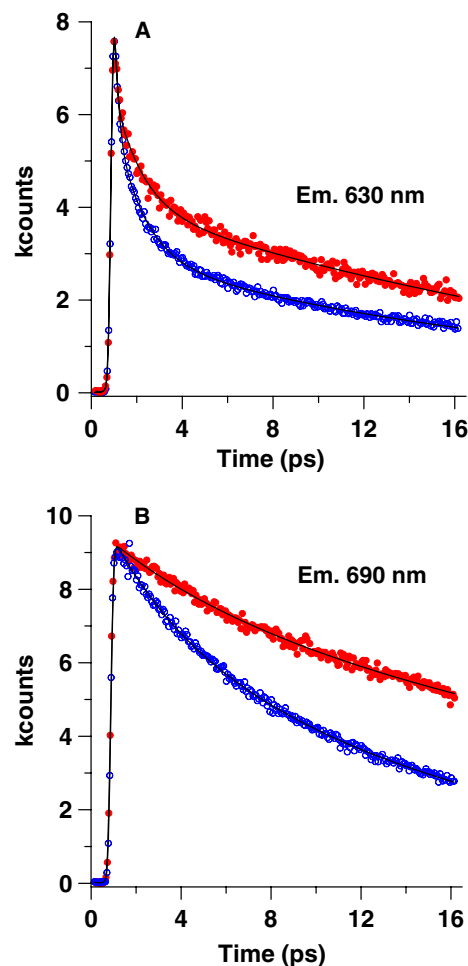

Fig. 4. fs-emission transients of TPPC (●●●) and TMPC (○○○) in THF at two selected observation wavelengths: (A) 630 and (B) 690 nm. The solid lines in A and B are from multiexponential fits of the transients.

In order to examine the effect of the alkyl-chain on the dynamics, we also studied the tetramethyl derivative (Fig. 1). Fig. 4 shows the fs-transients of propyl (TPPC) and methyl (TMPC) substituted compounds in THF at short and long observation wavelengths. The behavior of TMPC is only slightly different from that of TPPC. At 630 nm, the emission decay gives times of 70 fs, 1.1 and 17 ps. However, at 670 nm we got 1.2 and 17 ps, and at 690 nm the times are 3.4 and 17 ps. At these wavelengths, we have observed no rising component. Although the involved times and contributions of a particular component are slightly different when compared to those of

TPPC, both derivatives undergo dynamics in a similar time scale. At a longer time window of observation (Fig. 3B), the emission decays of both derivatives show the same trend. The fluorescence lifetime of TMPC is 17 ps, about half of that for TPPC (31 ps). Note that the shortest component measured for TMPC (1.2–3.4 ps) at this region (670–690 nm) is shorter than in TPPC (4.2–5.2 ps). This result suggests that these times in both derivatives reflect a similar channel, and which is related to the motion of the alkyl chain.

It is clear that the flow of the population from the Soret bands (S_3, S_4) to S_2 and S_1 is shorter than ~50 fs, suggesting that their lifetimes are $\leqslant 50$ fs. Recently, a fs-dynamics study of porphyrins in solution has reported a time shorter than 100 fs, assigned to the relaxation from B(S_3) state to Q_y(S_2) state [3]. Taking into account that the energy gap (~ 10,000 cm^{-1}) between S_3, S_4 and S_2 in TPPC is larger than in porphyrin (~5650 cm^{-1}) [14], and the similarity of the fs-conversion rate, one can not use the energy gap law to explain the origin of the fast internal conversion in porphycenes. Other factors like an increase in the density of vibronic states, enhanced by symmetry reduction, in-plane and out-of-plane motions of the rings should play a significant role in their fs-dynamics. Given the large viscosity effect on the S_1 fluorescence lifetime (in triacetin (viscosity η (293 K) = 20 cP) the emission lifetime of TPPC increases to hundreds of ps), the most probable mechanism of relaxation involves large amplitude motions distorting the porphycene skeleton, due to alkyl substituents positioned in close vicinity.

To study the isotope (N–H/N–D) effect on the DHT reactions and the depopulation of excited TPPC, we examined the fs-dynamics of the deuterated (N–D) compound. Deuteration was done by dissolving TPPC in CD$_3$OD and confirmed by monitoring the change in relative intensities of first two absorption bands of TPPC, characteristic for N–H → N–D exchange. The time-resolved (ps and fs) experiments were performed in CD$_3$OD and in THF. We have observed no (H/D) isotope effect on the lifetime. In addition to that, the fs-transients at 500 and 720 nm did not show any change upon deuteration. Because DHT reactions occur in *trans* (and *cis*) tautomers of TPPC in different environments: gas, liquids and cryogenic matrices [2,8], we explain these results in terms of a very low energy barrier to the migrations of both hydrogen (deuterium) atoms. Jet-cooled molecular-beam experiments suggested that this barrier is below 3.8 kcal/mol [15]. Furthermore, the system may undergo the photoreactions from high vibrational levels of S_1/S_2 states (Fig. 5). Our time-resolution suggests that the time constant for H or D atoms transfers is shorter than 50 fs.

Because of the strong overlapping of absorption bands in the Soret region and expected similarity of the absorption spectra of *trans* and *cis* tautomers, it is almost impossible to selectively excite one form. Therefore, the component of 4–5 ps observed in region IV can be also assigned to relaxation of the *cis* tautomer. In such a case, a shorter lifetime of *cis* would most probably be caused by its conversion to *trans*. Therefore it seems justified to focus on the photodynamics of excited *trans* (the most stable structure at S_0) (Fig. 5). After an ultrafast relaxation (< 50 fs) from S_4, S_3 to S_2 and S_1 states, VR/cooling takes place within 5 ps, and this time includes transitions to dark states. These are reached in 0.6–1.2 ps at higher vibrational levels due to an increase in the density of states. The presence of dark states has been postulated before [16]. It is now suggested by the low emission quantum yield
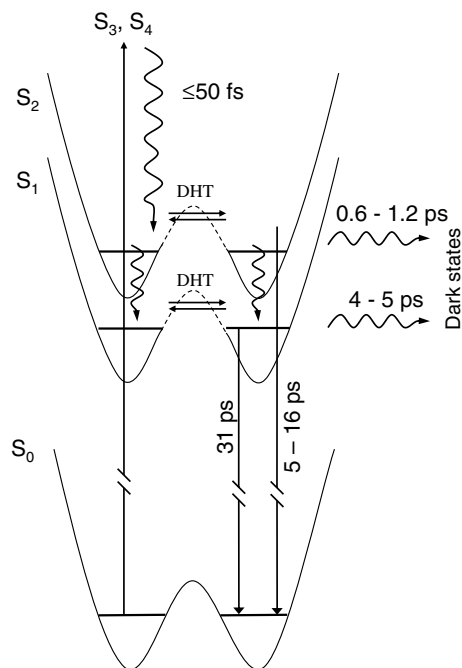

Fig. 5. A schematic representation of the energy diagram and the processes following excitation of *trans* tautomers of TPPC in THF. The numbers indicate the observed values for the involved processes, and DHT means double H-atom transfer (for details see text). Positions of the energy levels are not in scale.

(<10^{-3}), and by a large shortening of the room-temperature solution emission lifetime of TPPC (31 ps) and TMPC (17 ps) when compared to that of unsubstituted porphycene (8–11 ns) [8,17]. Furthermore, for TPPC in triacetin (η (293 K) = 20 cP) the emission lifetime reaches hundreds of ps [18]. The 5–16 ps component observed at 610–630 nm is assigned to an emission from high vibrational levels of S_1 and S_2 states.

4. Conclusion

Given that the energy spacing between the Q and Soret bands in porphycenes is much larger than in porphyrins, ultrafast $S_{3,4}$–$S_{1,2}$ relaxation (in < 50 fs) is not a result that could have been predicted a priori. The fast (1–5 ps) relaxation dynamics in $S_{1,2}$ is affected by the motion of the alkyl groups. For TPPC in THF, emissions from high vibrational states of S_2 and S_1 occur within 5–16 ps, while the emission lifetime from relaxed S_1 levels is 31 ps. Under our experimental conditions, we have observed no isotope (N–H/N–D) effect. This result is explained in terms of a low energy barrier to the DHT reaction.

References

[1] E. Vogel, M. Köcher, H. Schmickler, J. Lex, Angew. Chem., Int. Ed. Engl. 25 (1986) 257.

[2] J. Waluk, Tautomerization in porphycenes, in: R. Schowen, H.-H. Limbach (Ed.), Handbook of hydrogen transfer, Wiley-VCH, in press.

[3] J.S. Baskin, H.-Z. Yu, A.H. Zewail, J. Phys. Chem. A 106 (2002) 9837.

[4] H.-Z. Yu, J.S. Baskin, A.H. Zewail, J. Phys. Chem. A 106 (2002) 9845.

[5] J. Dobkowski, V. Galievsky, A. Starukhin, J. Waluk, Chem. Phys. Lett. 318 (2000) 79.

[6] J. Dobkowski, V. Galievsky, M. Gil, J. Waluk, Chem. Phys. Lett. 394 (2004) 410.

[7] J. Dobkowski, V. Galievsky, A. Starukhin, E. Vogel, J. Waluk, J. Phys. Chem. A 102 (1998) 4996.

[8] J. Waluk, E. Vogel, J. Phys. Chem. 98 (1994) 4530.

[9] A. Douhal, S.K. Kim, A.H. Zewail, Nature 378 (1995) 260.

[10] E. Vogel, M. Köcher, J. Lex, O. Ermer, Isr. J. Chem. 29 (1989) 257.

[11] J.A. Organero, L. Tormo, A. Douhal, Chem. Phys. Lett. 363 (2002) 409.

[12] J. Waluk, M. Müller, P. Swiderek, M. Köcher, E. Vogel, G. Hohlneicher, J. Michl, J. Am. Chem. Soc. 113 (1991) 5511.

[13] J. Sepioł, Y. Stepanenko, A. Vdovin, A. Mordziński, E. Vogel, J. Waluk, Chem. Phys. Lett. 296 (1998) 549.

[14] M. Gouterman, Optical Spectra and Electronic Structure of Porphyrins and Related Rings, in: D. Dolphin (Ed.), The Porphyrins, Part A, vol. III, Academic Press, New York, 1979.

[15] A. Vdovin, J. Sepioł, N. Urbańska, M. Pietraszkiewicz, A. Mordziński, J. Waluk, J. Am. Chem. Soc. 128 (2006) 2577.

[16] H. Levanon, M. Toporowicz, H. Ofir, R.W. Fessenden, P.K. Das, E. Vogel, E.M. Köcher, K. Pramod, J. Phys. Chem. 92 (1988) 2429.

[17] P.F. Aramendia, R.W. Redmond, S. Nonell, W. Schuster, S.E. Braslavsky, K. Schaffner, E. Vogel, Photochem. Photobiol. 44 (1986) 555.

[18] A. Douhal et al., to be submitted for publication.