Fluorescence studies of porphycene in various cryogenic environments

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Low temperature fluorescence of porphycene, a structural isomer of porphyrin, has been studied using polymer samples, matrix isolation, and fluorescence line narrowing (FLN) techniques. Contrary to the case of the chromophore embedded in a nitrogen matrix, the emission from polymer samples at temperatures above 10 K exhibits strong dependence on the wavelength of excitation: increasing the excitation energy leads to gradual broadening and, finally, loss of vibrational structure. A rather unusual observation is the similarity of the structured fluorescence spectra obtained for excitations into S_1 and S_2 states. This finding indicates a correlation between the site distributions in S_1 and S_2. A similar idea has been put forward earlier for tetraphenylporphyrin (I. Lee, G.J. Small, and J.M. Hayes, *J. Phys. Chem.* **94**, 3376 (1990)). We propose that the correlation is due to isotropic polarizability in the molecular plane; calculations confirm such hypothesis. For porphycene, an additional factor that can contribute to the effect is a rapid trans-trans tautomerization that leads to the rotation of x and y axes in-plane of the molecule. FLN spectra reveal significant band broadening for excitation into S_2. This suggests that the site correlation is not of 1:1 type or that at 4.2 K the site exchange dynamics is frozen in comparison with the situation at higher temperatures.

Keywords: fluorescence, porphycene, matrix isolation.

Introduction

Cryogenic techniques coupled with laser excitation provide a range of site selective methods, powerful tools for registration of electronic spectra with high spectral resolution, which enables obtaining, e.g., detailed information about the vibrational structure in the ground and excited states [1–12]. This is especially useful when the electronic absorption of the investigated system is unstructured due to inhomogeneous broadening, as is normally the case for molecules embedded in polymer films or glassy matrices. Spectrally narrow excitation allows obtaining highly resolved emission via selecting specific part of the population. This technique, however, usually works only for excitation into S_1, the lowest excited, emitting singlet state [10]. The correlation between narrow line excitation and structured emission is lost for $S_n \leftarrow S_0$ excitation with $n > 1$, indicating lack of correlation between excited and emitting populations.

However, exceptions to this rule exist. Photochemical hole burning experiments for tetraphenylporphyrin in a polystyrene matrix indicated that the site energy distribution functions are correlated for the two lowest electronic states, $Q_x(S_1)$ and $Q_y(S_2)$ [13]. This result was remarkable, especially in view of orthogonal polarizations of Q_x and Q_y transitions.

In this work, we present another example of a molecule in which such correlation is preserved for excitation into the excited state other than the emitting one. The chromophore is porphycene, a constitutional isomer of porphyrin (Fig. 1). Contrary to porphyrins, for which a variety of line-narrowing experiments have been performed [13–20], the corresponding data for porphycenes in condensed phase are scarce. Fluorescence spectrum of parent porphycene in a glassy tetrahydrofuran-toluene matrix at 4.2 K has been published, along with absorption and emission (of much lower spectral resolution) recorded for nitrogen and rare gas matrices [21]. Emission and fluorescence has also been obtained for porphycene embedded in superfluid helium droplets [22]. This rather limited pieces of data contrast with significant work carried out for porphycenes isolated in supersonic jets [23].
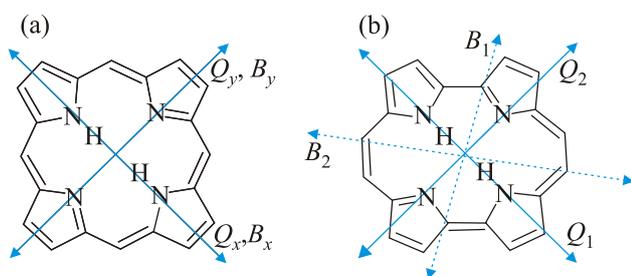
Fig. 1. Porphyrin (a); porphycene (b). The arrows show the transition moment directions for the *Q* and Soret (*B*) bands.

The characteristic spectral pattern for the two isomers is the presence of two electronic transitions in the low energy region (500–650 nm), usually referred to as *Q* bands, followed by stronger transitions — the so-called Soret bands — located at around 420 nm in porphyrins and at ca. 360 nm in porphycenes. A high — D_{2h} — symmetry of free base porphyrin imposes that these transitions can be polarized only along two orthogonal symmetry axes. This is not the case for porphycene, which has C_{2h} symmetry. Still, it has been demonstrated [24] that the polarizations of Q_x and Q_y transitions are nearly orthogonal and strongly resemble the pattern observed for porphyrin (Fig. 1). Another similarity is the possibility of intramolecular double hydrogen transfer between two chemically identical trans tautomers. This reaction, however, occurs according to very different mechanisms because of very strong intramolecular hydrogen bonds in porphycene and weak ones in porphyrin [23,25].

Our paper is divided into two parts. First, we report the low temperature fluorescence spectra obtained for porphycene in polymer films, obtained for "normal", xenon lamp excitation with moderate spectral resolution. In the second part, we discuss the emission and excitation spectra obtained in the regime of fluorescence line narrowing.

Experimental

Samples of porphycene in poly(methyl methacrylate) (PMMA) and poly(vinyl butyral) (PVB) have been obtained by co-solving the chromophore and polymer in toluene and tetrahydrofuran, respectively. Then, the solvent was allowed to slowly evaporate, leaving a good optical quality film of about 150 μm thickness.

Absorption spectra have been recorded using Shimadzu UV3100 spectrometer. Fluorescence was measured using Edinburgh Analytical Instruments FS900CDT spectrofluorometer. The excitation slits were 0.15–0.20 mm, corresponding to about 7–10 cm^{-1}.

Nitrogen matrices were prepared using Displex 202 closed-cycle helium cryostat. The sample was sublimed into the carrier gas by heating to about 420 K. Mixture of porphycene and nitrogen (Aldrich, 4.5) was deposited on a cold sapphire window of the cryostat at 30 K. The same cryostat has been used for low-temperature experiments with polymer films.

For fluorescence line narrowing (FLN) experiments, porphycene was embedded in 2-methyltetrahydrofuran as a host glassy matrix. The measurements were performed on samples immersed into liquid helium (4.2 K) in an optical cryostat.

Highly resolved fluorescence spectra were detected by the FLN method upon site selective laser excitation of porphycene in solid solutions at 4.2 K. The FLN technique is based on selective laser excitation within the absorption band of the 0–0 electronic transition of organic compounds, embedded in isotropic solid matrices at liquid helium temperature. Under such conditions, the inhomogeneous spectral broadening is removed and the fluorescence spectra transform from wide broad bands into a set of narrow zero-phonon lines (ZPL) [26]. The difference in frequency between the excitation laser and the ZPL line is equal to the frequency of the corresponding vibration in the ground state. For molecules with relatively high symmetry, the same set of modes is manifested in the FLN spectra as in the resonance Raman spectra.

The FLN spectra were recorded using a highly sensitive home-built experimental setup, based on a double monochromator of DFS-24 spectrometer [27]. A pulsed dye laser (DL-compact A, product of AS ESTLA, wavelength range of 400–800 nm, pulse width of ∼ 5 ns, line width of less than 0.02 nm) was used for fluorescence excitation. The position of the excitation line has been measured by high-resolution wide-range wavelength meter (SHR, product of SOLAR LASER SYSTEM, spectral range of 190–1100 nm, absolute accuracy ± 3 pm). The dye laser was pumped by the third harmonic of a Nd-YAG laser (LQ629, product of SOLAR LASER SYSTEM, 355 nm wavelength, pulse width of ∼ 10 ns, energy per pulse of about 50 mJ, repetition rate 100 Hz). The luminescence signals were detected with a photomultiplier tube (Hamamatsu, R-928) and a double channel SR200 Series Boxcar Averager System (Stanford Research Systems) coupled to a PC.

The molecular polarizabilities were calculated for ground state geometries optimized using density functional theory (DFT) model with the B3LYP functional and cc-pVTZ basis set. Gaussian 09 (Rev. E.05) software [28] was used.

Results and discussion

3.1. Low resolution spectra in polymers and nitrogen matrices

We started the experiments by recording the emission using the xenon lamp and the monochromator, which yielded the excitation bandwidth of the order of about 10 cm^{-1}. Figure 2 shows absorption and fluorescence spectra of porphycene embedded in PMMA at 10 K. The spectra recorded for PVB samples at 20 K are presented in Fig. 3. The absorption resembles that of room temperature solution. Fluorescence, however, reveals a structure for low energy
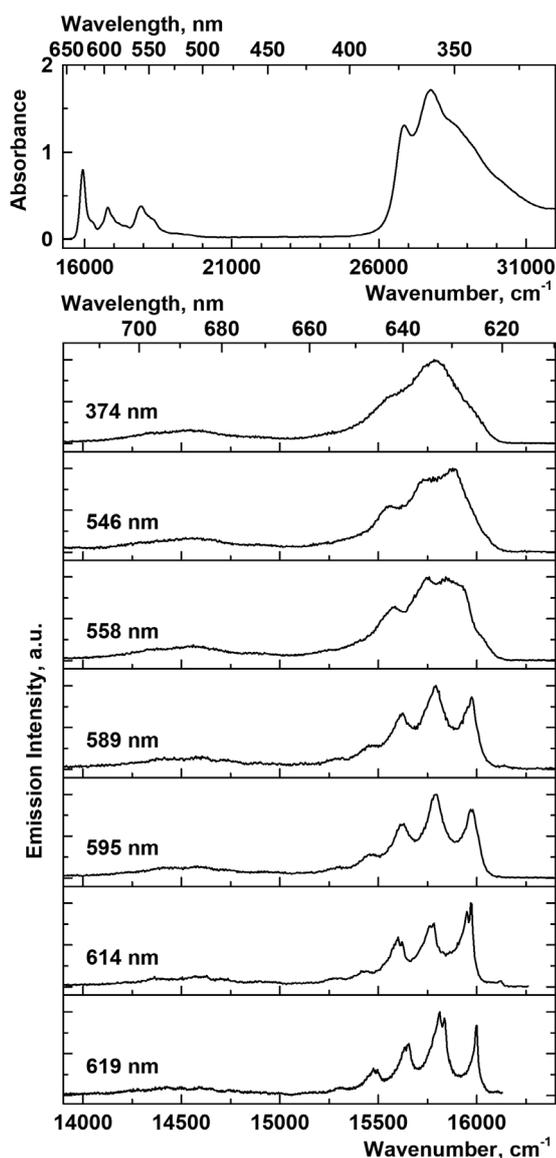
Fig. 2. Absorption and fluorescence spectra of porphycene in PMMA film at 10 K. For fluorescence, the wavelengths of excitation are indicated.
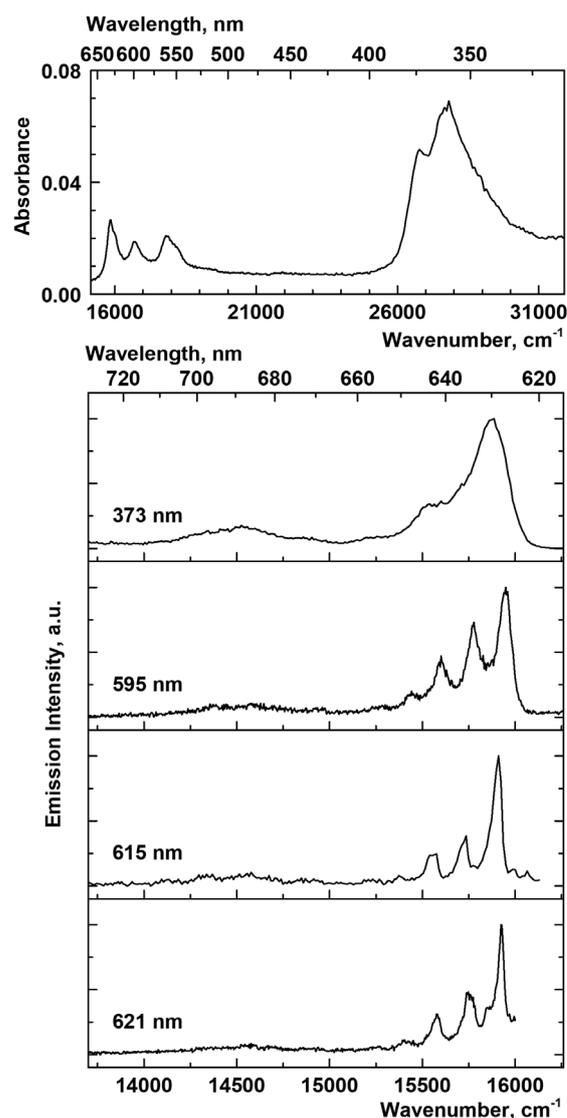

Fig. 3. Room temperature absorption spectrum and low-temperature (20 K) fluorescence spectra of porphycene in PVB film. For fluorescence, the wavelengths of excitation are indicated.

excitation, quite similar to that of the emission obtained from a nitrogen matrix (Fig. 4). The main difference between the two matrices is that for the chromophore embedded in solid nitrogen the emission is practically unchanged for various excitation wavelengths, while in the case of PMMA and PVB samples fluorescence becomes structureless for higher energy excitation. While exciting in the low energy range, the origin of the fluorescence of porphycene in polymers follows the excitation wavelength, which indicates that even using a low-resolution bandwidth it is possible to selectively excite subpopulations in the inhomogeneously broadened molecular ensemble.

The difference between excitations to Q_1 and Soret bands could have been expected, but the pattern observed for excitation at 595 and 589 nm, i.e., close to the origin of Q_2 [21] (Table 1) is rather unusual: fluorescence looks very much the same as for $S_1 \leftarrow S_0$ excitation (slight differ-

ences in the relative intensities of two highest energy peaks are due to reabsorption). The main vibronic features may still be distinguished for shorter excitation wavelengths, 558 and 546 nm, which certainly correspond to contributions from Q_2.

These results indicate that the site specificity is not lost upon Q_2 excitation and that a correlation exists between the site distributions in S_1 and S_2. In this respect, porphycene resembles tetraphenylporphyrin as an "unusual" chromophore. For the latter, it has been argued that the origin of $S_1–S_2$ correlation can be explained by isotropic interactions with the environment in the molecular plane [13]. Apparently, porphycene behaves in a similar way. We recall that both molecules exhibit similar solvent shifts in the Q_1 absorption measured in solutions at room temperature (blue shift with increasing solvent polarity). Since the dipole moment is zero in both cases, similar shifts indicate similar polarizabilities.
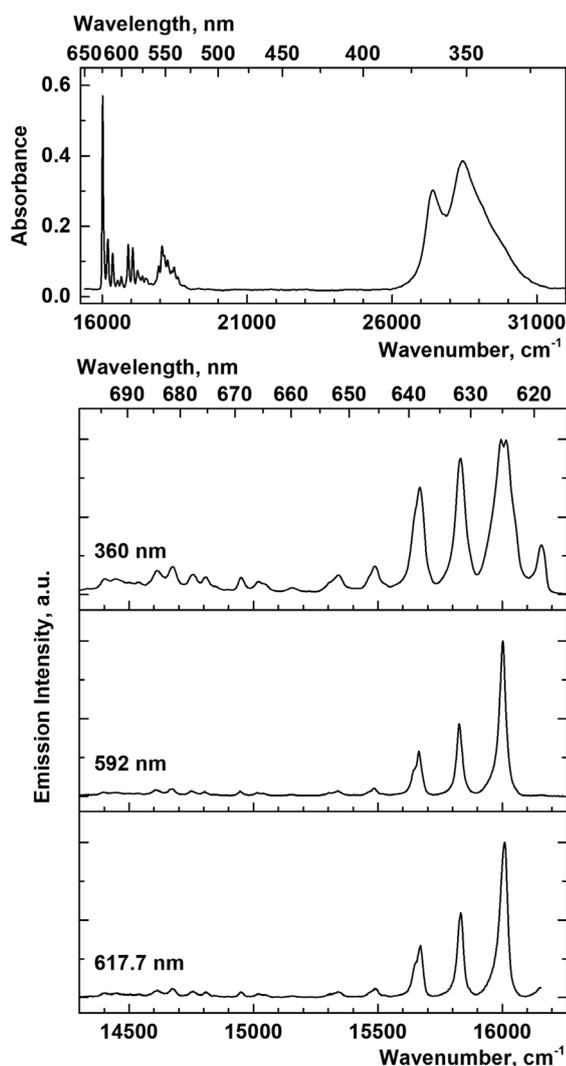
Fig. 4. Absorption and fluorescence spectra of porphycene in the nitrogen matrix at 30 K. For fluorescence, the wavelengths of excitation are indicated. Slits of 0.3 mm (~ 15 cm^{-1}) were used for recording the fluorescence spectrum excited at 360 nm.

We have calculated the polarizabilities of porphyrin and porphycene using the density functional theory. For porphyrin, the following values were obtained for the principal components of the polarizability tensor (in atomic units): $\alpha_{xx} = 465.2$, $\alpha_{yy} = 455.7$, $\alpha_{zz} = 110.1$, where the x axis coincides with the NH···HN direction and y is the other in-plane axis. The corresponding values for porphycene

Table 1. The origins of transitions to S_1 and S_2 in different environments, determined form the absorption spectra

	T, K	$S_1 \leftarrow S_0$		$S_2 \leftarrow S_0$	
		nm	cm^{-1}	nm	cm^{-1}
PMMA	10	627.5	15936	596	16779
PVB	20	631	15848	599.5	16681
Nitrogen	30	624.5	16013	592	16892
2-methyltetra-hydrofuran	4.2	630.6	15858	598.7	16703

are: $\alpha_{xx} = 486.6$, $\alpha_{yy} = 448.0$, $\alpha_{zz} = 109.2$. These results confirm that the in-plane polarizability is close to being isotropic in both molecules, with porphycene exhibiting slightly less isotropic behavior.

Another effect that can effectively symmetrize the polarizability tensor in the molecular plane of porphycene is the trans-trans tautomerization, a process that rotates the x and y in-plane axes. Kinetic pump-probe experiments demonstrated that this reaction can occur, via tunneling, in glasses even at low temperatures, in a subnanosecond time scale [29]. On the other hand, single molecule studies indicate that in a polymer matrix the reaction rate can be slowed down by orders of magnitude, so that the time scale of the process is controlled by polymer motions [30–32].

Gradual loss of vibronic structure upon higher energy excitation (cf. the spectra recorded for excitation at 558 and 546 nm, Fig. 1) is, most probably, a consequence of population transfer between various sites, activated by vibrational excitation.

The spectra described above have been obtained in the regime far from high spectral resolution. Therefore, in the next step, we applied the fluorescence line narrowing technique in order to check the hypothesis of S_1–S_2 site correlation.

3.2. Fluorescence line narrowing in glassy samples. Dependence of fluorescence spectra on the excitation wavelength

The methods of low-temperature site-selection spectroscopy such as fluorescence line narrowing and spectral hole burning (SHB) [33] open additional possibilities for the study of structural properties and photophysical processes of organic compounds.

The optical absorption and fluorescence spectra of free base porphycene in solid solution (2-methyltetrahydrofuran) at 4.2 K upon non-selective excitation in the spectral region near 355 nm are characterized by the so-called inhomogeneous broadening in the spectrum (see Fig. 5). The spectrum consists of wide bands with the spectral bandwidth of ~ 150 cm^{-1}, caused by the interaction of the chromophore with the matrix.

Inhomogeneous broadening in the fluorescence spectra is removed upon narrow band laser excitation in the range of the $S_1 \leftarrow S_0$ absorption spectrum at liquid helium temperature. As a result, the fluorescence spectrum is transformed from wide bands into the set of narrow zero-phonon lines (ZPL). Well-resolved fluorescence spectrum of porphycene upon excitation into the $S_1 \leftarrow S_0$ absorption band consists of ZPL with half-width lines of about 10 cm^{-1}, as presented in Fig. 5.

When shifting the excitation to the region of vibronic sublevels of the S_1-state (for example, $\lambda_{exc} = 605.07$ nm), a so-called multiplet is observed within the region of pure $S_1 \rightarrow S_0$ electronic band of the fluorescence spectrum (Fig. 6). The differences between the positions of multiplet components and the position of the line of excitation in the
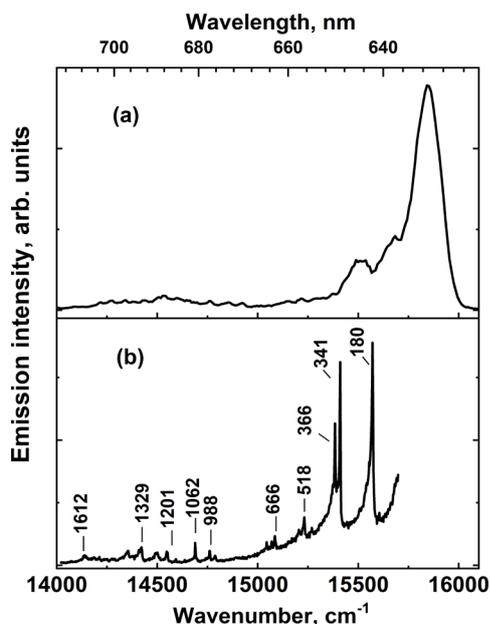
Fig. 5. Fluorescence spectra of porphycene in 2-methyltetra-hydrofuran at 4.2 K upon non-selective broad-band excitation at 355 nm (a) and laser selective excitation at 634.9 nm (b).

energy scale determine the frequencies of vibrational modes in the S_1-state [34,35]. The half-width of lines in the multiplet is about 10–15 cm^{-1}. Manifestation of multiplet lines corresponds to the case when various sublevels of different sites are excited and emitting simultaneously [35].
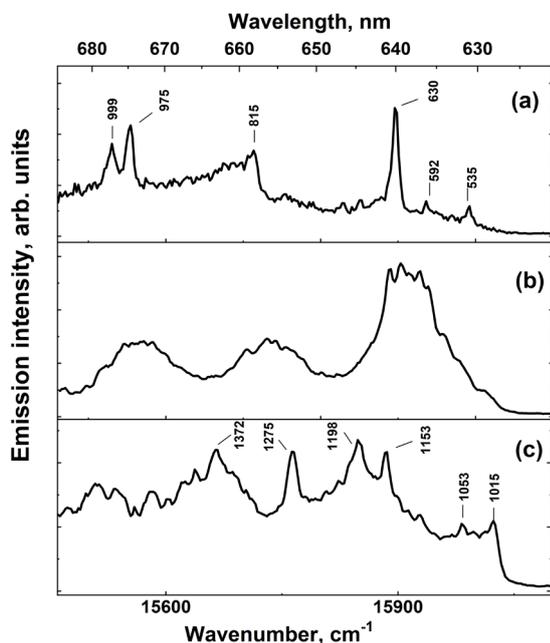

Fig. 6. Fluorescence spectra of porphycene in 2-methyltetra-hydrofuran at 4.2 K in the spectral region of the origin of S_0–S_1 electronic transition with laser selective excitation; λ_{exc} = 605.07 nm (a), 597.07 nm (b), and 586.9 nm (c). The numbers correspond to the difference between the excitation energy and the position of a fluorescence band.

The spectra shown in Fig. 6 may contain contributions from both S_0 and S_1 states. For instance, the energy differences between the peaks labelled 815, 975 and 999 cm^{-1} and the feature at 630 cm^{-1} (Fig. 6(a)) are 185, 345, and 369 cm^{-1}, respectively. These values correspond to $2A_g$, $3A_g$, and $4A_g$ modes of porphycene, of which the frequencies are very similar in both ground and the lowest excited singlet states [36]. Interestingly, the low energy part also exhibits a broad background, an indication of vibrational broadening upon excitation to S_2.

Upon shorter wavelength laser excitation (λ_{exc} = = 597.07 nm), the FLN structure disappears (Fig. 6) and the fluorescence spectrum consists of broad bands. In this case the fluorescence spectrum is analogous to that measured upon broadband excitation in the region at 405 nm. Further shift of the laser excitation line to higher energy (λ_{exc} = 586.9 nm) leads again to the FLN effect.

The effect of FLN disappearance upon excitation at 597 nm may be interpreted as manifestation of the disappearance of selectivity upon excitation in the spectral region of the $S_2 \leftarrow S_0$ electronic transition. This interpretation is based on the results of studies [35,37] which demonstrated that the interaction of molecules with the matrix at 4.2 K manifests itself in the difference of the energy gap ΔE (S_1–S_2) for each site. As a result, after nonradiative $S_2 \rightarrow S_1$ internal conversion, the site-selectivity of excitation is lost and it is no longer observed in the emission from the S_1: the spectra become substantially inhomogeneously broadened.

The effect of band broadening, corresponding to the excitation to the second lowest electronic state, is also manifested in the fluorescence excitation spectrum of porphycene. Figure 7 shows that, upon selectively monitoring the fluorescence signal in the spectral region of $S_1 \rightarrow S_0$ (λ_{fl} = 630.5 nm), the fluorescence excitation spectrum is the superposition of the FLN spectrum with the origin at 630.5 nm (15860 cm^{-1}) and an essentially broader spectrum with the origin about 597 nm (16750 cm^{-1}) and with a set of broad bands which correspond to vibronic levels. The spectral position of the origin of the broad spectrum coincides well with the spectral position of the $S_2 \leftarrow S_0$ electronic transition, whose position can thus be determined based on FLN data. The obtained difference between the Q_1 and Q_2 band origins amounts to 890 cm^{-1}, in excellent agreement with the previously reported value of 882 cm^{-1}, based on the spectra obtained for porphycene isolated in a nitrogen matrix [21].

An interesting difference between porphyrin and porphycene was observed in the line narrowing features: no spectral holes could be burned for the latter, contrary to the case of porphyrin, for which such effect is well established. We interpret the inability to permanently deplete some sites as manifestation of tautomerization proceeding even at helium temperatures. Numerous works demonstrated the occurrence of this reaction for porphycene at low temperatures [23].
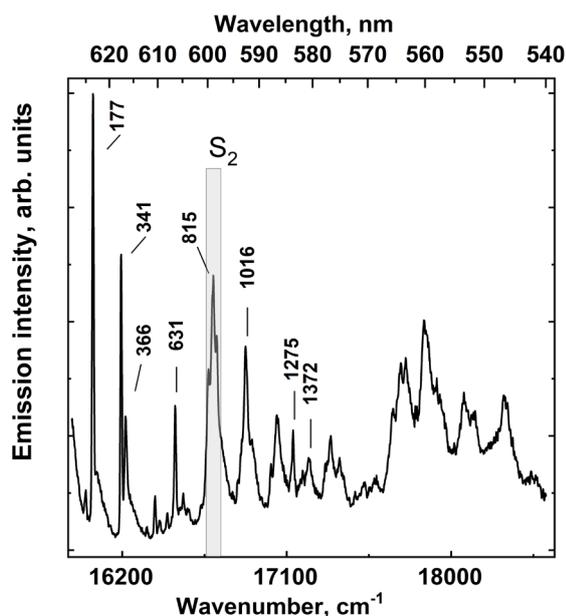
Fig. 7. Fluorescence excitation spectrum of porphycene in 2-methyltetrahydrofuran at 4.2 K obtained upon selective monitoring of fluorescence at 630.5 nm. The rectangle shows the position of the S_2 origin band, and the arrows indicate the S_1 frequencies (those of S_2 are not shown, because of larger error in their determination due to broader bands).

Summary and conclusions

The cryogenic experiments have been carried out for two somewhat different regimes: (i) spectroscopy with moderate spectral resolution for polymer samples and nitrogen matrices at temperatures not lower than 10 K; (ii) fluorescence line narrowing for glassy matrices at liquid helium temperature. The results obtained using these two setups may at first seem somewhat contradictory: based on the spectra obtained for porphycene in polymers, correlation between the sites has been postulated for the S_1 and S_2 states. On the other hand, the FLN experiments show a clear effect of the site selectivity loss while exciting to S_2.

In order to reconcile these results, we first note that the comparison of the two regimes is not straightforward, due to different spectral resolutions. The data obtained with lower resolution suggest a correlation between S_1 and S_2 sites, but they do not imply that it has to be of 1:1 type. The FLN experiments with higher spectral resolution seem to exclude a 1:1 scenario, but not a possibility that a particular S_1 site is correlated to a certain subset of sites in S_2. Such situation can explain the observation that even though line broadening occurs for S_2 excitation, the fluorescence excitation spectrum is still much more structured than the absorption (cf. Fig. 2 and 7).

Second, one cannot exclude that the sites can interconvert at temperatures exceeding 10 K, but not at 4.2 K. In order to assess the role of temperature and environment in the site structure, further experiments are required, carried out in parallel for different matrices in the temperature range as high as possible.

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Дослідження флуоресценції порфіцену в різних кріогенних матрицях

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Низькотемпературна флуоресценція порфіцену, структурного ізомеру порфірину, була вивчена з використанням полімерних зразків, матричної ізоляції та техніки звуження ліній флуоресценції (ЗЛФ). На відміну від хромофору, вбудованого в азотну матрицю, випромінювання полімерних зразків при температурах вище 10 К сильно залежить від довжини хвилі збудження: збільшення енергії збудження призводить до пос-
тупового розширення та, в кінцевому підсумку, до втрати коливальної структури. Досить незвичним спостереженням є подібність структурованих спектрів флуоресценції, отриманих при збудженні в S_1 і S_2 стани. Це вказує на кореляцію між розподілами позицій в S_1 і S_2. Аналогічну ідею було висунуто раніше для тетрафенілпорфірину (I. Lee, G.J. Small, J.M. Hayes, *J. Phys. Chem.* **94**, 3376 (1990)). Ми припускаємо, що кореляція обумовлена ізотропною здатністю до поляризації в площині молекули; розрахунки підтверджують таку гіпотезу. Для порфіцену додатковим фактором, який може сприяти ефекту, є швидка транс-транс таутомеризація, яка призводить до зміни осей x та y у площині молекули. Спектри ЗЛФ показують значне розширення смуги при збудженні в S_2. Це говорить про те, що кореляція позицій не відноситься до типу 1:1, або що при 4,2 К динаміка обміну позиціями заморожена в порівнянні з ситуацією при більш високих температурах.

Ключові слова: флуоресценція, порфіцен, матрична ізоляція.

Исследования флуоресценции порфицена в различных криогенных матрицах

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Низкотемпературная флуоресценция порфицена, структурного изомера порфирина, была изучена с использованием полимерных образцов, матричной изоляции и техники сужения линии флуоресценции (СЛФ). В отличие от хромофора, встроенного в азотную матрицу, излучение полимерных образцов при температурах выше 10 К сильно зависит от длины волны возбуждения: увеличение энергии возбуждения приводит к постепенному уширению и, в конечном итоге, к потере колебательной структуры. Довольно необычным наблюдением является сходство структурированных спектров флуоресценции, полученных при возбуждении в S_1 и S_2 состояния. Это указывает на корреляцию между распределениями позиций в S_1 и S_2. Аналогичная идея была выдвинута ранее для тетрафенилпорфирина (I. Lee, G.J. Small, J.M. Hayes, *J. Phys. Chem.* **94**, 3376 (1990)). Мы предполагаем, что корреляция обусловлена изотропной поляризуемостью в плоскости молекулы; расчеты подтверждают такую гипотезу. Для порфицена дополнительным фактором, который может способствовать эффекту, является быстрая транс-транс таутомеризация, которая приводит к смене осей x и y в плоскости молекулы. Спектры СЛФ показывают значительное уширение полосы при возбуждении в S_2. Это говорит о том, что корреляция позиций не относится к типу 1:1, или что при 4,2 К динамика обмена позициями заморожена по сравнению с ситуацией при более высоких температурах.

Ключевые слова: флуоресценция, порфицен, матричная изоляция.