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## Dynamic process in a hexameric benzo-porphyrin studied by femtosecond transient absorption

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### Abstract

The fast kinetics of a hexameric benzo-porphyrin compound was investigated by femtosecond transient absorption spectroscopy. Using polychromatic detection, a sequence of spectra acquired at different delays revealed complex kinetic processes on the timescale of approximately 20 ps. The samples were then investigated at selected wavelengths by using a dual-colour femtosecond pump–probe setup. The same sequence of measurements was carried out under identical conditions on a benzo-porphyrin model sample. The comparison of the transient absorption decays recorded for both compounds revealed that only in the hexamer a 20 ps decay component is present which is attributed to an intramolecular interchromophoric excited-state process. © 1999 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

Porphyrins and porphyrin-based systems have attracted considerable attention. In particular, porphyrin assemblies have been prepared and investigated to understand better the activity of more complex biological systems [1–5]. It has recently been shown that the spectral properties [6] and the fluorescence decay processes [7] of the porphyrin chromophore within a multi-chromophoric synthetic assembly are controlled by the spatial arrangement of the molecules. In this contribution, the dynamics of a

hexameric porphyrin array (BP6; see Fig. 1, insert A) in which each of the six porphyrin chromophores is covalently bound to a central benzene ring is reported. Previous NMR investigations [8] indicated the occurrence of interactions among the porphyrin moieties. The observation of a splitting of the Soret band at low temperatures for the hexamer and the absence thereof in the model compound [8] was indicative of an electronic interaction between the porphyrin chromophores. Comparison of the fluorescence properties of the hexamer and the corresponding monomer in chloroform using single photon timing (SPT) detection with a time increment of 42 ps resulted in a decay time of 3.8 ns for BP6, which as the quantum yield of fluorescence is unchanged indicates an enhanced  $k_f$  for the hexamer.

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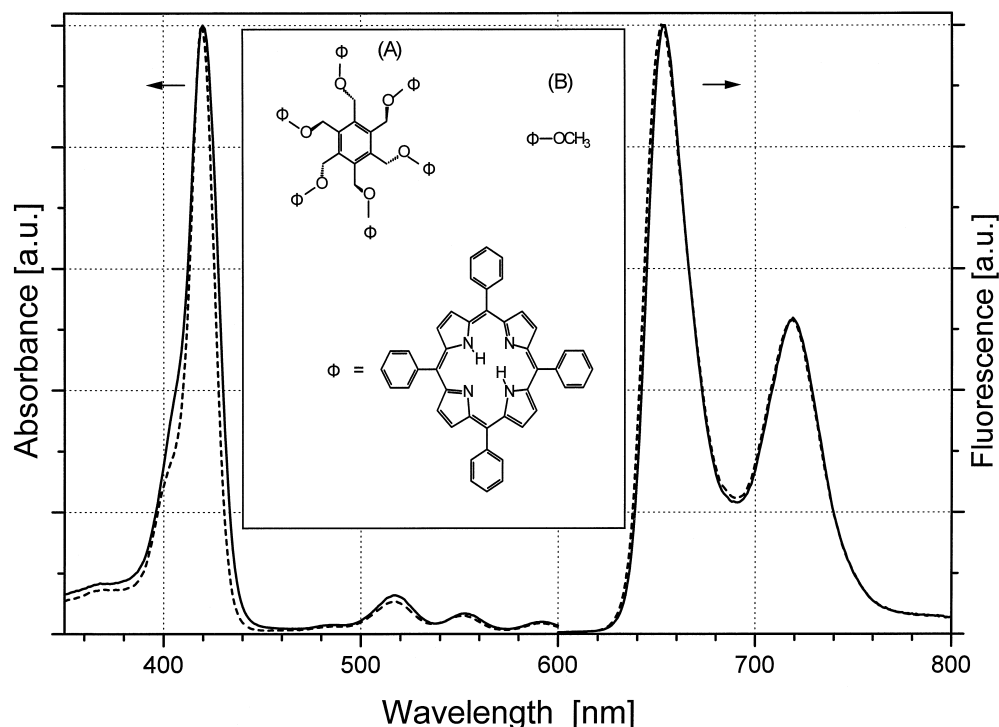


Fig. 1. Ground-state spectra of MeOPP (dotted lines) and BP6 (solid lines). Left: Absorption spectra; right: fluorescence emission spectra. Insert: Molecular structures of (A) BP6 and (B) MeOPP.

In order to clarify the mechanism of the relaxation processes within the hexamer, a femtosecond transient absorption study has been carried out on BP6. By a polychromatic detection setup using white-light continuum generation and a CCD camera as detector, transient absorption spectra in the range from 430 to 490 nm have been acquired at different delays after excitation. Furthermore, transient absorption decays at selected probe wavelengths have been recorded by a more sensitive monochromatic detection setup. The same set of measurements was also performed on a mono-chromophoric model benzo-porphyrin molecule (Fig. 1, insert B).

## 2. Experimental

The molecular structures of both samples investigated are shown in Fig. 1 (inserted). The synthesis of the hexakis-porphyrinato benzene (BP6; see Fig. 1,

insert A) and the methoxy-substituted porphyrinato monomer (MeOPP; Fig. 1, insert B) has been reported previously [8]. As a solvent for all samples chloroform (HPLC grade, Biosolve) was used without further purification. The ground-state spectra recorded by a Lambda6 spectrophotometer (Perkin Elmer) are shown in Fig. 1. Besides a very small broadening of the absorption spectrum of BP6 as compared to MeOPP which is most pronounced in the Soret band, both the absorption and emission spectra of the monomeric compound are almost identical to the corresponding ones of the hexameric system.

The amplified femtosecond double OPA laser system has been described in detail previously [9]. In brief, a NdYVO<sub>4</sub>-pumped Ti:Sapphire laser (Millenia and Tsunami, Spectra Physics) was regeneratively amplified giving pulses at 1 mJ, 800 nm, ca. 120 fs length and 1 kHz repetition rate. One half of this energy was used to pump an optical parametric amplifier (OPA) including a final stage for fourth

harmonic generation, which was tuned to the excitation wavelength of 420 nm. Using an induced transient Kerr effect in a sample of CS<sub>2</sub>, the pulse length at the position of the sample was determined as ca. 250 fs under the present experimental conditions.

Two different schemes were used for monochromatic and polychromatic detection. For the former, a dual-color transient absorption setup as described in Ref. [9] was employed, with the addition of fourth harmonic generation stages into both OPAs allowing for selection of wavelengths from 350 to 550 nm. For the latter, 50% of the 800 nm light from the amplified laser system was used in one OPA giving the light at the pump wavelength of 420 nm, while the other half served for generation of a fs white-light continuum for probing the absorption changes. The actual detection was done by a CCD Camera (EEV 30, Princeton Instruments) mounted at the exit of 30 cm spectrograph (SP300i, Acton Research) which was used both for probe and reference light detection.

The samples were prepared to have an optical density of 0.8–1.0 at the excitation wavelength. All measurements have been carried out in a flow cell of 1 mm optical path length at 50 ml/min, to ensure refreshing of the solution at each laser shot, and under N<sub>2</sub> gas atmosphere. In air-equilibrated conditions a photo-oxidation product was efficiently formed by either BP6 and MeOPP. The formation of the photoproduct was spectrophotometrically detected and it shows up as a sharp absorption band at 450 nm. In order to reduce the photodegradation of the samples, all the measurements have been carried out under N<sub>2</sub> gas atmosphere. Under these conditions the side reaction was practically eliminated as revealed by the ground-state absorption spectra recorded before and after each set of time-resolved measurements.

Single-photon timing measurements have been carried out with the setup already described [10]. Briefly, the second harmonic of a Ti:Sapphire laser (Spectra Physics) has been used to excite the samples at 420 nm at a repetition rate of 4 MHz. Using a double-grating monochromator (Jobin Yvon, DH10 Double VT), the emitted light was collected and guided by a fiber to a microchannel plate photomultiplier (Hamamatsu R3809U-50). A channel width of 2 ps/channel has been chosen in order to

resolve the decays. In these conditions an instrumental response function, FWHM, of 60 ps has been obtained.

### 3. Results and discussion

The ground state of BP6 and MeOPP in chloroform show the same absorption spectrum (cf. Fig. 1) which is typical for a metal-free porphyrin [11]: the Soret band has its maximum at 420 nm and four Q-bands at 518, 555, 595 and 645 nm. Due to the high extinction coefficient of the Soret band, the transient absorption measurements have been carried out by exciting at 420 nm.

#### 3.1. Transient absorption spectra

The result of the polychromatic measurements for the model compound MeOPP is depicted in Fig. 2, in which a set of spectra extending from 430 to 490 nm detected at different delay times (as indicated in Fig. 2) is shown. Already 2 ps after excitation, a prompt rise of an excited-state absorption band extending from 435 to 490 nm with a maximum at 445 nm can clearly be determined. After this fast initial increase, there are no additional processes going on in the time window monitored: all other spectra detected at longer delays (20, 35 and 120 ps) are identical within the signal-to-noise level given by the detection. These findings are easily rationalized by a prompt population of an excited state which is long living. The comparison of the spectra with literature data [12,13] suggested the assignment of the signal to an S<sub>1</sub>–S<sub>n</sub> transition. The S<sub>1</sub> signal decays in a nanosecond timescale as observed by time-resolved fluorescence measurements for the free base tetraphenyl porphyrins [8] and also for a cobalt(II) tetraphenyl porphyrin [14].

The spectra recorded for BP6 under identical conditions presented a more complex time evolution as shown in Fig. 3. Also in this case, immediately after excitation a prompt rise of the excited-state absorption is found in a spectral region from 435 nm extending to 490 nm. However, at longer delays ( $\geq 10$  ps) a decay of the absorption signal is observed, which is most clearly seen at wavelengths below 470 nm.

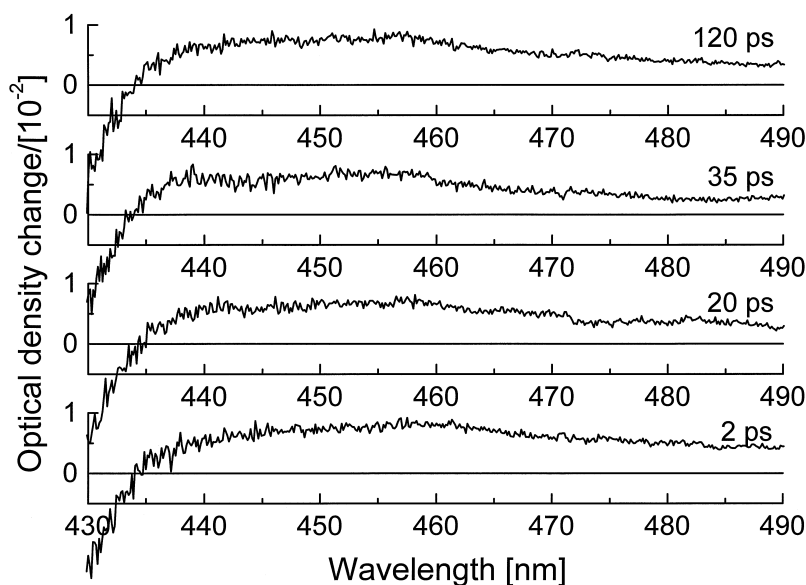


Fig. 2. Transient absorption spectra of MeOPP at delay times of 2, 20, 35 and 120 ps after excitation at 420 nm.

### 3.2. Transient absorption decays

In order to gain more precise information on the kinetics of the dynamic process of the porphyrin

derivatives, transient absorption decays were recorded on the samples by a monochromatic detection setup. The pump wavelength was retained at 420 nm, while for the probe wavelengths 436, 450 and 475

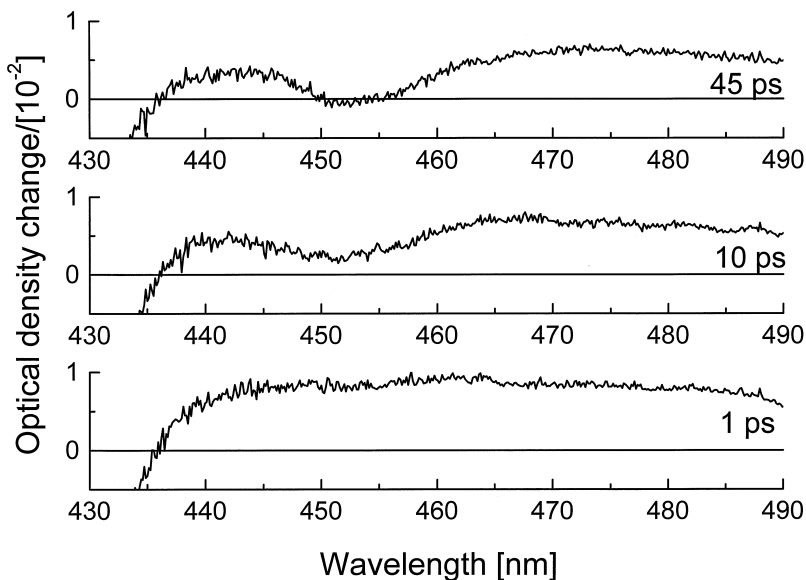


Fig. 3. Transient absorption spectra of BP6 at delay times of 1, 10 and 45 ps after excitation at 420 nm.

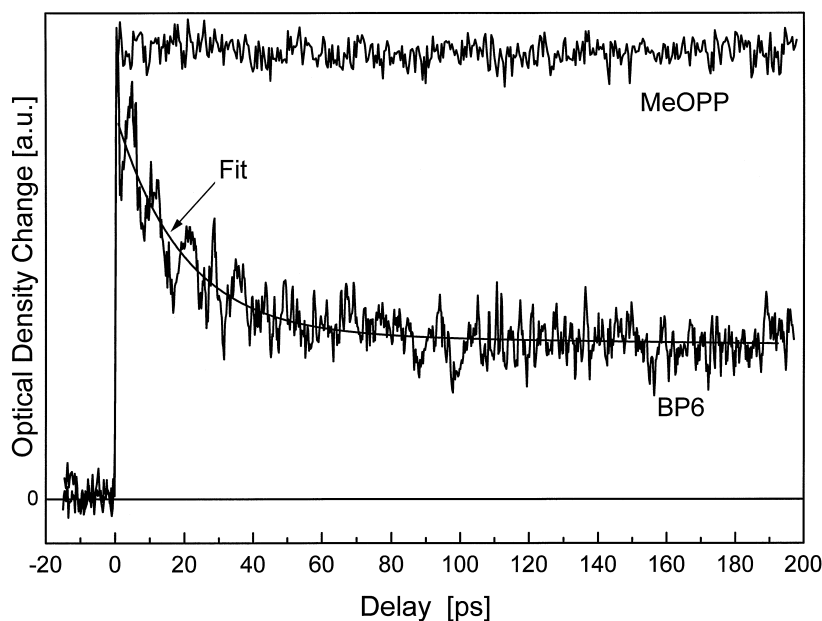


Fig. 4. Time-resolved absorption changes of MeOPP (top line) and BP6 (bottom line, incl. fit) at probe wavelength 475 nm.

nm were selected. All measurements were performed under magic-angle polarization configuration.

### 3.3. Detection at 475 nm

The traces obtained for the MeOPP model compound are shown in Fig. 4 (top line). As expected from the polychromatic measurements, a prompt increase of the transient absorption signal is observed, which remains unchanged in the measurement windows experimentally accessible (200 ps in Fig. 4, and also up to 1.5 ns, data not shown). As the transient produced upon excitation is long living compared to these experimental time windows, its decay time ( $> 5$  ns) could not be determined. These observations confirmed the assignment of the transient absorption signal to a transition starting from the  $S_1$  state which decays with a time of ca. 8.1 ns as observed by single-photon timing measurements [8].

The result of the measurement for the hexameric sample BP6 under identical experimental conditions is shown in Fig. 4 (bottom line). In contrast to the model compound, it clearly exhibits an additional fast decay after the initial rise of the transient absorp-

tion signal. The data could be satisfactorily fitted (cf. Fig. 4) using a sum of two exponentials. The results of this data analysis are summarized in Table 1. The decay time of the short-living component (1) is determined to  $20 \pm 4$  ps, while for the long component (2) the decay time cannot be determined from these measurements and was kept constant at 3.8 ns in the fits. 58% of the total amplitude relates to the fast component, while the remaining 42% result from the long-living component 2.

Table 1  
Results of the fits for both samples at three different wavelengths

Detection (nm)	Sample	Component 1		Component 2	
		$a_1$ (%)	$\tau_1$ (ps)	$a_2$ (%)	$\tau_2^a$ (ns)
$475 \pm 2$	BP6	58	20	42	3.8
	MeOPP	—	—	100	8.1
$436 \pm 2$	BP6	95	23	5	3.8
	MeOPP	—	—	100	8.1
$450 \pm 2$	BP6	59	24	41	3.8
	MeOPP	—	—	100	8.1

<sup>a</sup> Determined from SPC measurements [8].

Error in  $\tau_1 \pm 4$  ps.

### 3.4. Detection at 436 and 450 nm

Absorption decays were also recorded by probing both samples at 436 and 450 nm, while all other parameters were kept unchanged. For the model compound, the excited-state absorption decay traces at both wavelengths showed a behaviour very similar to the one observed at 475 nm (data not shown). The excited-state absorption decays of BP6 under identical conditions are shown in Fig. 5 (bottom line: 436 nm; top line: 450 nm). Also at these wavelengths, a fast decay component is observed in addition to the long-living component already attributed to the decay of the  $S_1$  state. By fitting in the same way as described above, time constants of 23 ps (436 nm) and 24 ps (450 nm) were determined, which are identical within the experimental error to the one found at 475 nm detection. All times and amplitudes resulting from the fits are summarized in Table 1. As can be seen, for 450 nm detection the relative amplitudes are almost unchanged in comparison to 475 nm, while for 436 nm the relative contribution of the long-living component to the total amplitude decrease drastically.

The presence of the fast component in BP6 and the absence in MeOPP can be attributed to the

formation of an intramolecular inter-chromophoric excited state which decays on a longer timescale in 3.8 ns.

In order to verify this assignment SPT measurements have been performed. Exciting at 420 nm and detecting at 640 nm a rising component could be observed. With the time resolution of the SPT measurements (ca. 20 ps) the rise time could not be resolved.

These findings can be rationalized by assuming an excited-state process in the hexamer, which takes place with a time constant of 20 ps resulting in the formation of a different excited state having a different electronic configuration with a red-shifted absorption band as seen in the transient spectra. This view is supported by the finding that the model compound does not exhibit a 20 ps component, which excludes an attribution to a relaxation from higher excited states ( $S_2$  to  $S_1$ ) in a single porphyrin chromophore.

Additional support of this view arises from comparison to literature data. For a linked porphyrin system, O'Keefe et al. [15] found a time constant of  $13 \pm 5$  ps, however, excited into the Q-band of their dimeric molecules. Recently, Young et al. [16] published a study on *p*-phenylen-linked porphyrin sys-

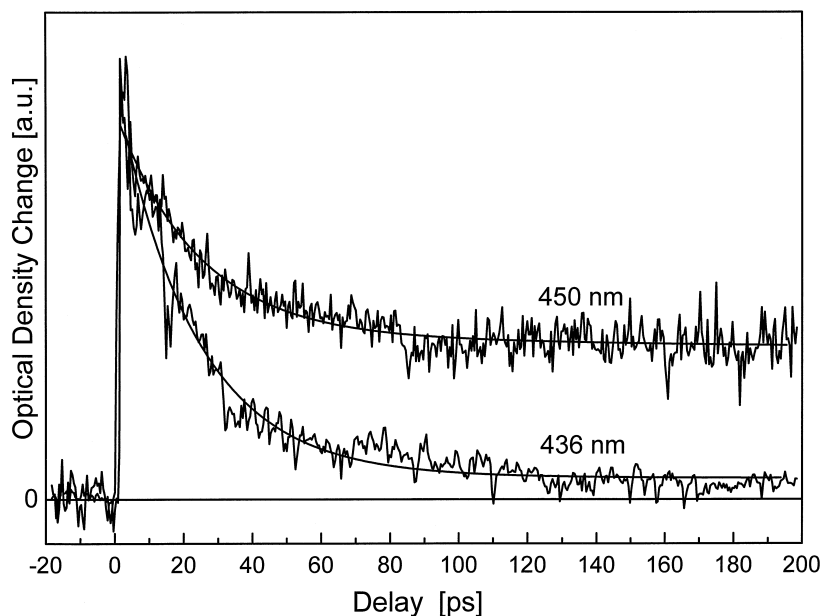


Fig. 5. Time-resolved absorption changes of BP6 at probe wavelengths of 436 nm (top line, incl. fit) and 450 nm (bottom line, incl. fit).

tems. In hetero dimers of free base and zinc porphyrins, they also find a time constant of 3.5 ps (fluorinated: 10 ps) which they attribute to an intramolecular energy transfer.

#### 4. Conclusions

A hexameric benzo-porphyrin compound and a model compound containing only one chromophore have been investigated by means of transient absorption measurements. In the former, probing at various probing wavelengths between 436 and 475 nm, a 20 ps kinetic component is clearly observed, which is not existent in the latter. This component is attributed to an excited-state process in the hexamer leading to a state in which the localized excitation is to a certain extent delocalized.

#### References

- [1] J. Zimmerman, J. von Gersdorff, H. Kurreck, B. Roder, J. Photochem. Photobiol. B 40 (1997) 209.
- [2] J. Deisenhofer, O. Epp, K. Miki, R. Huber, H. Michel, Nature 318 (1986) 618.
- [3] G. Feher, J.P. Allen, M.Y. Okamura, D.C. Rees, Nature 339 (1989) 111.
- [4] G. McDermott, S.M. Prince, A.A. Freer, A.M. Hawthornthwaite-Lawless, M.Z. Papiz, R.J. Cogdell, N.W. Isaacs, Nature 374 (1995) 517.
- [5] N.W. Isaacs, R.J. Cogdell, A.A. Freer, S.M. Prince, Curr. Opin. Struct. Biol. 5 (1995) 794.
- [6] E.I. Zenkevich, A.M. Shulga, S.M. Bachilo, U. Rempel, J. von Richthofen, C. von Borczyskowski, J. Luminesc. 76 (1998) 354.
- [7] R.W. Wagner, J. Seth, S.I. Yang, D. Kim, D.F. Bocian, D. Holten, J.S. Lindsey, J. Org. Chem. 63 (1998) 5042.
- [8] H.A.M. Biemans, A.E. Rowan, A. Verhoeven, P. Vanoppen, L. Latterini, J. Foekema, A.P.H.J. Shennings, E.W. Meijer, F.C. De Schryver, R.J.M. Nolte, J. Am. Chem. Soc. 120 (1998) 11054.
- [9] G. Schweitzer, L. Xu, B. Craig, F.C. De Schryver, Opt. Commun. 142 (1997) 283.
- [10] L. Latterini, G. De Belder, G. Schweitzer, M. Van der Auweraer, F.C. De Schryver, Chem. Phys. Lett. 295 (1998) 11.
- [11] M. Gouterman, The Porphyrins, in: D. Dolphin (Ed.), Physical Chemistry A, vol. 3, New York, 1978, Chap. 1.
- [12] J. Rodriguez, C. Kirmaier, D. Holten, J. Am. Chem. Soc. 111 (1989) 6500.
- [13] A.M. Brun, A. Harriman, V. Heitz, J.P. Sauvage, J. Am. Chem. Soc. 113 (1991) 8657.
- [14] H.Z. Yu, J.S. Baskin, B. Steiger, C.Z. Wan, F.C. Anson, A.H. Zewail, Chem. Phys. Lett. 293 (1998) 1.
- [15] G.E. O'Keefe, G.J. Denton, E.J. Harvey, R.T. Phillips, R.H. Friend, J. Chem. Phys. 104 (1996) 805.
- [16] S.I. Yang, R.K. Lammi, J. Seth, J.A. Riggs, T. Arai, D. Kim, D.F. Bocian, D. Holten, J.S. Lindsey, J. Phys. Chem. B 102 (1998) 9426.