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Study of resonance effects in copper phthalocyanines

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Abstract

The purpose of this paper is to follow the influence of chlorine or fluorine substituents of phthalocyanine dyes on their spectroscopic, photothermal and photoelectric properties. Such influence is discussed in term of the resonance effects occurring in organic macrocycles. The domination of mesomeric effect was indicated due to the large enhancement of photocurrent created by the studied systems and other changes in spectroscopic and photothermal properties of the investigated phthalocyanines. The occurrence of steric effect was supported by the photothermal experiments. The differences between electronegative substituents of phthalocyanine dyes on photophysical properties of macromolecular systems are also discussed.

Keywords: Resonance effects; Spectral methods; Photoelectric examination; Fluorinated phthalocyanines

1. Introduction

The subject of substituent effects in conjugated compounds gets more and more attention in the last decade. Particular interest is put on the chemical activity and photophysical behaviour of fluorinated compounds investigated both by experimental methods [1,2] and theoretical calculations [2,3–7].

Fluorine is a unique atom due to its extreme electronegativity [8–10]. The importance of the effect of fluorine on the physico-chemical properties of molecules is described e.g. in the review paper by Smart [8]. Although the influence of the fluorine atoms on some chemical and physical properties of compounds are rather firmly understood, the effect of fluorine substituents on photophysical properties of molecules on the molecular level are rather very little known [4]. Electron-withdrawing and electron-donating substituents exhibit very marked effects on the spectral and electronic behaviour of many molecules. The electron-withdrawing effect in fluorinated molecules is not surprising. However, its electron-donating influence on some spectroscopic and electronic behaviour seems to be rather unique. There are some papers concerning the resonance effects of electron-withdrawing and electron-donating substituents on the macroring of porphyrin dyes and other organic molecules [1–5,7,11] but only modest knowledge on these effects in fluorinated phthalocyanine dyes is reported [8,12].

It was previously shown that phthalocyanine (Pc) substituted with fluorine atoms exhibits particular spectroscopic and photoelectric properties when compared with those of its non-substituted counterparts. Some phthalocyanines such as fluorinated zinc phthalocyanines also exhibit a marked enhancement of photocurrent generation with respect to other porphyrin/phthalocyanine dyes when embedded in a photoelectrochemical cell (PEC). It was preliminary regarded as a strong resonance interaction between electronegative fluorine atoms attached to the indole units and the π-electron system of the macrocyclic molecular ring [12]. It has also been reported that halogenation with fluorine, bromine, chlorine or iodine of porphyrins and phthalocyanines can influence fluorescence quantum yield and lifetime, formation of triplet state and other photophysical properties [13–15]. Bonett et al. showed a strong effect of bromination or chlorination on the intersystem crossing process of octaethyl porphyrins [13].

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

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The influence of the substituents on the photophysical properties of porphyrins and phthalocyanines, usually referred to the mesomeric [2,7], inductive [5,9,10,16,17] or steric [1,18] effects, can be studied with various physical and chemical methods. In the present paper three phthalocyanines containing copper as the central ion, two of them substituted with 16 fluorine or chlorine atoms, were subjected to spectroscopic and photoelectrochemical investigations. Absorption, fluorescence, photoacoustic and laser-induced optoacoustic spectroscopy (LIOAS), as well as photocurrent generation study in the PEC, were used for examinations of substituent effects in phthalocyanines on absorption and fluorescence features, photothermal properties, population of triplet state and its thermal deactivation and also on some photoelectric behaviour. As far as we know the LIOAS experiment for the dyes under consideration is done for the first time. The present study has potentially further implication for the design of a suitable phthalocyanine for certain applications, like organic photovoltaics, photodynamic therapy and other biological activities.

2. Materials and methods

2.1. Materials

The molecular structure of the three dyes investigated (CuPc, $CuPcCl_{16}$, $CuPcF_{16}$) is shown in Fig. 1.

In our chemical procedure we have modified the CuPc receipt described in [19,20] because we wanted to avoid chlorine impurities. The synthesis procedure of CuPc was as follows: a mixture of 0.68 mol (100 g) of phthalic anhydride, 2.2 mol (130 g) of urea, 20 g (0.1 mol) of cuprous chloride, 0.2 g of ammonium molybdate and 400 ml of tricholorobenzene was agitated and gradually heated to 150–180 °C for 5 h and then cooled bellow 100 °C. The product was filtered, vacuum dried and ground and then reslurried in 1500 parts of 4% aqueous sodium hydroxide. The slurry was heated, maintained at boiling for 1 h in contact with the steam and filtered. After that the slurry was filtered and washed alkali-free with hot water. The filtered product was dried at 80 °C. This product corresponds to the copper phthalocyanine and represented 98% of the theoretical yield [19,20].

The synthesis procedure for $CuPcCl_{16}$ was as follows: tetrachlorophthalonitrile (2 g; 0.01 mol) and cuprous chloride (0.5 g; 0.005 mol) were boiled under reflux in *N*-methyl pyrrolidone for 2 h. The mixture was poured into aqueous hydrochloric acid and the resulting suspension was filtered. The perecipitate was washed with boiling water, and dried at 120 °C. The dark blue powder weighted 2 g. The product was identified as copper hexadecachloro phthalocyanine with the following elemental analysis: $C_{32}Cl_{16}N_8Cu$ found: C 44.5%, Cl 34.6%; N 13%, Cu 7.9% requires: C 44.4%, N 13%, Cu 7.5%, Cl 35.1% [21].

The $CuPcF_{16}$ were purchased from Aldrich and used without further purification.

2.2. Spectroscopic measures

The absorption spectra were measured with a Specord M40 (Carl Zeiss Jena, Germany) in the range of 300–900 nm.

Fluorescence was registered with a fluorescence spectrophotometer Hitachi F4500 (Japan) in the region of 620–900 nm (excitation wavelength was 609 nm for all samples).

The steady-state photoacoustic spectra were registered with a single-beam photoacoustic spectrometer PAC 300 (MTEC, Iowa, USA). Three light modulation frequencies were used (8, 15 and 30 Hz) at the constant phase shift. The samples were embedded in a photoacoustic cell filled with helium atmosphere and a signal was detected with a very sensitive microphone. A black body was used to correct the photoacoustic spectra for the device response.

The kinetics of photothermal processes and triplet state population were studied with the laser-induced optoacoustic spectroscopy (LIOAS). The dyes were illuminated by a

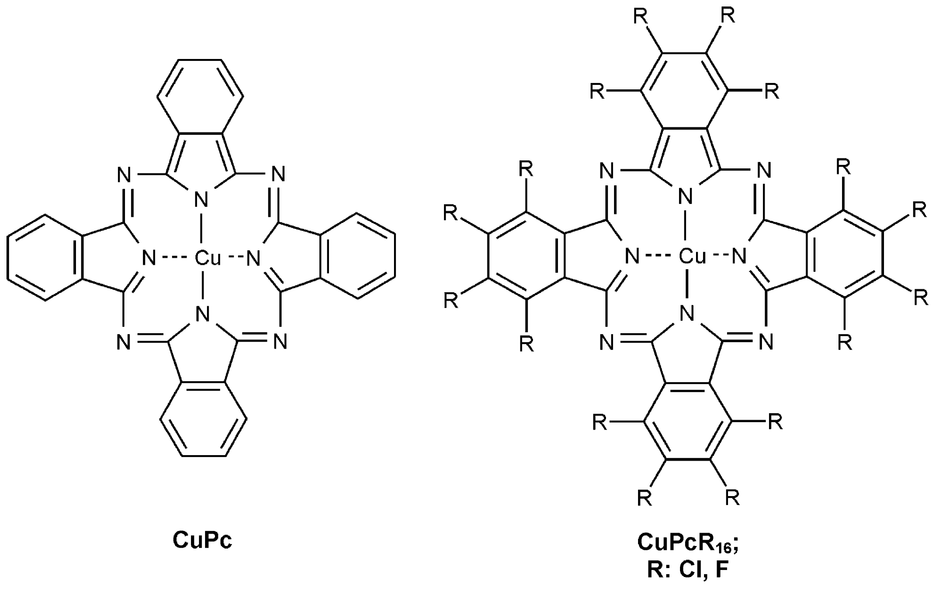

Fig. 1. Molecular structures of copper phthalocyanines.

subnanosecond flashes of a nitrogen laser combined with the dye laser ($\lambda_{ex} = 415$ nm for all dyes). The laser pulse duration was 0.2 ns and the time resolution of the LIOAS apparatus was 0.4 μs. Bromocresol purple (BCP) dissolved in DMSO was used as standard. BCP was characterized by the supposition of that whole absorbed energy is changed into heat in the time shorter than the time resolution of the LIOAS apparatus. The photothermal measurements were done in nitrogen atmosphere at 20 °C and all samples were located in a thermostated cuvette.

The dyes were dissolved in dimethylsulfoxide (DMSO) since this very polar solvent lets to avoid dye aggregation [22]. The dye concentrations used were 1 mM and 10 μM and the spectroscopic measurements were done in 1 mm and 1 cm quartz cuvettes, respectively.

2.3. Analysis of LIOAS signals

The analysis of the LIOAS waveform was carried out according to the method of Marti et al. [23] and to the deconvolution analysis of Rudzki-Small et al. [24]. In the first approach two waveform signals of the dye and of the standard sample were compared [23]. The first maximum (H_{max}) of the LIOAS signal measured for the investigated sample and for the reference is given by the following equation:

$$H_{max} = k\alpha E_L(1 - 10^{-A}), \tag{1}$$

where k is a proportional factor which contains the influence of geometry and electric impedance of an apparatus on measured signals, α is the part of energy changed into heat in time shorter than the time resolution of the LIOAS aparature, A is the absorbance of the sample and E_L is the laser energy (calculated for 415 nm).

The quantum yield of the triplet state generation (ϕ_T) was estimated according to the following equation [25]:

$$\phi_T E_T = (1 - \alpha)E_L - \phi_F E_F - \phi_D E_D, \tag{2}$$

where ϕ_F is the fluorescence quantum yield, E_F and E_T are the energies of the fluorescence and of the triplet state, respectively. The ϕ_D and E_D parameters describe the quantum yield and energy of additional effects occurring in the investigated samples (except fluorescence, internal conversion and intersystem crossing) [25]. These effects are not measurable directly with our experimental equipment.

As a result of the deconvolution of the LIOAS signals, using the procedure proposed by Rudzki-Small et al. [24], it is possible to get information about the kinetics of thermal relaxation of the triplet state and the possible participation of other processes occurring in the time longer than 5 μs can also be indicated.

2.4. Photoelectrochemical experiments

Photovoltaic and photocurrent measurements of dyes are done in the photoelectrochemical cell (PEC) which was constructed of the semiconducting electrode (In_2O_3) and gold electrode (Au). The electrodes were spaced out with a 60 μm teflon spacer [26].

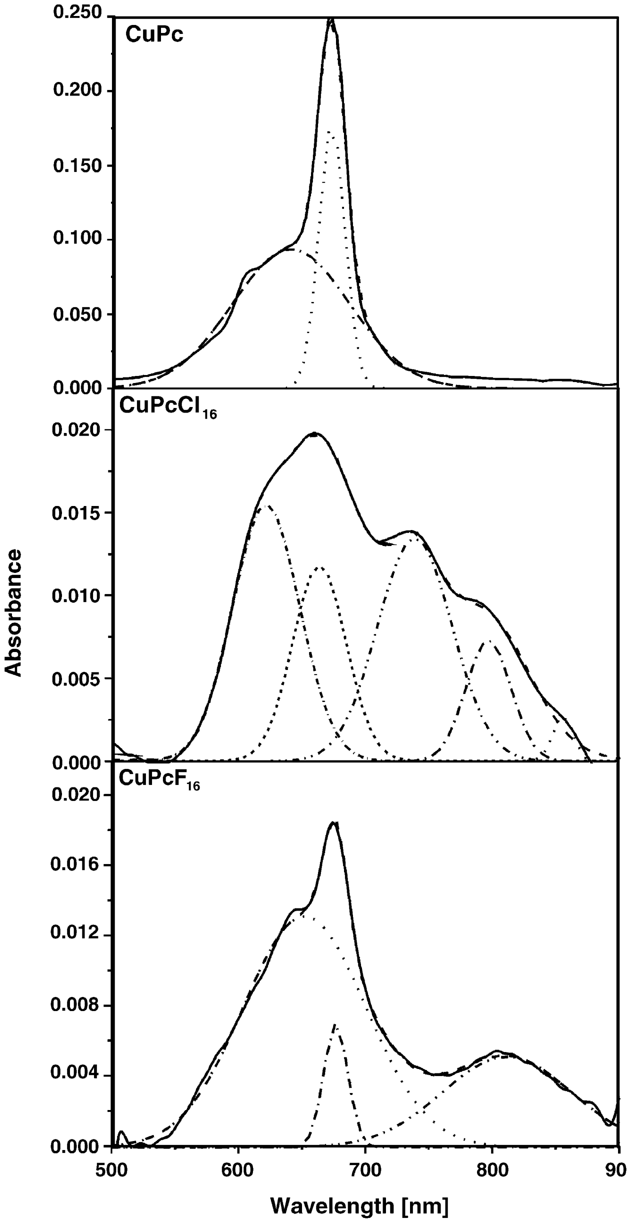

Fig. 2. Absorption spectra of copper phthalocyanines in DMSO ($c = 10$ μM) (Gaussian components are also shown).

3. Results

3.1. Spectrophotometric studies

Fig. 2 shows the set of absorption spectra (in the range of 500–900 nm) of all investigated dyes dissolved in DMSO. The results of the Gaussian analysis are also shown. The main absorption bands are observed in the blue region of the spectra at 300–450 nm (Soret band—not shown, see Table 1) and in the range of Q bands (500–900 nm) [27]. The band locations depended on the dye nature. The unsubstituted dye CuPc is characterised by a band with the maximum at 673 nm as usually observed in the literature for CuPc [19,20]. The dye $CuPcCl_{16}$, containing chlorine substituents showed a shortwavelength shift

Table 1
Spectroscopic and photothermal parameters of the investigated dyes

Dye	λ_{max} (nm)		$\varepsilon \times 10^4$ (M^{-1} cm^{-1})		A (S/Q)	PAS (S/Q)	TD (Q)	R (Q)
	S	Q	S	Q				
CuPc	345	673	1.11	1.70	0.65	0.59	0.41	0.90
$CuPcCl_{16}$	369	659	0.22	0.17	1.29	0.57	0.73	0.91
$CuPcF_{16}$	334	674	0.32	0.18	1.78	0.93	0.82	0.96

$\Delta\varepsilon = \pm 0.1 \times 10^4$ M^{-1} cm^{-1}; ΔTD = ±0.4, $\Delta R = \pm 0.01$. S, Soret band; Q, Q band; R, correlation factor; A, absorbance; PAS, photoacoustic signal intensity; TD = PAS/A.

with the band positioned at 659 nm, whereas $CuPcF_{16}$ exhibit the band with a maximum at 674 nm. As shown, the variation in the absorption band intensities, their half widhts and their locations are due to the different peripheral atoms or groups attached to the main phthalocyanine core. In the absorption spectra of chlorinated and fluorinated dyes ($CuPcCl_{16}$, $CuPcF_{16}$) the changes in the spectral bands are observed; both in their shifts and in the broadness. The extra bands in the longwavelength region beyond 700 nm for $CuPcCl_{16}$ and $CuPcF_{16}$ could be attributed to the extra electronic transition owing to the resonance effects of fluorine and chlorine. In the halogen group, the polarizability is increasing from fluorine to chlorine. Under such circumstances, increase of macrocycle polarizability support the absorption blue shift. Moreover, because $CuPcCl_{16}$ has a coordination covalent bond, and chlorine has an ionic character, it is possible to form some electrostatic bonds, which could be a proof for increased number of the absorption bands [28]. The presence of chlorine and fluorine in the molecular skeleton of phthalocyanines ($CuPcCl_{16}$, $CuPcF_{16}$) decreases the extinction coefficients with respect to those for CuPc. Absorption parameters are gathered in Table 1.

The investigated dyes do not show fluorescence. This result is in contrast to the fluorescence emission monitored for ZnPc and $ZnPcF_{16}$ dyes in DMSO [12]. The lack of fluorescence emission of CuPc and its derivatives is assigned to the presence of the Cu ion incorporated in the centre of the molecular skeleton [26]. The result for the copper Pc dyes presented in this paper evidently indicates large participation of non-radiative processes of the excited states of these dyes in energy deactivation.

3.2. Steady-state photoacoustics

To date little is known about the thermal behaviour of the phthalocyanines studied in this paper. The photoacoustic spectra (PAS), monitored at three light modulation frequencies (8, 15, 30 Hz), are presented in Fig. 3 together with the Gaussian components. Photoacoustic examination gives information on the global thermal deactivation channels in which both the singlet and triplet states of a molecule can be involved. The results in Fig. 3 clearly show that a part of absorbed energy is transformed into heat as a result of non-radiative ways of dye excited state deactivation due to internal conversion and intersystem crossing processes. The comparison of the PAS and absorption spectra evidently shows the participation of dyes in thermal processes and allows to determine thermal deactivation (TD) parameters as a ratio of the photoacoustic signal (PAS) to absorbance (A), i.e. TD = PAS/A. For evaluation of the TD parameters the corresponding Gaussian components of the absorption and photoacoustic bands were used. Among the investigated dyes, CuPc turns out to be less effective in thermal processes than the remaining dyes. It is clear that the presence of fluorines or chlorines in the molecular structure changes the PAS markedly;

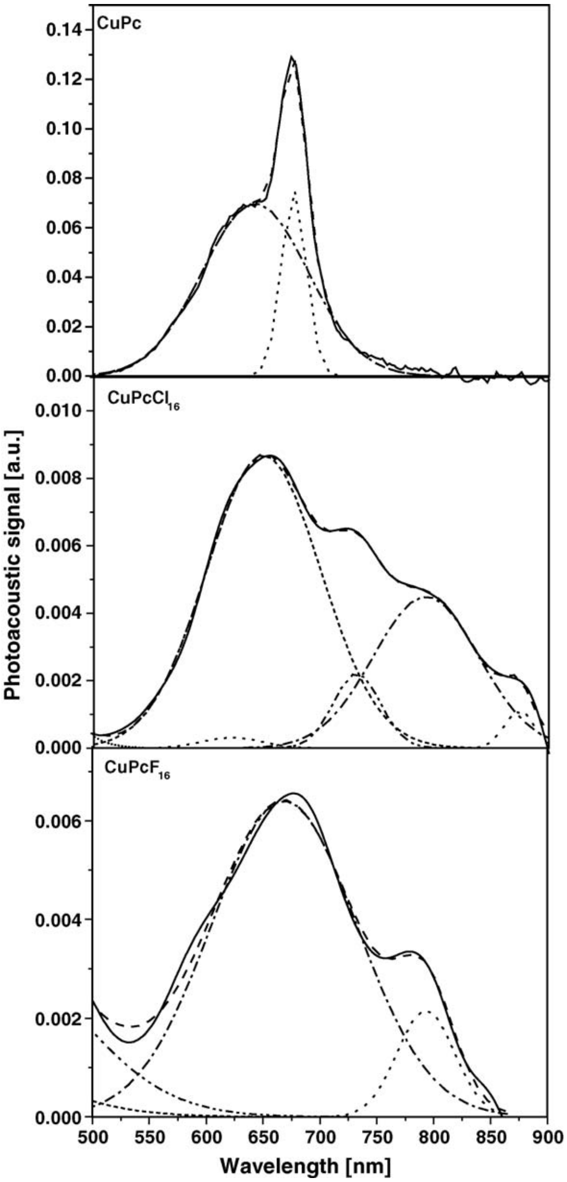

Fig. 3. Photoacoustic spectra of copper phthalocyanines in DMSO (c = 1 mM) (Gaussian components are also shown).

the presence of the electronegative elements increases the photothermal deactivation parameters TD. Also the shift and broadening of the PAS bands are evidently observed with respect to those in the CuPc spectra. This result evidently shows: firstly, the existence of correlation between the molecular structure of dyes and their participation in photothermal processes and secondly, thermal properties are markedly affected by the presence of halogen elements in the molecular structure. Moreover, the relations between PAS band and absorption band intensities in the Soret and Q regions for $CuPcF_{16}$ and $CuPcCl_{16}$ are reversed (Table 1), i.e. the Soret band intensity is higher than that of the Q band in absorption (S/Q = 1.29 and 1.78 for $CuPcCl_{16}$ and $CuPcF_{16}$, respectively), whereas for their corresponding PAS bands, the intensity of the Q band is higher than that of the Soret band (S/Q = 0.57 and 0.93 for $CuPcCl_{16}$ and $CuPcF_{16}$, respectively). It is not a case for CuPc. To explain this observation the correlation factor between the experimental data and theoretical prediction is estimated. In accordance with Rosencwaig-Gersho theory, the PAS amplitude should linearly decrease in the increasing light modulation frequency (in reversed square root) provide that only one spectral dye species takes part in thermal processes (e.g. internal conversion). However, it is not a case for the investigated dyes since the estimated correlation factors *R* (see Table 1) do not reach the value of unity and they are in the range from 0.90 to 0.96 depending on dye. The deviation of the correlation factor from unity, as well as the reversed relations between PAS and absorption band intensities in the Soret and Q regions, indicates at least three events which have to be taken into consideration: (i) the co-existence of more than one spectral species which are involved in thermal relaxation, which can relax with different decay, (ii) not only one fast process contributes to thermal relaxation, but also slow relaxation processes with triplet state participation are involved in thermal deactivation to the ground state, (iii) generation of different moieties (e.g. chemical products) due to some photochemical processes and/or conformational changes in the molecules. The use of low concentrated samples and DMSO as the solvent, which protect against dye aggregation [22], allow us to assume a lack (or a very modest amount) of the aggregated species and to neglect the event (i). Thus in further considerations we will take into account only events (ii and iii).

3.3. Triplet state generation

The LIOAS experiment allows to distinguish the prompt thermal effects occurring in the range time shorter than the apparatus resolution (0.4 μs) from those occurring in time longer than 0.4 μs and lets us to get information on participation of the singlet–triplet transitions in thermal deactivation (ii). Also we are able to estimate the yield of triplet population and thermal relaxation decay (ii and iii).

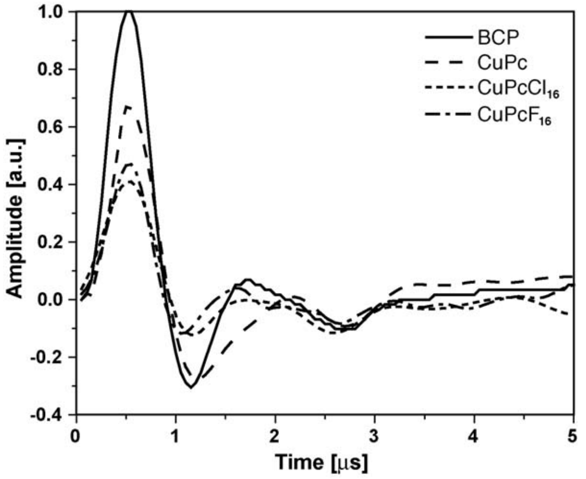

Fig. 4. LIOAS waveform of copper phthalocyanines and BCP in DMSO ($c = 10\,\mu M$).

Fig. 4 shows the LIOAS waveforms for the three dyes, CuPc, $CuPcCl_{16}$ and $CuPcF_{16}$, and for the standard BCP. The α value (Eq. (1)) for the standard is equal to 1. The LIOAS signals for the dyes and reference were measured at the several laser flash intensities with using a grey filter of known transmittance. On the basis of the dependence of dH_{max}/dE_L versus $(1 - 10^{-A})$ the part of energy which changed into heat in time shorter than 0.4 μs was estimated (Eq. (1)). Under the supposition that the *k* factor is the same for the reference and for the dyes and that the whole energy absorbed by BCP is changed into heat [29], the α values for the dyes can be estimated with Eq. (2). As expected Marti et al. (α values) and Rudzki-Small et al. (k_1 values) methods give similar α and k_1 values, which are comparable in the range of the experimental accuracy. These values are 0.67–0.70, 0.37–0.41, and 0.41–0.50 for CuPc, $CuPcCl_{16}$ and $CuPcF_{16}$, respectively, and indicate that about a half of absorbed energy (depending on dye) is converted into heat in prompt processes in time shorter than 0.4 μs. All LIOAS data are gathered in Table 2. The deconvolution analysis was done for two or three exponential components. The best results were obtained for the two-component deconvolution procedure with $\tau_1 \leq 0.4\,\mu s$ and τ_2 ranging from about 6.72 to 1.26 μs. The time range of the order of microseconds can be interpreted as thermal deactivation with participation of the long-lived triplet states of the monomeric dye species and/or could be connected with a heat released in other processes.

Eq. (2) can be used to calculate the yield of triplet state population, Φ_T. In the Φ_T estimation, E_T is the energy of the triplet state taken from the literature on the basis of phosphorescence data for phthalocyanine dyes [30] and Φ_F is taken as 0, since the dyes under examination do not fluoresce. These parameters are also collected in Table 2. The Φ_T value for CuPc is about 0.88 and it is consistent with that of porphyrins [31,32] and other phthalocyanines not substituted with fluorine or chlorine [33].

Table 2
LIOAS parameters of the investigated dyes estimated on the basis of Marti et al. procedure [23] and Rudzki-Small et al. deconvolution [24]

Dye	α	ϕ_T	k_1	τ_1 (μs)	k_2	τ_2 (μs)	k_D
CuPc	0.67	0.88	0.70	≤0.4	0.06	1.69	0.24
$CuPcCl_{16}$	0.41	~1	0.37	≤0.4	0.30	6.72	0.33
$CuPcF_{16}$	0.50	~1	0.41	≤0.4	0.20	1.26	0.39

$\Delta\alpha = \pm 0.06$; $\Delta\phi_T = \pm 0.10$; $\Delta k_1 = \pm 0.01$; $\Delta k_2 = \pm 0.01$; $\Delta\tau_2 = \pm 0.01$; $k_D = 1 - (k_1 + k_2)$.

However, the Φ_T values for the remaining phthalocyanines studied in this paper which are substituted with fluorines or chlorines seem to be overestimated. The k_2 values estimated for $CuPcCl_{16}$ and $CuPcF_{16}$ are higher than those for CuPc. Moreover, the sum of k_1 and k_2 does not reach the unity as expected. These results indicate that other processes than intersystem crossing, in which the triplet state could be involved, should be taken into consideration. The processes which could affect the estimated Φ_T values and the value of the sum of $(k_1 + k_2)$ will be discussed in Section 4.

3.4. Photoelectric behaviour

Photoelectric properties of the dyes were investigated with the PEC for photocurrent examination. The PEC system and the mechanism of photocurrent generation by dyes immersed in the PEC were widely described in our and other papers [26,27,31,34]. The kinetics of photocurrent rise and decay in the second time scale under illumination are presented in Fig. 5 and they confirm participation of the dyes in this process. The values of the photocurrent intensity per cm^2 of the illuminated PEC surface are recalculated for a number of incident photons and absorbance of dyes. The extremely high photocurrent, 116 nA/cm^2 was revealed for fluorinated phthalocyanine ($CuPcF_{16}$), whereas, the remaining dyes give much lower signal (2 and 11 nA/cm^2 for CuPc and $CuPcCl_{16}$, respectively). Such a significant difference in the ability of the dyes in photocurrent generation is due to the marked differences in the groups attached to the main molecular core of phthalocyanines. As seen from the presented results fluorines play an essential role in the ability of dyes in photoresponse as to the great enhancement of photocurrent was also monitored for fluorinated zinc phthalocyanine [12]. Also the effect of the presence of the chlorine atoms attached to the indole units (although not so significant as in fluorinated dyes) could also be taken into account.

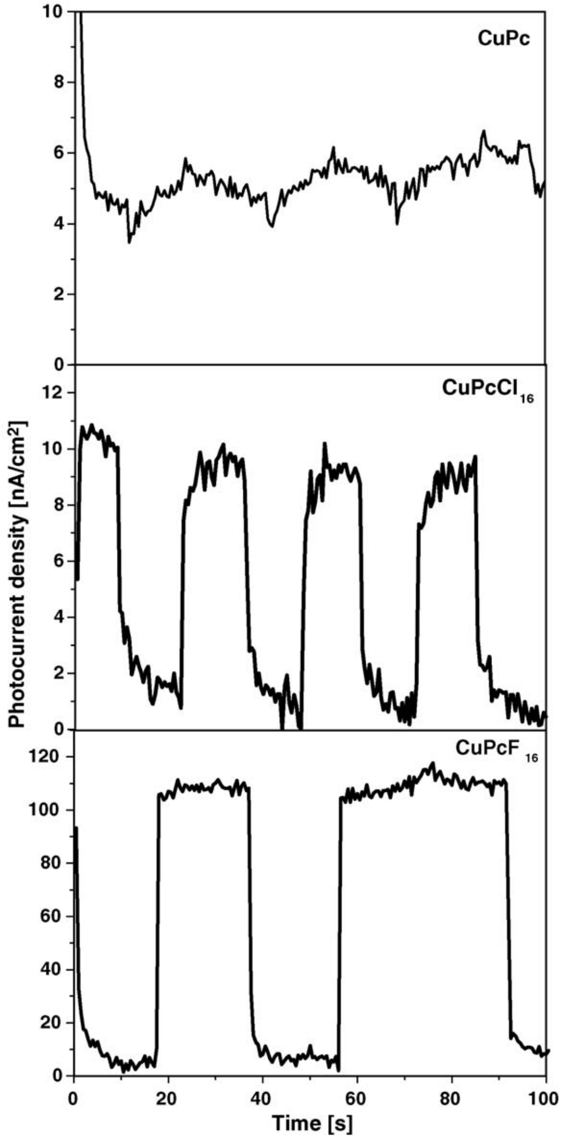

Fig. 5. Kinetics of photocurrent generation in the PEC with copper phthalocyanines in DMSO ($c = 1$ mM).

4. Discussion

Mesomeric, inductive and/or steric effects, named in the literature as resonance effects, occurring in fluorinated or chlorinated phthalocyanines are very fine phenomena and therefore they are rather difficult to be unambiguously recognized. In this paper we have tried to follow them by means of spectral and photoelectric studies.

We begin to address this problem with our spectroscopic results. All dyes studied in this paper are complexed with Cu and they differ one from each other with the substituted hydrogen atoms by electronegative atoms (16 fluorines or 16 chlorines) linked to the indole units. We will start our consideration with the changes observed in the absorption spectrum of $CuPcF_{16}$ with respect to the corresponding spectrum of CuPc (the latter one could be a standard dye without any substituent). We showed that the shapes and energetic positions in the absorption spectra depend on the kind of the external atoms (F or Cl). The fluorine or chlorine substituents cause a substantial decrease in the molar absorption coefficients. The shapes of $CuPcF_{16}$ and $CuPcCl_{16}$ spectra differ from those obtained for the standard CuPc. The differences are particularly observed in the position of the Soret bands and in their halfwidths (which are much broader) and in the bands which arrive beyond the wavelength of 700 nm. It could be assigned to the marked influence of the F and Cl atoms, which have ionic character. Thus, they are able to form some electrostatic bonds, which caused the increased number of the absorption bands. Moreover, the Q band for the $CuPcCl_{16}$ dye (659 nm) is shifted toward shortwavelength of about 14 nm with respect to the Q band of the maternal dye CuPc (673 nm). The spectral parameter changes for $CuPcF_{16}$ with respect to those corresponding to CuPc are much discrete when compared with the large spectral alteration observed for fluorinated $ZnPcF_{16}$ both in the band shapes and band positions [12]. Some changes can also be found in $CuPcCl_{16}$. In our consideration we have also to take into account a strong tendency of phthalocyanines to create aggregates reflected as a shift in absorption spectra. Nevertheless, in our spectroscopic experiments the dye concentration is rather low ($c = 10\,\mu$M) and DMSO, which protects against aggregation owing to its high polarity [22,26], was used as a solvent. Thus, we have every reason to believe that the observed changes in electronic properties are due to mesomeric effects rather than aggregation. Even though the observed changes in $CuPcF_{16}$ and $CuPcCl_{16}$ are not so huge as observed in $ZnPcF_{16}$ [12], they indicate both perturbation of electron density distribution and conjugation of the fluorine/chlorine electrons with the π-electrons in the macrocyclic system of the main dye core. Also, the longwavelength shifts observed in the dye photoacoustic spectra with respect to those of their counterpart CuPc confirm our suggestion about the occurrence of the resonance effects induced by the fluorine and chlorine presence.

Changes in electron density and electron conjugation after introducing heteroatoms are accompanied with alteration in photocurrent in the PEC based on the dyes. The electronegativity of the fluorine and chlorine atoms are obvious and reflects their inductive electron-withdrawing character. However, the unique photoelectric ability of fluorinated/chlorinated phthalocyanines monitored as photocurrent created in the PEC needs special comments. In our papers [12,27,31] we evidently showed the close correlation between the molecular structure of porphyrin/phthalocyanine dyes and their ability in photocurrent generation. For fluorinated $ZnPcF_{16}$ extreme enhancement of current generated in the PEC upon illumination was also observed [12]. $CuPcF_{16}$ also reveals highly intensive photocurrent (116 nA/cm^2) when compared with the standard CuPc (2 nA/cm^2), as shown in this paper. Peculiarities in $CuPcF_{16}$ photoconversion of light to electric energy may be concluded to originate from the combination of the inductive and mesomeric effects of the heteroatoms in substituted phthalocyanines. The changes in the triplet state behaviour upon the fluorine and chlorine atom linkage to the main molecular structure can also suggest the occurrence of a mesomeric effect. Fluorine and chlorine are rather electron withdrawing, but the resonance conjugative effects make them electron donating fragments which cause drastic changes in photoelectric behaviour. The question arrives with the stronger influence of the presence of the fluorine atoms on the photoelectric ability of $CuPcF_{16}$ when compared to that for $CuPcCl_{16}$. It could be explained by several factors, e.g.: differences in Pauling's electronegativities (4.0 and 3.0 for F and Cl, respectively), differences in the atomic radius values (42 and 79 pm for F and Cl, respectively), differences in the covalent radii (71 and 99 pm for F and Cl, respectively) and differences in electron configurations [35,36].

The final aspect of this paper is related to fluorine/chlorine steric effects. It was reported that the presence of heteroatoms in some porphyrin molecules or in molecular groups (e.g. alkyl chains) changed the fluorescence parameters (the fluorescence quantum yield, lifetime) [13]. Unfortunately, the dyes under investigation do not fluoresce, therefore we are not able to follow directly the effect of fluorination/chlorination on their first excited singlet states like in substituted phthalocyanines by fluorescence spectroscopy. For that reason we have done PAS and LIOAS experiments to get insight in triplet state population and triplet thermal relaxation decay and their alternation upon fluorine/chlorine substitutes. Bonett et al. indicated the effect of bromination on the intersystem crossing rate in some porphyrins [13]. Moreover, Türker [4] showed the effect of halogens on the charge distribution of zinc porphyrins by means of the semiempirical orbital calculations. From our PAS study we have evidently shown that global thermal relaxations with both singlet and triplet participation are not the same for all investigated dyes. Thus, the value of the TD parameter is rather low for CuPc when compared to that of the fluorinated/chlorinated dyes. Moreover, our LIOAS data showed an increase in the quantum yield formation of the triplet state for $CuPcF_{16}$ and $CuPcCl_{16}$ with respect to those in the parent CuPc. It could be assigned to the steric effects upon fluorination/chlorination. Bondi [37] and Wiliams and Houpt [38] reported that fluorination can also increase the steric size of alkyl groups. The steric effects are dependent on the nature of the process that determines the degree of coloumbic interaction between atoms and overlapping of van der Waals radii [8]. Thus we could expect the occurrence of steric effects in phthalocyanines in the presence of fluorine/chlorine attached to the π-electron macroring system. We can find the confirmation of the occurrence of the steric effects in the ϕ_T values and the sum of k_1 and k_2. The Φ_T value obtained for CuPc in this paper is 0.88 as usually obtained for many non-substituted porphyrin and phthalocyanine dyes investigated in some papers [26,31,32]. However, in fluorinated and chlorinated phthalocyanines ($CuPcF_{16}$, $CuPcCl_{16}$), Φ_T is drastically increased indicating the occurrence of the effect of fluorination/chlorination on the intersystem crossing rate.

With our LIOAS device we are not able to follow experimentally the decay time above 5 μs. It could be a reason why the sum of k_1 and k_2 does not reach unity. This result suggests that some thermal processes with the longer decay time with triplet state participation and/or other non-radiative deactivation processes should be taken into consideration: (i) creation of singlet oxygen, (ii) exothermic photochemical reactions, (iii) changes in the electron distribution in the molecular skeleton due to internal electron transfer, (iv) deformation in the molecular skeleton. Also radiative processes, such as phosphorescence, could participate in deactivation of the excited triplet state, but in our LIOAS experiment we observed photothermal processes.

The values for k_D taken as the difference of $1-(k_1+k_2)$ are found to be 0.24, 0.33 and 0.39 for CuPc, $CuPcCl_{16}$ and $CuPcF_{16}$, respectively (Table 2). This indicates that other processes mentioned above (i–iv) can take place in the investigated dyes, but with different effectiveness. Creation of singlet oxygen (i) cannot be excluded as to such a reaction is often reported for other phthalocyanine-like dyes. Since the singlet oxygen production is not very much sensitive to the presence of the substituents therefore, we can suppose that it affects all investigated dyes in the same degree [29]. Thus, the differences among the k_D values for the investigated CuPc, $CuPcF_{16}$ or $CuPcCl_{16}$ could be explained by the processes (ii–iv). If we take into consideration the rise of the k_D values for $CuPcCl_{16}$ and $CuPcF_{16}$ with respect to that for CuPc we cannot neglect some photochemical reactions (ii) in $CuPcF_{16}$ and $CuPcCl_{16}$ due to very high electronegativity of the F and Cl atoms. Thus, the difference in the k_D values for $CuPcF_{16}$ (0.39) and $CuPcCl_{16}$ (0.33) could be explained by the difference in F and Cl electronegativity.

Nevertheless, the highest k_D value for $CuPcF_{16}$ could also evidently indicate the changes in electron distribution in the molecular skeleton (iii) and conformational alteration in the dye molecules (iv). The point (iii) is confirmed by the change in the absorption features of this dye when compared to those of the parent CuPc. Moreover, the very huge rise in photocurrent created by $CuPcF_{16}$ in the PEC (with respect to that for the PEC with CuPc) is a great evidence of the occurrence of the steric and mesomeric effects in the fluorinated phthalocyanines ($CuPcF_{16}$). These effects cannot either be excluded in $CuPcCl_{16}$, although they are a little weaker (the k_D value for $CuPcCl_{16}$ is lower than that for $CuPcF_{16}$). Also, the presence of the Cl atoms in the phthalocyanine structure affects the photocurrent intensity much less spectacularly than that of the fluorinated $CuPcF_{16}$. The observed differences in fluorinated and chlorinated phthalocyanines could be explained by both the electronegativities of F and Cl and also by the more expanded molecular structure of $CuPcCl_{16}$ with respect to that of $CuPcF_{16}$ [36].

Summarizing, we showed that the spectroscopic behaviour and high photoactivity of $CuPcF_{16}$ in photocurrent creation could be assigned to the occurrence of the mesomeric and steric effects in the fluorine substituted dye. Mesomeric effect for $CuPcF_{16}$ was evidently proved by the high photocurrent generated when compared with the photocurrent in the PEC for CuPc, whereas the occurrence of the steric effect was showed with the LIOAS experiments even though it was not so spectacular. We also showed that fluorination rather than chlorination has a great influence on the photoactivity of the dye in photocurrent generation. It could be explained by the differences in F and Cl electronegativity and in the molecular size of $CuPcF_{16}$ and $CuPcCl_{16}$. We can rather exclude the influence of the inductive effect on photoelectric behaviour since we observed the rise of photocurrent in the PEC based on $CuPcF_{16}$/$CuPcCl_{16}$ with respect to CuPc (but not its decrease).

Our study seems to be essential in searching for very good dyes as photoconverters in organic photovoltaics and also in other fields of molecular optoelectronics. We have shown that $CuPcF_{16}$ could be potentially used as good photoconverter in organic photovoltaics due to its efficient photocurrent generation. Moreover, the high quantum yield of triplet state population indicates the advantage of $CuPcCl_{16}$ and $CuPcF_{16}$ in photodynamic therapy of cancer but not in diagnosis of cancer because the dyes presented in this paper do not show fluorescence.

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