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# Relaxation in excited states of porphycene in low-temperature argon and nitrogen matrices

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## Abstract

Picosecond transient spectroscopy was used to study excited state deactivation processes of porphycene embedded in solid argon and nitrogen matrices at low temperatures. Comparison of time profiles of the signals due to ground state bleaching and stimulated fluorescence reveals that the latter is delayed by about 100 ps with respect to the former when the molecule is excited into the  $S_3$  or  $S_4$  electronic states, corresponding to Soret bands. No delay between the two signals is observed for excitations into Q bands, corresponding to  $S_1$  and  $S_2$  transitions. This is evidence of slow vibrational relaxation from  $S_3$  and  $S_4$  into  $S_1$  and  $S_2$ , due to the considerable  $S_1$ – $S_3$  energy gap and similarity of the potential energy profiles in different electronic states. On the contrary, for nonrigid dibenzo-derivatives of porphycene which have an ‘intruder’ state located between the Q and Soret bands, the relaxation from excited electronic states is faster than the experimental time resolution of about 30 ps. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Intramolecular vibrational relaxation following electronic excitation in large polyatomic molecules occurs in solutions within picoseconds or even faster. However, in certain environments at low temperatures the process may be significantly slowed down [1]. It has been observed, for instance, that naphthazarin embedded in solid Ne and Ar matrices emits unrelaxed fluorescence from higher vibronic levels, of which the lifetimes can be as long as 250 ps [1–4]. Similar behaviour has been found for 9-hy-

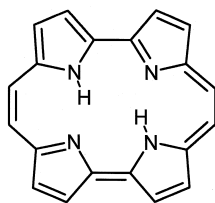
droxyphenalenone [5] and several halobenzene radical cations [6]. Vibrational relaxation process involving phenyl torsion in 3-hydroxyflavone isolated in Ar matrices at 10 K takes about 100 ps [7].

The above findings, and most of other experimental evidence of slow vibrational relaxation in large molecules, were obtained for not too high excess vibrational energies, up to  $\sim 2000\text{ cm}^{-1}$ . The behaviour for larger excess energies is less known. In this Letter, we present the results of study that enabled to probe the relaxation involving vibrational energies larger than  $10\,000\text{ cm}^{-1}$ . Transient picosecond spectra have been measured for porphycene, a constitutional isomer of porphyrin (see Scheme 1). Unusually slow vibrational relaxation from the higher electronic states is detected in solid matrices at temperatures below 20 K. A delay of the order of 100 ps is observed between excitation into the UV Soret

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Scheme 1. Porphycene.

bands and the appearance of stimulated  $S_1 \rightarrow S_0$  fluorescence. On the contrary, no such delay can be detected when the molecule is excited into  $S_1$  or into a nearby  $S_2$  electronic transition. This behaviour is explained by, on one hand, a relatively large energy gap between the  $S_1$  and  $S_3$  electronic states, about  $11\,000\text{ cm}^{-1}$ , and, on the other hand, by the lack of significant changes in the potential energy curves for different electronic states. The photophysical characteristics of porphycene are completely different from those of previously studied dibenzoporphycene derivatives, for which a fast ( $< 30\text{ ps}$ ) recovery of the ground state population after excitation into the higher energy electronic states has been observed [8]. For the latter, the energy gap between the Q and Soret transitions is bridged by introducing an additional electronic state lying in between. Another source of the differences may be the lack of conformational rigidity in dibenzoporphycenes.

## 2. Experimental details

Porphycene was synthesized and purified according to procedures described in Ref. [9]. Solid gas matrices were obtained after deposition of a stream of gas containing porphycene vapour onto a sapphire window held at 30 K in a Displex 202 cryostat. The compound, contained in a glass tube, was heated to 320 K.

Absorption spectra were recorded on a Shimadzu UV 3100 spectrophotometer. Fluorescence spectra were obtained using either an FS900 Edinburgh Instruments spectrofluorimeter or a CCD camera (Princeton Instruments) attached to an Acton SpectraPro-275 spectrograph. The excitation in the latter case was provided by the third harmonic (355 nm) of a Nd:YAG laser (Surelight I10, Continuum).

A home-built picosecond spectrometer has been described previously [10]. Briefly, pump pulses of 30 ps duration are provided by an EKSMA/EKSPLA Nd:YAG laser, working at about 1 Hz. Pulse energy is 30, 15, 2 and 7 mJ at the fundamental, second, third and fourth harmonic, respectively. The probing beam, generated by focussing the fundamental frequency pulse onto a cylindrical cell, containing a mixture of normal and heavy water, is optically delayed with respect to the excitation. Two home-built polychromators equipped with Reticon linear photodiode arrays detect the portion of the continuum used to probe the sample and the reference portion, respectively. This system has now been supplemented with an optical parametric oscillator (PG411 VIR, EKSPLA, Vilnius, Lithuania), pumped by the 4th harmonic of the Nd:YAG laser, which enables tuning of the excitation between 300–500 and 570–2300 nm; pulse energy at 600 nm is 0.4 mJ.

After prolonged irradiation with pumping laser pulses, we observed a slight deterioration of the matrix quality, accompanied by a decrease in the signal. Therefore, for experiments that required longer accumulation, different areas of the matrix were probed at different times. Care was also taken to avoid possible artifacts due to polarization of pumping and probing beams.

## 3. Results and discussion

Electronic absorption spectra of porphycene in *n*-hexane solution at room temperature and in a nitrogen matrix at 17 K are shown in Fig. 1. Previous magnetic circular dichroism [11] and matrix isolation [12] studies enabled the assignment of the four lowest electronic states. In analogy with porphyrin Q bands, two weaker transitions are observed at low energies. The Soret band of porphyrin also has a counterpart: two strong transitions are detected in the near UV region. Several differences are observed in the electronic spectra of the two compounds. The  $S_1$  and  $S_2$  transitions in porphycene have similar oscillator strengths and lie much closer to each other than in porphyrin ( $\sim 900$  [12] vs.  $\sim 3200\text{ cm}^{-1}$  [13], respectively). The relative intensities of the Q bands with respect to the Soret bands

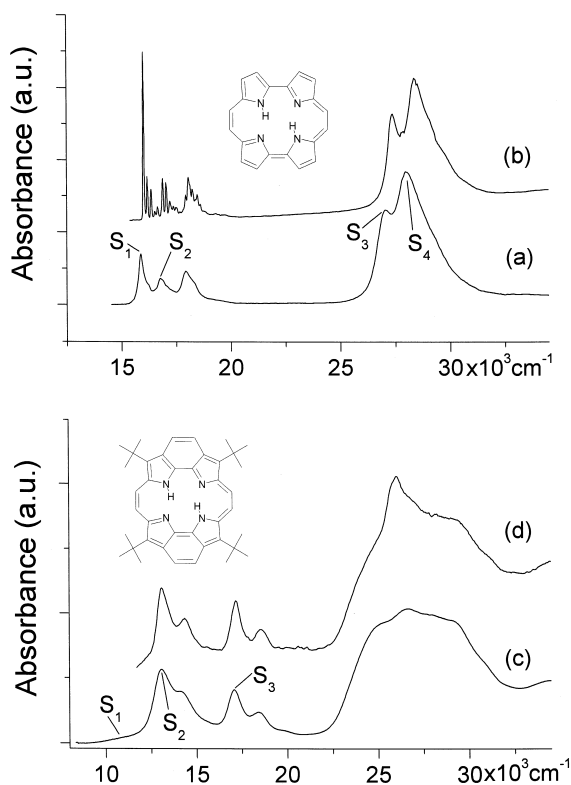


Fig. 1. Absorption spectra of porphycene (top) and 2,17,12,17-tetra-*t*-butyl-3,6,13,16-dibenzo-[cde,mno]porphycene (bottom) recorded in *n*-hexane at 293 K (a, c) and in solid nitrogen at 15 K (b, d). The positions of lowest electronic transitions are indicated, based on the assignments in Refs. [8,11,12].

are much stronger in porphycene than in porphyrin. Finally, the energy separation between Q and Soret bands is much larger in porphycene: it exceeds  $10\,000\text{ cm}^{-1}$  for both  $S_1$ – $S_3$  and  $S_2$ – $S_3$  gaps.

Fig. 2 presents a comparison between stationary absorption spectra recorded for porphycene embedded in a solid nitrogen matrix at 17 K and a transient signal observed 80 ps after excitation into the Soret band (using the third harmonic of the laser at 355 nm). The time-resolved spectrum consists mostly of absorption bleaching, as evidenced by its shape. A weak and broad transient  $S_1 \rightarrow S_n$  absorption signal is observed at wavelengths below 510 nm. Both of these signals appear instantaneously for all excitation wavelengths. Additionally, negative bands appear to the red of the (0–0) energy of the  $S_0$ – $S_1$  transition. For these bands, however, the risetime is crucially

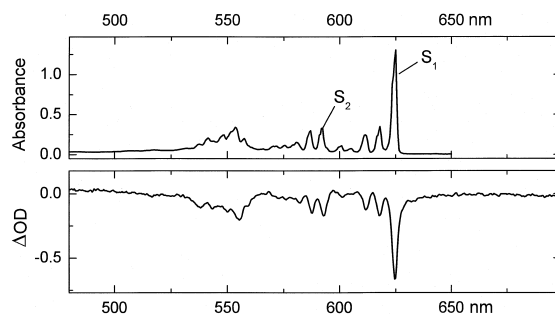


Fig. 2. Top, stationary absorption of porphycene in an  $N_2$  matrix at 15 K. Bottom, transient absorption and bleaching observed 80 ps after excitation at 355 nm.

dependent on the excitation wavelength. For excitation into the Soret transitions (Figs. 2 and 3b) these components are delayed with respect to the bleaching by about 100 ps. On the contrary, if porphycene is excited into  $S_1$  or  $S_2$  states, no delay is observed

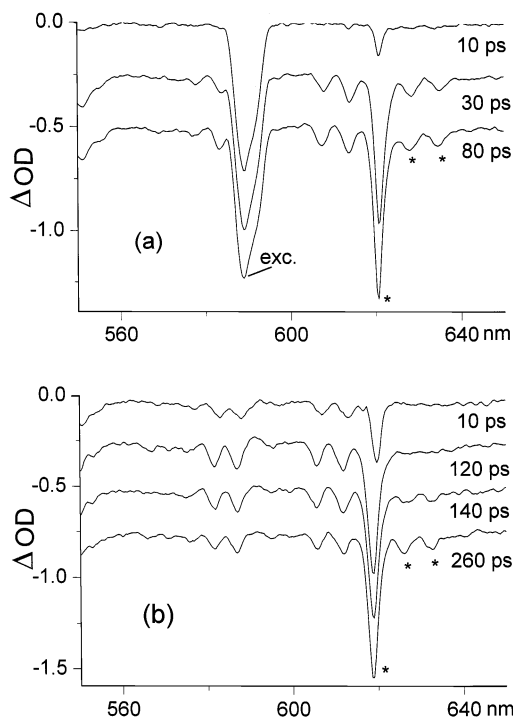


Fig. 3. Comparison of transient spectra obtained for excitation into different electronic states: (a) excitation at 591 nm; and (b) excitation at 355 nm. Delay times from the moment of excitation are indicated for each curve. An artifact due to scattering of the pumping beam is marked by 'exc.'.

(Fig. 3a), which, taking into account the time resolution of our instrument, implies that the time separation between the two signals must be smaller than 30 ps.

The signal that is delayed for higher-energy excitation but appears simultaneously with bleaching for excitation into Q bands corresponds to stimulated  $S_1 \rightarrow S_0$  fluorescence, generated by the probing pulse of our spectrometer. This can be clearly seen by the inspection of Fig. 4, where the stationary fluorescence spectrum is compared with the difference between the transient signals obtained at 260 ps and at 80 ps delays, using the excitation into Soret bands. Such subtraction leads to practically complete cancelling of signals due to ground state bleaching and  $S_1 \rightarrow S_n$  transient absorption, because the difference in delay times of the two transient signals is much shorter than the  $S_1$  lifetime, about 15 ns. This procedure also reveals a strong 0–0 fluorescence signal,

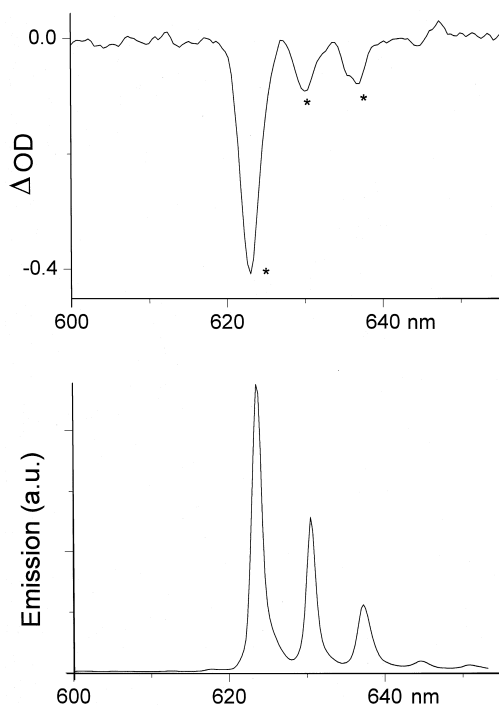


Fig. 4. Bottom: high-energy portion of stationary fluorescence of porphycene in an  $N_2$  matrix at 15 K excited at 355 nm. Top: the results of subtracting the transient spectrum observed at 80 ps delay from the signal recorded at 260 ps delay. The asterisks mark the same spectral positions as in Fig. 3.

which otherwise would have been difficult to detect, since it coincides with the 0–0 band of  $S_0 \rightarrow S_1$  absorption, and thus overlaps with the strongest bleaching feature (cf. Figs. 2 and 3).

Closer examination of the time evolution of the stimulated fluorescence signal monitored for higher energy excitations reveals not only changes in intensity, but also in spectral shape. At shorter delay times, up to about 120 ps, this emission is broad and weak, and may be observed as a structureless shoulder on the low-energy side of the 0–0 band of the  $S_0 \rightarrow S_1$  transition (cf. Fig. 2 for the signal obtained at 80 ps delay). At longer delays, the two most prominent vibronic bands of the fluorescence become visible. Their intensity increases for about 60 ps and then remains constant during the time window available in our instrument (up to 3 ns). The spectral evolution of the emission, difficult to analyse quantitatively by the transient absorption technique, was also observed by monitoring time-resolved fluorescence with picosecond resolution. These results will be described separately [14]. Upon exciting into  $S_1$  or  $S_2$  levels, the stimulated fluorescence appears simultaneously with the bleaching signal (Fig. 3a). No evidence of the broad emission at small delay times is found. The emission is structured from the earliest moments of observation.

Qualitatively the same results as in solid nitrogen were obtained in argon matrices. Thus, the relaxation into the lowest excited singlet state of porphycene is fast, shorter than 30 ps, if the process starts from the neighbouring  $S_2$  state, but becomes unusually long ( $> 100$  ps) when the molecule is initially excited into higher energy third or fourth transitions. These findings are completely different than those we recently obtained for two dibenzoporphycene derivatives [8]. For the latter molecules, all the excited state relaxation processes are very rapid, both in room temperature solutions and low temperature solid matrices. The recovery of the ground state population depletion is very fast, comparable to the 30 ps time resolution of our spectrometer, even when the chromophore is excited (at 355 nm) into a higher excited state (cf. Fig. 1, which shows the absorption spectrum of 2,17,12,17-tetra-*t*-butyl-3,6,13,16-dibenzo-[cde,mno]porphycene). The difference in relaxation behaviour observed for the two chromophores in the same matrices suggests that the

properties of the environment are not the main factor responsible for the slow relaxation in porphycene. The origin must be of intramolecular nature. Several cases may be envisaged: (i) slow internal conversion (IC) from  $S_3/S_4$  into  $S_1/S_2$ , followed by rapid intramolecular vibrational relaxation (IVR); (ii) fast IC from  $S_3/S_4$  into  $S_1/S_2$ , followed by slow IVR; and (iii) a combination of (i) and (ii).

Our results show that the bottleneck for reaching the lowest excited singlet state in porphycene is most probably created by slow vibrational relaxation. If the IC processes were slow, one would expect to observe fluorescence in the Soret region. Assuming a lifetime of 100 ps for the  $S_3$  and the same radiative constant as for the lowest excited singlet state ( $k_r = \phi/\tau$ , where  $\phi$  and  $\tau$  are fluorescence quantum yield and lifetime) leads to the value of 0.004 for the expected of  $S_3 \rightarrow S_0$  fluorescence quantum yield. The actual value might even be 2–3 times larger, judging by the intensity ratio of the oscillator strengths for the  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_3$  transitions (Fig. 1). Fluorescence of such intensity should be readily detectable by our set-up based on a CCD camera. However, attempts to measure  $S_3 \rightarrow S_0$  fluorescence in  $N_2$  matrices were unsuccessful. We are thus left with the explanation that the slow process starts after the IC from  $S_4/S_3$  and is thus due to vibrational relaxation. Such conclusion is also in conformity with the observation that a structureless  $S_1 \rightarrow S_0$  fluorescence is detected at small delay times after excitation into the higher energy region. This emission needs about 100 ps to evolve into a structured spectrum.

The origin of the low rate of vibrational relaxation may be related to large energy gaps between  $S_1/S_2$  and  $S_3/S_4$  states (Figs. 1 and 5). The  $S_1$ – $S_3$  separation is about  $11\,000\text{ cm}^{-1}$ , and the  $S_2$ – $S_3$  energy distance is smaller by only  $900\text{ cm}^{-1}$ . These values are comparable to  $14\,000\text{ cm}^{-1}$ , the value of the  $S_1$ – $S_2$  energy gap in azulene, a molecule famous for its slow  $S_2 \rightarrow S_1$  relaxation [15]. It is to be expected that a presence of an additional electronic state between the Q and Soret regions would lead to the increase of the relaxation rate. Such is indeed the case for dibenzoporphycenes, where an ‘intruder’ state has been located halfway between the Q and Soret bands (see Fig. 1). For these molecules, the relaxation has been shown to occur very rapidly [8].

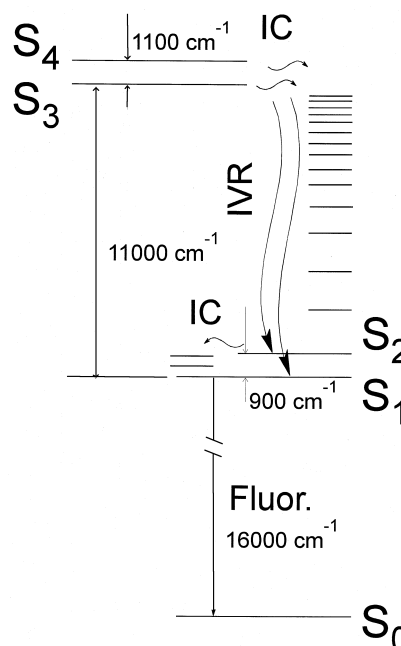


Fig. 5. Scheme of excited state energies and relaxation processes in PC. IC, internal conversion; IVR, intramolecular vibrational relaxation; Fluor., fluorescence.

However, the case of dibenzoporphycenes also shows that the explanation of slow relaxation entirely in terms of energy gaps is not sufficient. The  $S_1 \rightarrow S_0$  relaxation process in these compounds is also exceptionally fast, even though the energy spacing is  $11\,000\text{ cm}^{-1}$ , very similar to the  $S_1$ – $S_3$  energy separation in porphycene. The explanation for the fast relaxation in dibenzoporphycenes is based on the non-rigidity of the molecular skeleton, which also implies different shapes of the potential energy curves in different electronic states. These characteristics conform to the model of ‘strong coupling’ between electronic states in the theory of radiationless transitions [16]. In porphycene, the situation is very different and close to the ‘weak coupling’ limit. The molecule is known to be planar in the ground state. No evidence for large geometry distortion in the excited states is found: the spectra obtained by matrix isolation technique are dominated by strong (0–0) transitions for both  $S_1$  and  $S_2$  [12].

Finally, each of the two dibenzoporphycenes that we studied had four alkyl substituents (methyl or *t*-butyl) on the macrocyclic skeleton. It has been

observed earlier that alkyl substitution can lead to a significant increase of vibrational relaxation in the  $S_1$  state. In neon and argon matrices, vibrationally unrelaxed fluorescence was observed for 9-hydroxyphenalenone, but not for its 5-methyl derivative [5].

In conclusion, the unusually slow relaxation from higher excited electronic states of porphycene in low-temperature argon and nitrogen matrices is explained by the combination of at least two factors: (i) large energy gaps between the Q and Soret transitions; and (ii) lack of substantial changes in the shape of potential energy in different electronic states. In order to separate the role of both contributions, it would be instructive to study a porphycene derivative that would retain only one of the above features. 9,10,19,20-tetra-*n*-propylporphycene seems to be a good candidate in this respect, revealing, on the one hand, large separation between  $S_1$  and  $S_3$  states, and, on the other, rapid radiationless depopulation from  $S_1$ , of which the rate is strongly viscosity-dependent [17]. Finally, we are planning comparison of the low-temperature matrix data with the results obtained in solutions. Recent studies of Zn-tetraphenylporphyrin have shown that, in room temperature ethanol solution, the vibrational relaxation in  $S_1$ , probed after  $S_0 \rightarrow S_2$  excitation, occurs with lifetimes much shorter than 2.35 ps [18].

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