

Modification of electronic structure in supramolecular fullerene–porphyrin systems studied by fluorescence, photoacoustic and photothermal spectroscopy

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Abstract

Three fullerene–porphyrin hybrids (fullerene–porphyrin, fullerene–porphyrin dyad, two fullerenes–porphyrin dyad) in dimethylsulfoxide and chloroform were investigated. Strong interaction in the porphyrins covalently linked to the fullerene C₆₀ was studied with the electronic absorption and fluorescence examinations as well as with the steady-state photoacoustic and time-resolved optoacoustic spectroscopy (LIOAS). Analysis of LIOAS waveforms was done with Marti et al. approach and Rudzki-Small et al. deconvolution procedure. The basic spectral parameters of the fullerene–porphyrin systems were evaluated: locations of absorption/fluorescence bands, fluorescence quantum yields, thermal deactivation parameters, yields of triplet state population, thermal relaxation of triplet states of porphyrin moieties and their alteration upon the presence of covalent linkage to fullerene. Formation of an excimer with participation of the porphyrin second excited singlet state was shown. The changes in triplet state behaviour were discussed in terms of changes in fullerene–porphyrin hybrids electronic structure due to the strong interaction of porphyrin and fullerene subunits. It was also shown that LIOAS experiment can be used not only in establishing the basis spectral features of molecular triplet states, but it is an excellent tool for investigation of the changes in the electronic molecular structure in porphyrin species in the presence of fullerene covalent linkage.

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1. Introduction

The unique photophysical and photochemical properties of the fullerene C₆₀ itself and particularly, when covalently linked to some organic moieties make it a perfect system for investigations in various fields. Since the C₆₀ is able to create the strong rigid bonding with electron-donating organic molecules and to form supramolecular donor–acceptor complexes the multistep electron transfer and/or energy transfer can be followed. Fullerenes covalently linked to photoactive organic molecules such as, e.g. porphyrins and phthalocyanines can be very attractive molecular systems for investigations of

nature and kinetics of intramolecular interactions upon photoexcitation [1–3]. These materials can find many applications as energy conversion systems in artificial photosynthesis (in modeling energy/electron transfer in photosynthetic reaction centers [4–8]) or in molecular organic photovoltaics (in which light energy can be efficiently converted into electric energy [9–11]). To date fullerene–porphyrins were studied using various methods in order to characterize basic spectral properties and intramolecular interactions [1,2,4,9,12–17].

In this paper, we extend spectroscopic studies with the steady-state fluorescence, photoacoustic spectroscopy (PAS) and time-resolved spectroscopy (light-induced optoacoustic spectroscopy—LIOAS) to get insight in radiative and non-radiative thermal processes occurring in the fullerene–porphyrin systems as a result of photoexcitation. These methods give information on global photothermal processes. In particular internal conversion and intersystem crossing transitions with contributions of the singlets and triplets (PAS) and kinetics of the

Abbreviations: BCP, bromocresol purple; DMSO, dimethylsulfoxide; LIOAS, laser-induced optoacoustic spectroscopy; PAS, photoacoustic spectroscopy/signal; TD, thermal deactivation

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non-radiative processes (LIOAS) can be studied. To our knowledge thermal relaxation processes were not yet investigated for fullerene–porphyrin hybrids.

The general purpose of our investigations is to get knowledge in understanding of thermal processes in the C_{60} -porphyrin hybrids and establishing the influence of C_{60} on photothermal properties of porphyrin in fullerene–porphyrin systems due to strong interaction between two moieties. On the basis of our PAS and LIOAS examinations supported by fluorescence and our previous optical spectroscopic studies we have determined the basic spectral parameters such as population of triplet states and their thermal decays [12,15]. We also showed that PAS and LIOAS are excellent tools in determining electronic processes occurring in fullerene–porphyrin systems upon photoexcitation.

To realize our task, we have chosen three fullerene–porphyrin hybrids constituted of one porphyrin and one fullerene species, one porphyrin and two fullerene moieties and porphyrin dyad linked to two fullerenes. Porphyrin and porphyrin dyad were also examined as standard references.

2. Materials and methods

The molecular structure of the investigated fullerene–porphyrin systems **2**, **4**, **5** and the reference porphyrinic samples **1**, **3** are presented in Fig. 1. The molecules **1**–**5** were synthesized by the Zürich group following the procedure reported elsewhere [18].

The absorption, fluorescence and photothermal properties were studied in organic solvents. The samples were dissolved in chloroform and dimethylsulfoxide (DMSO) with the dye concentrations of 0.1 mM (PAS experiment) and 0.01 mM (the remaining experiments). The latter solvent was used in order to prevent the sample against aggregation [19]; the concentra-

tion of DMSO solutions was lower than enable for perceptible aggregation. In the paper [20], it was evidently shown by the concentration dependence measurements, that DMSO is able to prevent aggregation in the wide range. The absorption spectra were measured with a Specord M40 spectrophotometer in the range of 240–800 nm. The steady-state fluorescence emission and excitation spectra were recorded with a Hitachi F4500 spectrofluorimeter at different excitations and observation wavelengths, respectively. The steady-state photoacoustic spectra were obtained with a single-beam photoacoustic spectrometer PAC300 at three light modulation frequencies: 8, 15 and 30 Hz at the same phase shift, $\varphi = 100^\circ$. The black body was used to correct photoacoustic spectra for device response. The thermal deactivation parameter (TD) was estimated as the ratio of photoacoustic signal intensity to the absorbance of the sample for given wavelength.

The LIOAS experiments were performed with an apparatus described in Ref. [21]. Two methods of the data analysis were applied: Marti et al. approach [21] and Rudzki-Smal et al. deconvolution procedure [22]. Marti et al. approach gives information on a part of energy changed into heat promptly (α parameter) in the time range from 0 to 0.4 μs (resolution of the LIOAS device) and allows also to determine the quantum yield of triplet state population, Φ_T in porphyrin/porphyrin dyad according to Eq. (1) [21]:

$$\Phi_T E_T = (1 - \alpha) E_L - \Phi_F E_F, \quad (1)$$

where Φ_F and E_F are the quantum yield of fluorescence and fluorescence energy of porphyrin moieties, respectively (taken from the fluorescence experiment), E_T the energy of the first triplet state for zinc porphyrin (taken from the literature [23]) and E_L is the absorbed energy of a laser. Coumarin was used

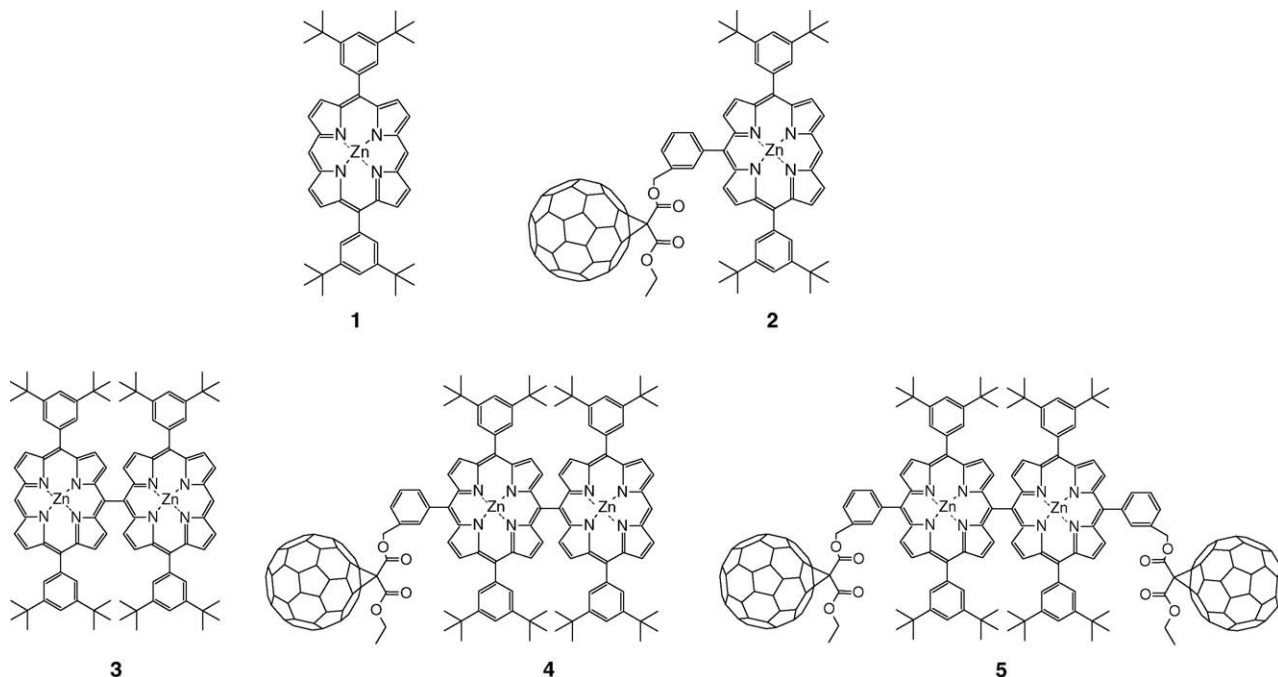


Fig. 1. The molecular structure of the investigated samples.

as a standard sample for estimation of the fluorescence quantum yield. Bromocresol purple (BCP) was taken as a reference sample under supposition that whole energy absorbed by this molecule is changed into heat in prompt processes in time shorter than $0.4 \mu\text{s}$ ($\alpha = 1$).

On the basis of the method elaborated by Rudzki-Small et al. [22] deconvolution of the sample and reference responses for the exponential components of thermal deactivation was conducted (Eq. (2)):

$$y = R(t) \times \sum K_i e^{-t/\tau_i}, \quad (2)$$

where $R(t)$ is the weight factor of deconvolution.

Such an approach lets to determine the following parameters: K_1 (a part of energy changed promptly into heat in time duration from 0 to $0.4 \mu\text{s}$); (it is equivalent to the α parameter), K_2 (a part of energy changed into heat in slow processes in time range of $0.4\text{--}5 \mu\text{s}$), τ_1 (thermal relaxation times of the excited singlet and/or excited triplet states to the ground state). The samples were illuminated at the excitation wavelength of 415 nm (and additionally at 337 nm for the sample **5**).

3. Results

3.1. Electronic absorption and fluorescence spectra

Fig. 2 shows the absorption spectra (normalized to unity) of the samples **2**, **4** and **5** in DMSO (A) and in chloroform (B).

The spectra of the porphyrin samples **1** and **3** are also shown for comparison. The spectra are dominated by the Soret band in the range from 400 to 450 nm (band locations depend on solvent and a kind of sample); this band is responsible for the ground state to second excited singlet state transition of the porphyrin moieties. The much less intensive Q bands (seen in the inserts) are positioned in the range of $500\text{--}600 \text{ nm}$ as expected for the $S_0\text{--}S_1$ transition in porphyrins [24]. In the spectrum of **2** the single Soret band is observed, whereas in the spectra of the samples **4** and **5** this band is splitted into a doublet with maxima at about 420 and 450 nm due to splitting of the second electronic level owing to the strong interaction in porphyrin dyad as shown in Fig. 2(A and B) for **3** and in Refs. [12,15]. The Soret absorption band in **2** and the doublets in **4** and **5** are bathochromically shifted when compared to the porphyrin

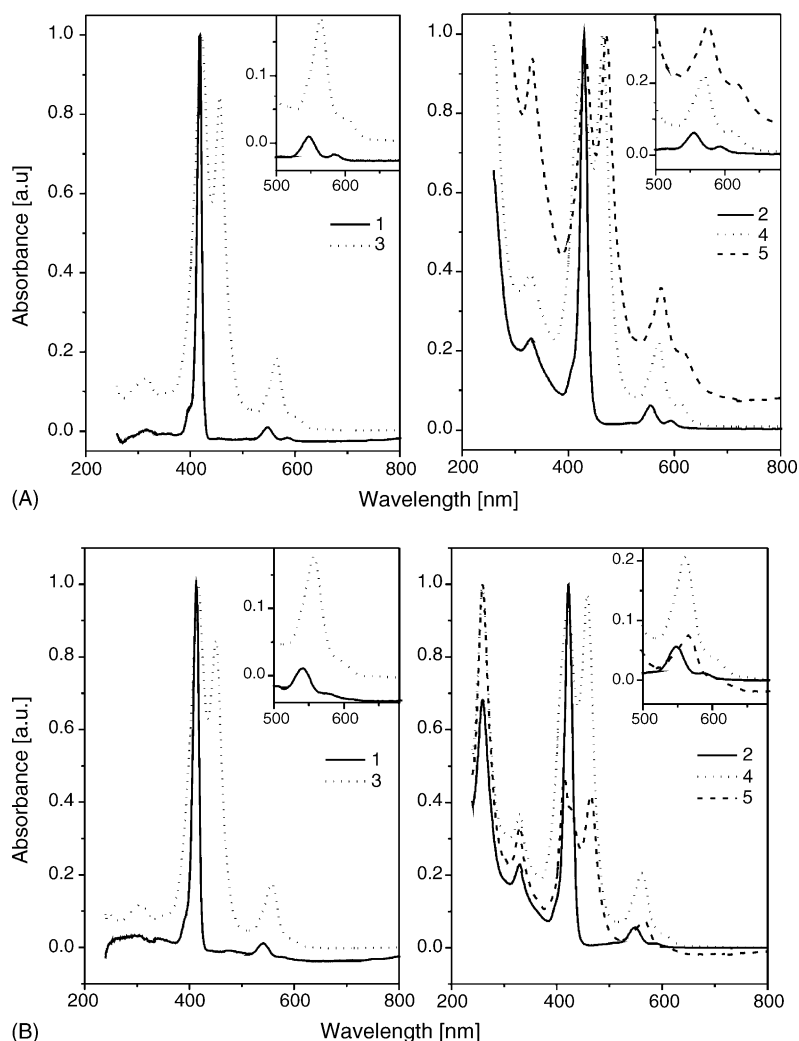


Fig. 2. The absorption spectra (normalized to unity) of the fullerene-porphyrin systems **2**, **4**, **5** and adequate porphyrins **1**, **3** (A, in DMSO; B, in chloroform). The Q band is shown in the insert.

Table 1
Absorption, fluorescence and photoacoustic parameters of the samples 1–5 in DMSO (in chloroform)

Sample	Absorption						PAS _P /PAS _{P'} (for $\nu=15$ Hz)	Fluorescence	
	$\lambda_{\text{max}}^{\text{Fu}}$	$\lambda_{\text{max}}^{\text{P}}; \lambda_{\text{max}}^{\text{P}'}$	$\lambda_{\text{max}}^{\text{Q}}$	$I_{\text{P}}/I_{\text{Q}}$	$I_{\text{P}'}/I_{\text{Q}}$	$I_{\text{P}}/I_{\text{P}'}$		λ_{max}	Φ_{F}
1	–	419; – (413; –)	546 (542)	31.0 (23.2)	–	–	–	590; 640 (587; 633)	0.08
2	–/330 (259/330)	430; – (423; –)	556 (549)	22.5 (17.8)	–	–	–	591; 650 (535; –)	0.01
3	–	421; 457 (417; 450)	564 (556)	5.6 (6.0)	5.7 (6.0)	0.99 (1.2)	1.08	622; 662 (620; 651)	0.12
4	–/330 (259/330)	426; 465 (421; 458)	570 (561)	4.2 (4.7)	4.5 (5.4)	0.93 (0.86)	0.78	625; 666 (622; 651)	0.01
5	– (259/330)	433; 472 (414; 465)	574 (566)	2.3 (5.4)	2.5 (4.6)	0.93 (1.2)	0.74	590; 647 (535; 639)	0.04

I , intensity of absorption band; Φ_{F} , fluorescence quantum yield; indices: Fu, fullerene band; P, P', Soret porphyrin bands; Q, longwavelength porphyrin band; $\Delta\Phi_{\text{F}} = \pm 0.02$. The absorption and fluorescence data are taken on the basis of Figs. 2 and 3, respectively.

samples **1** and **3** indicating very strong interaction between porphyrin and fullerene species (the exception is **5** in chloroform). The bands in the absorption region between 250 and 350 nm are assigned to the fullerene moiety [12,14,15]. The supplementary bathochromic shifts in DMSO versus chloroform are trivial and due to the differences in solvent polarity. The character of these spectra is slightly dependent on the kind of medium; the spectra in solutions are similar to those presented in our previous paper

for the samples in KBr [12,15]. The absorption data are gathered in Table 1.

The fluorescence spectra presented in Fig. 3 confirm the marked influence of the C₆₀ on the porphyrin species—fullerene strongly quenches fluorescence of porphyrin in the hybrids **2**, **4** and **5**. The fluorescence bands at about 590 nm (in DMSO)/587 nm (in chloroform) and nearly at 640 nm (in DMSO)/633 nm (in chloroform) in the sample **1** are assigned

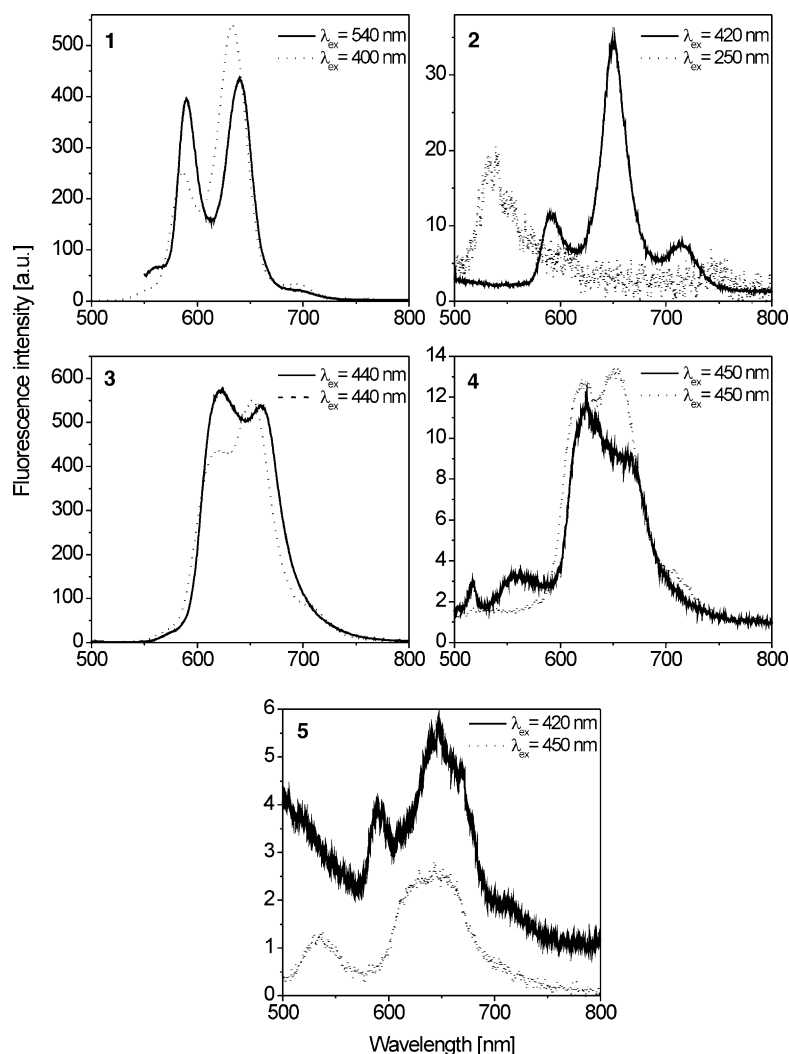


Fig. 3. The fluorescence emission spectra of the fullerene–porphyrin systems **2**, **4**, **5** and adequate porphyrins **1**, **3** for appropriate excitation wavelengths (solid line, in DMSO; dotted line, in chloroform).

to the monomeric porphyrin species as found in the literature [19,23]. In the dyad **3** these bands are bathochromically shifted with respect to those in **1**, both in DMSO and chloroform, due to the strong interaction between two porphyrin units. Moreover, the band positions and intensity relationships in **3** are influenced by the solvent. The bathochromic shift in fluorescence band positions in DMSO with respect to those in chloroform are due to higher polarity of DMSO than that of chloroform. Differences in the relative band intensities in DMSO and in chloroform could be assigned to dissimilarities in vibronic transitions in the samples when solvated by various solvents. The fullerene also exhibits fluorescence and thus indicates its excited states participation in radiative processes but fullerene fluorescence is much weaker than porphyrin moiety radiative emission. The fluorescence parameters important and needed for our further investigations of non-radiative processes occurring after light excitation are gathered in Table 1.

Very interesting results are obtained for the fullerene–porphyrin samples **2**, **4**, **5**. All samples both in DMSO and chloroform were excited in the porphyrin absorption range for appropriate excitation wavelengths from 400 to 540 nm. Also 250 and 320 nm wavelengths were used for excitation. In Fig. 3, we have shown the fluorescence results for some selected excitation wavelengths as examples. In the case of the sample **2** in chloroform (Fig. 3, **2**) the result is similar to that obtained in DMSO (not shown). The shapes of the fluorescence spectra depend more or less on the excitation range and also on solvent polarity. The fluorescence features of porphyrins **1** and **3** are strongly affected in the presence of fullerene as seen for **2**, **4** and **5**. The most spectacular alteration in the fluorescence spectra is very strong quenching of porphyrin/porphyrin dyad emission after covalent linkage to the fullerene. Fluorescence intensity of porphyrin decreases more than ten times when compared to that of the porphyrinic samples **1** and **3**. It is a proof for occurrence of other processes which compete with the radiative pathways of excitation energy deactivation resulted from non-radiative transitions (internal conversion and intersystem crossing) and/or other non-radiative processes which can occur after photon absorption. The low values of the fluorescence quantum yields of some fullerene–porphyrins were also found by Tkachenko et al. [25]. On the basis of the quenching results we can confirm the occurrence of intramolecular electron transfer from the porphyrin moiety as an electron donor to the fullerene species as an electron acceptor; previously it was suggested on the ground of electron and vibrational spectra [13].

The sample **5** (the hybrids constituted of two porphyrin dyads and two fullerene moieties) when its fluorescence is excited in the Soret absorption region of the porphyrin dyad (420 or 450/460 nm) is the excellent example of fullerene affection on porphyrin properties. The results are presented in Fig. 3, **5**; an intense band is observed in the range of 535 nm (in chloroform) and 590 nm (in DMSO), which is not seen in the fluorescence spectra of **3**. Similar features are observed for **4**; they are well seen mainly in DMSO solution but in chloroform a broad weak hump at 535 nm can be also observed (Fig. 3, **4**). The new band locations and fluorescence intensities depend on a kind of sample and are affected by solvents used in the experiment (highly

polar DMSO and chloroform of low polarity). This result could be explained either by excimer creation or by the strong shift of porphyrin fluorescence in the presence of fullerene; on the basis of above results presented in Fig. 3 we cannot neglect the shift of the porphyrin fluorescence bands in the presence of fullerene but occurrence of excimer cannot be excluded. We can suppose that appearance of these extra bands in the energy range below the porphyrin second singlet excited state and a marked influence of solvent polarity could indicate a creation of the fullerene–porphyrin excimer with the porphyrin second excited singlet state as a result of strong interaction between the ground and excited states of the systems. Excimer formation characterized by extremely fast formation rate from the singlet excited state of porphyrins was shown by Tkachenko et al. [25], but unfortunately short-lived species are beyond circumstances of our experiments. The excimer presence is also observed in the sample **2** as a sharp peak located at 535 nm. The most spectacular excimer band we have observed when the sample was excited at 250 nm in chloroform and DMSO; the result is shown in Fig. 3, **2** in chloroform as an example. The less intense band at 535 nm is also seen for excitation at 320 nm (not shown). When the sample **2** dissolved in DMSO is excited in the range of porphyrin absorption region (e.g. at 420 nm) porphyrin fluorescence is clearly observed. The example of that is also shown in Fig. 3, **2**. In the fullerene–porphyrin dyad **4**, excimer formation is not as spectacular as seen in **2** and **5**. The differences might be explained by the kind of porphyrin (dyad) and a number of porphyrin species per fullerene unit in **4** (two porphyrins per one fullerene) against **2** and **5** (one porphyrin per one fullerene). The fluorescence spectra of the sample **2** (e.g. Fig. 3, **2**) and also in **4** and **5** (not shown) indicate also that intramolecular energy transfer from the fullerene to the porphyrin moiety can occur as suggested in [12] because we observe emission with the sharp peak at about 535 nm located on the background of the 550–750 nm wing of the porphyrin moiety spectrum, when the sample is excited in the fullerene absorption range (250 nm). Confirmation of this effect was also found in the same sample in DMSO for other excitation wavelengths (not shown). However this topic needs deeper insight and could be a subject of our further investigation.

Since it is rather difficult unambiguously to judge about excimer formation on the basis of fluorescence spectra we have also measured emission excitation spectra. A few examples of the obtained results are presented in Fig. 4 (both in DMSO and chloroform). The changes in the spectra shapes and in the band relationships with the fluorescence wavelengths result in contribution of fluorescence coming from various moieties. The excitation spectra shapes depend also very strongly on the observation wavelengths and the kind of sample, what indicates co-existence of more than one emitting species. When emission of the samples is observed in the range of porphyrin/porphyrin dyad fluorescence ($\lambda_{\text{obs}} > 600$ nm), the spectra shapes coincide more or less with the porphyrin moieties absorption spectra and domination of porphyrins is observed (e.g. Fig. 4, **1** for $\lambda_{\text{obs}} = 650$ nm, **2** for $\lambda_{\text{obs}} = 670$ nm, **3** for $\lambda_{\text{obs}} = 630$ nm; in chloroform). On the other hand, when the observation wavelengths match the range of 540–590 nm the intense band at about 520–540 nm is

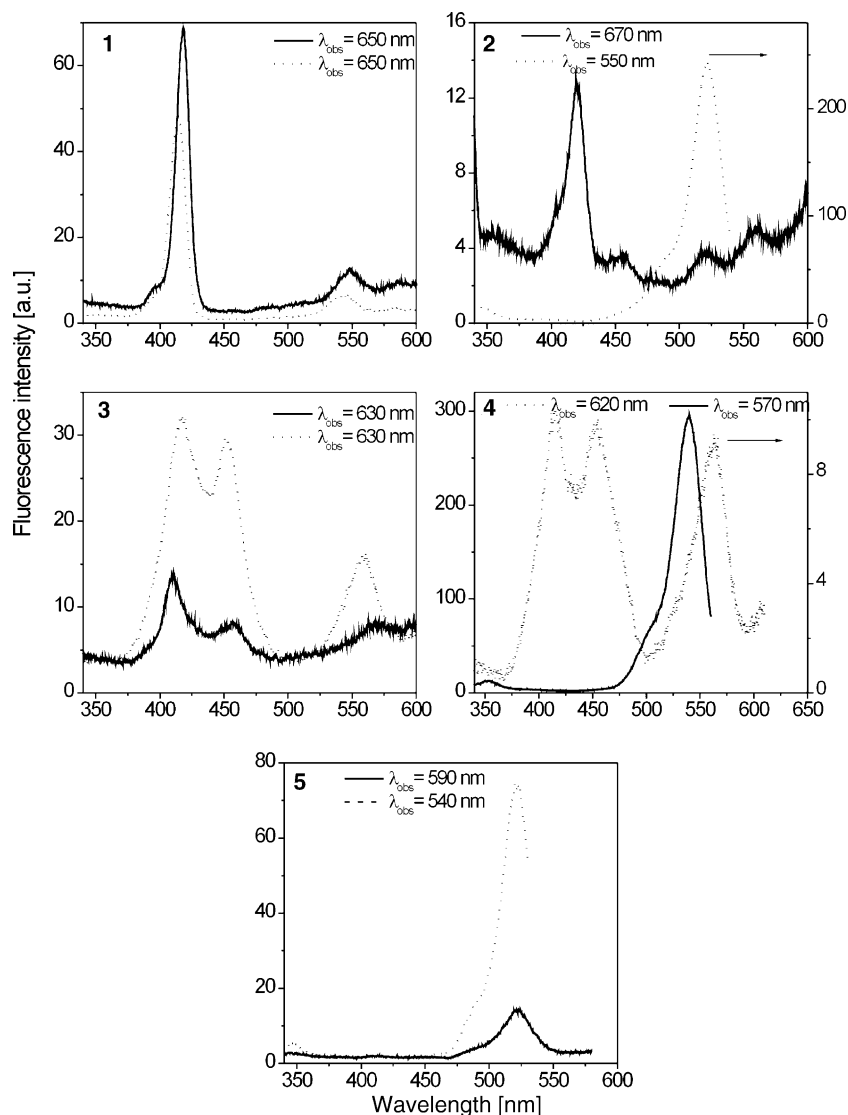


Fig. 4. The fluorescence excitation spectra of the fullerene–porphyrin systems **2**, **4**, **5** and adequate porphyrins **1**, **3** for appropriate observation wavelengths (solid line, in DMSO; dotted line, in chloroform).

observed originating from emission of the excimer (e.g. Fig. 4, **4** for $\lambda_{\text{obs}} = 570$ nm, **5** for $\lambda_{\text{obs}} = 590$ nm; in DMSO).

3.2. Photoacoustic investigations

Photoacoustic examination provides us information on global thermal deactivation of the systems under investigation. The photoacoustic spectra were measured for three light modulation frequencies ($\nu = 8, 15$ and 30 Hz). The typical results are presented in Fig. 5 for the samples in DMSO, measured at the modulation frequency of 15 Hz.

The spectra in chloroform are similar to those in DMSO however they are less intense and more noisy as well as interfered by chloroform evaporation therefore we concentrate on the PAS in DMSO. In the spectra of **2**, **4** and **5** the wide bands ranged from 300 to 350 nm can be assigned to thermal processes occurring in the fullerene moiety. The bands in the range of 400 – 500 nm and at about 580 nm originate from the por-

phyrin species. Fig. 5 confirms participation of both fullerene and porphyrin species in photothermal deactivation since we observe the bands at 300 – 350 nm and bands at 400 – 700 nm. Moreover, a great influence of the fullerene on non-radiative processes in the fullerene–porphyrin hybrids is observed. The bands in **2** and **4**, **5** are broader and bathochromically shifted with respect to those in **1** and **3**, respectively; the Soret bands of porphyrin are shifted from 420 (in **1**) to about 430 nm (in **2**) and from $420/460$ nm (in **3**) to $440/475$ nm (in **4** and **5**). The maximum of the Q band is also bathochromically shifted from 550 nm (in **1**) to 560 nm (in **2**) and from 560 nm (in **3**) to about 575 nm (in **4** and **5**). As it appears from Table 1, the relative intensity ratios of the photoacoustic bands $440/475$ nm (0.78 in **4** and 0.74 in **5**) are markedly changed when compared to that of the band $420/460$ nm (1.08 in **3**). The changes in photoacoustic signals for the samples **2** and **4**, **5** in comparisons with **1** and **3**, respectively, evidently confirm a great influence of fullerene on porphyrin/porphyrin dyad thermal behaviour.

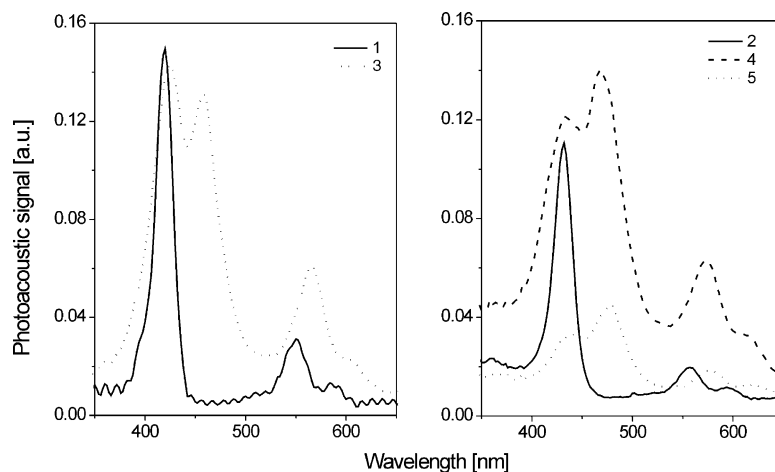


Fig. 5. The photoacoustic spectra of the fullerene–porphyrin systems **2**, **4**, **5** and adequate porphyrins **1**, **3** in DMSO, at light modulation frequency 15 Hz.

Some conclusions concerning thermal relaxation in the samples under investigation can be drawn when PAS bands are correlated with their corresponding absorption bands (absorbance ratios are 0.99, 0.93 and 0.93 for the samples **3**, **4** and **5**, respectively). Thermal relaxation process can be expressed by the thermal deactivation parameter as a ratio of absorbance and photoacoustic signal intensity. The difference in absorption and PAS ratios for **3**, **4** and **5** indicates variation in thermal deactivation in porphyrin dyads upon linkage to fullerene. The results obtained for **2**, **4** and **5** and presented in our previous paper [12] support strong interaction in fullerene–porphyrin hybrids and a great affection of porphyrin/porphyrin dyad thermal deactivation in the presence of fullerene. The PAS results are coherent with observation of porphyrin fluorescence quenching upon linkage with fullerene (and possible intramolecular energy transfer from fullerene to porphyrin moieties). The changes in porphyrin/porphyrin dyad thermal deactivation parameters can be assigned to changes in charge distribution in molecular skeleton upon fullerene linkage. An interesting result is the difference in thermal deactivation in the Soret region (420–460 nm) and in the Q band (550–575 nm). Usually thermal deactivation parameters, in the Soret and in the Q band regions, are expected to be rather similar when one species is present in a sample. The differences in thermal deactivation parameters in the Soret band region and in the Q band (**2**, **4** and **5**) can be assigned to the formation of an excimer from the second excited singlet of porphyrins owing to the fact that a part of energy of the second excited state is used for excimer formation instead for thermal deactivation. According to Rosencwaig-Gersho theory [26] the product of the photoacoustic signal and $\nu^{1/2}$ is expected to be constant when thermal relaxation comes from one origin in prompt processes. The correlation factors (for the relation of the photoacoustic signal versus $1/\nu^{1/2}$) estimated on the basis of the PAS experimental data and Rosencwaig-Gersho theory [26] do not reach unity and they are in the range of 0.90–0.99. This indicates that at least not only fast processes contribute to thermal processes but also slow relaxation with triplet state participation is involved in thermal deactivation to the ground state. Also other processes (such as: electron transfer, molecular

conformation, existence of different molecular species) cannot be excluded.

3.3. LIOAS studies

In the LIOAS experiment, we focus our attention on the following features of the hybrid systems: the changes in the yields of triplet state population (Φ_T), in thermal relaxation decays (τ_2), in parameters describing parts of energy changed into heat in prompt and slow processes (the K_1 and K_2 parameters, respectively). Only the samples dissolved in DMSO were used for the LIOAS experiments to minimize changes in molecular volume [27] and to avoid formation of aggregated structure. The LIOAS results are shown in Fig. 6 for all samples in DMSO. The obtained LIOAS waveforms are typical as found for porphyrin dyes [26]. Table 2 collects the LIOAS data evaluated with the use of Marti et al. approach [21] and Rudzki-Small et al. deconvolution [22]. In the samples **2**, **4** and **5** the evaluated data show marked shortening of thermal decay times of

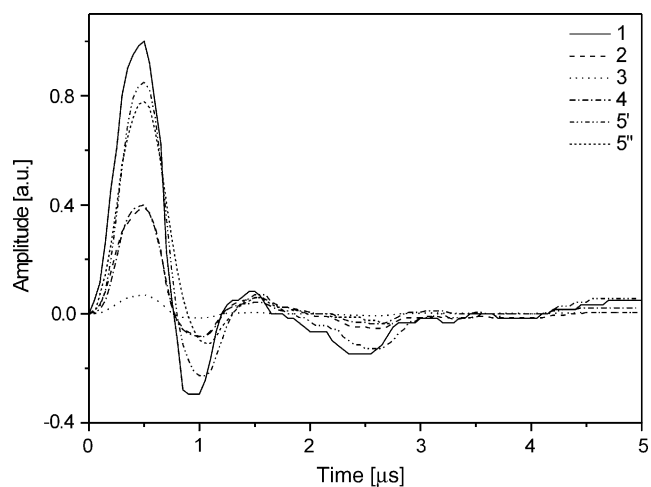


Fig. 6. The photothermal waveforms of the investigated samples in DMSO for excitations: $\lambda_{\text{ex}} = 415$ nm (samples **1–4**, **5'**), and $\lambda_{\text{ex}} = 337$ nm (sample **5''**); BCP was used as a standard.

Table 2
The results of photothermal data analysis of the samples in DMSO for $\lambda_{\text{ex}} = 415$ nm (in brackets— $\lambda_{\text{ex}} = 337$ nm)

Sample	α	K_1	K_2	ΣK_i	Φ_T	τ_2 [μs]
1	0.39	0.36	0.20	0.56	0.50	2.08
2	0.07	0.06	0.01	0.07	0.92	0.70
3	0.40	0.37	0.13	0.50	0.43	7.54
4	0.41	0.40	0.06	0.46	0.58	0.64
5	0.78 (0.85)	0.74 (0.84)	0.07 (0.09)	0.81 (0.93)	0.09 (0.16)	1.43 (1.09)

$\Delta\alpha = \pm 0.06$, $\Delta\Phi_T = \pm 0.10$, $\Delta K_1 = \pm 0.01$, $\Delta K_2 = \pm 0.01$, $\Delta\tau_2 = \pm 0.01$, $\tau_1 \leq 0.4 \mu\text{s}$.

the porphyrin triplet states (τ_2) and the increase in triplet state population (Φ_T) in **2** and **4** or decrease in **5** when compared to those for the reference samples **1** and **3**, respectively. The τ_2 value for porphyrin **1** is characteristic for porphyrin dyes as found in Ref. [28]. The porphyrin linkage to fullerene shortens τ_2 in the samples **2**, **4** and **5**. These results confirm once more a strong interaction between fullerene(s) and porphyrin(s) in the hybrids. In this point, we have to underline that the sum of K_1 and K_2 is expected to be equal to 1 provide that only thermal processes participate in deactivation of singlet and triplet states due to internal conversion and intersystem crossing. It is not a case in our experiment. In the sample **5**, the sum of ($K_1 + K_2$) reaches nearly 1; ($K_1 + K_2$) = 0.81 ($\lambda_{\text{ex}} = 415$ nm) or 0.93 ($\lambda_{\text{ex}} = 337$ nm). The difference in ($K_1 + K_2$) estimated for different excitation wavelengths is due to various species when excited either in the porphyrin absorption region ($\lambda_{\text{ex}} = 415$ nm) or in the fullerene and porphyrin absorption region ($\lambda_{\text{ex}} = 337$ nm). Also distribution of energy in fast or slow processes can be different upon different excitations. This indicates that in **5**, energy absorbed by the system is predominantly (but not only) deactivated as a result of thermal processes. On the other hand, the sum of K_1 and K_2 in **4** does not reach 0.50. For the sample **2**, the particular small ($K_1 + K_2$) value is estimated (0.07). The values of ($K_1 + K_2$) in **2**, **4** and **5** evidently proof the occurrence of other processes which have to be taken into consideration as competitive processes to non-radiative thermal relaxation.

4. Discussion

The absorption and fluorescence studies presented in this paper evidently show strong interaction between fullerene and porphyrin moieties in the fullerene–porphyrin hybrids. As shown in the emission and excitation spectra the strong interaction in fullerene–porphyrin hybrids leads to formation of an excimer with participation of the porphyrin second excited singlet state. However we focus our discussion on the steady-state photoacoustics and time-resolved photothermal spectroscopy since they excellently support conclusions on the great influence of fullerene on photophysical behaviour of porphyrin species.

The values of correlation factors estimated on the basis of the PAS results and Rosenzweig-Gersho theoretical prediction [26] indicate complex thermal relaxation with contribution of both fast (e.g. internal conversion) and slow processes (e.g. intersystem crossing) with participation of the singlet and triplet states, respectively. The higher TD values estimated for the sample **3**

(when compared to TD of **1**) confirm efficient thermal deactivation in molecular dyads as observed also in other associated molecular structures [19]. However, this process is very much enhanced in the presence of fullerene; it is seen especially clearly for the samples **4** and **5** against **3**. The changes in the relationships of the photoacoustic band intensities (Fig. 5), when compared the results for the samples **2** and **4**, **5** with those for **1** and **3**, respectively, indicate markedly how fullerene influences thermal properties of porphyrin moieties. These results confirm a strong influence of fullerene on porphyrin photophysical properties, but also participation not only the singlet states but also triplet states in all deactivation processes and contribution of other processes occurring after light excitation is also noticeable.

In the light of the LIOAS experiments it is evident that not only thermal deactivation is important but also other processes have to be taken into consideration. Firstly, we consider the values of Φ_T . We have to mention that it is very difficult to evaluate their proper values because we are not able to separate the contribution of the porphyrin triplet states from those of the fullerene; thus the Φ_T values are rather rough. Moreover, in our estimation we put (Eq. (1)) the E_T value taken from the literature for zinc porphyrin when not covalently linked to fullerene [23]. Additionally, the values estimated from Eq. (1) are rather overestimated because this equation is fulfilled under the assumption that whole excitation energy, which is lost neither in radiative process of fluorescence nor in non-radiative processes from the singlet state, is converted into heat with triplet state participation; it means that Eq. (1) does not include other deactivation pathways such as: photochemical reaction, conformational changes, electron transfer, inter- and intramolecular energy transfer. In Ref. [29] the authors proposed to use an extended form of Eq. (1) with a factor which takes into consideration other possible processes globally and interactions that could occur in systems upon light excitation. However, in the paper [29] the attention was mostly concentrated on oxygen generation from the triplet states in much simpler systems (chlorines in solutions) than our hybrids. The fullerene–porphyrin hybrids are very complex units and therefore we concentrate on the sum of ($K_1 + K_2$). There are some reasons why ($K_1 + K_2$) values could be less than unity: (i) changes in molecular volume, (ii) generation of singlet oxygen, (iii) inter- and intramolecular energy/electron transfer and formation of a charge-separated state, (iv) formation of other molecular species, (v) electronic redistribution owing to changes in electronic molecular structure, (vi) occurrence of some thermal processes in time duration longer than it is available in the

LIOAS experiment; the (vi) is beyond our reach and therefore we cannot discuss this.

In the LIOAS experiments, we have used DMSO as a solvent for the samples in order to minimize the effect of molecular volume changes (i) [27]. Of course we cannot neglect point (ii) since singlet oxygen evaluation always accompanies processes in which triplet states are involved. However, we minimized singlet oxygen creation by carrying on the LIOAS experiments under nitrogen atmosphere. The changes in absorption/fluorescence spectra resulting in a strong interaction in the fullerene–porphyrin hybrids provide an evidence for the intramolecular electron/energy transfer between fullerene and porphyrin moieties (iii). Moreover the differences in Φ_T and $(K_1 + K_2)$ for the samples **2**, **4** and **5** regards to those for the references **1** and **3** can be assigned to occurrence of other molecular species like for example an excimer (iv). In discussion of (iii) and (iv) we have to underline importance of the results presented by, e.g. Imahori et al. [4,9], El-Khouly et al. [30], Tkachenko et al. [31,32] and Gabrielsson et al. [33]. Fullerene–porphyrin systems are known to be donor–acceptor supramolecular systems which are able to form charge-separated state, $P^{•+}-C_{60}^{•-}$ from the first singlet and/or triplet states of porphyrin P and with contribution of C_{60} singlet/triplet transient species [4,9]. The formation of transient fullerene–porphyrin forms were evidently shown with transient-absorption spectroscopy in [34]. Moreover, fluorescence spectroscopy presented in this paper shows unambiguously electron transfer (iii) and creation of an excimer formed with participation of the porphyrin second excited singlet state (iv). Thus in the light of our results and results presented in Refs. [4,9,12,30–34] we have every reason to believe in formation of a fullerene–porphyrin excimer in fullerene–porphyrin (**2**) and fullerene–porphyrin dyads (**4** and **5**). Moreover, essential fluorescence quenching due to electron transfer was also observed in a system of porphyrin and strong electron acceptor [7,8,35]. We realize that the fullerene–porphyrin hybrids under investigation in this paper are not the same ones as investigated in [7,8,35], however the occurrence of intramolecular electron transfer in strongly interacting species in hybrids is obvious on the basis of fluorescence quenching. Thus, we can claim that intramolecular energy transfer and excimer formation can modify the values of Φ_T and $(K_1 + K_2)$. Thus a part of excitation energy is used for these processes and it leads to diminishing $(K_1 + K_2)$ values.

The LIOAS experiments prove the opposite behaviour of the samples **2** and **4** with respect to **5** in terms of an increase in triplet state population. Moreover the $(K_1 + K_2)$ reaches nearly 1 for **5** but not for the remaining samples **2** and **4**. This finding seems to be inconsistent with the decrease in triplet state population of **5**. One possible explanation of this incoherence in $(K_1 + K_2)$ and Φ_T could lie in the population and depopulation rate constants in **5** with respect to those processes in **2** and **4**. However we are not able to judge these events at this stage of the presented paper. In consideration of our LIOAS results we have also to take into account the electro-vibration harmonic and anharmonic interactions in such large systems like fullerene–porphyrin samples. In our experiments we are not able to distinguish the channels for energy deactivation in which anharmonic states of the first

excited singlet and harmonic states of the second excited singlet could be involved and overlapped. Due to the time resolution of the LIOAS device we are not able to determine a part of energy which is lost with contribution of the electro-vibration harmonic and anharmonic interactions and which could make also the differences in the LIOAS data of **5** against **2** and **4**.

In the last stage of our discussion, we have to recall observations done for the fullerene–porphyrin systems with the vibrational spectroscopy presented in Ref. [15]. The shifts of some electronic bands, observed in the electronic spectra in this paper and in the vibrational bands presented in [15] in comparison with respective porphyrin and fullerene bands were assigned to redistribution (v) of the charges occurring in both fullerene and porphyrin moieties due to covalent linkage. Similar effects were observed in fullerene substituted with tetrathiafulvalenes [36]. Thus, we can suggest occurrence of modification in the electronic molecular structure in fullerene–porphyrin hybrids owing to the strong interaction between fullerene and porphyrin species which are confirmed by our absorption, fluorescence and photothermal spectroscopy presented in this paper and by vibrational spectroscopy showed in [13,15].

5. Conclusions

On the basis of presented results we can draw some conclusions. The presence of fullerene influences markedly photophysical properties of porphyrin/porphyrin dyad due to the strong interaction between fullerene and chromophore covalently linked. We showed intramolecular energy transfer from fullerene to porphyrinic moieties; electron transfer between dye species and fullerene can be suggested. Strong interaction in the investigated systems can lead to the charge redistribution and also to creation of an excimer.

The LIOAS examination is usually used for determination of the basic parameters such as: the quantum yield of triplet states population and thermal relaxation decay of triplet states which can be essential, e.g. in molecular photovoltaics [4–11], in modeling energy/electron transfer in photosynthesis [4,7,8] and in photodynamic therapy of cancer [29]. In this paper, we show that LIOAS experiment can also be an excellent tool for investigation of electronic processes in supramolecular materials such as, e.g. covalently linked fullerene–porphyrin systems but can also provide data very useful in designing molecular light converting systems.

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