# Spectroscopic study of electron and energy transfer in novel silicon phthalocyanine—boron dipyrromethene triads<sup>†</sup>

Eugeny A. Ermilov,\*<sup>ac</sup> Jian-Yong Liu,<sup>b</sup> Dennis K. P. Ng<sup>b</sup> and Beate Röder<sup>a</sup>

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Phthalocyanines (Pcs) and boron dipyrromethenes (BDPs) are two versatile classes of functional dyes suitable for design of artificial light harvesting and charge separation systems. In the present work, we report the results of photophysical investigations of two novel non-sandwich-type BDP-Pc heterotriads, in which two BDP or mono-styryl BDP moieties are linked to the central atom of a silicon(IV) phthalocyanine core (triad 4 and 5, respectively). It was found that the photophysical properties of the triads in toluene and N,N-dimethylformamide (DMF) are strongly affected by two different types of interaction between the BDP and the Pc parts, namely excitation energy transfer (EET) and photoinduced charge transfer (CT). The first process delivers the excitation to the first excited singlet state of the Pc-part upon initial BDP-part excitation. The probability of EET supersedes that of CT in toluene, whereas the latter transfer process dominates in BDP-part depopulation when triads are dissolved in polar DMF. The direct or indirect (via EET) population of Pc moiety is followed by the hole transfer to the charge-separated state in 4 (in DMF) and in 5 (in DMF and toluene). At the same time, it was found that CT is energetically unfavorable for the triad 4 in toluene upon excitation of the Pc-part. The charge-recombination in DMF occurs very fast with a decay time of 40 and 30 ps for 4 and 5, respectively, whereas toluene stabilizes the charge-separated state, prolonging the lifetime to 4.5 and 1.7 ns, respectively.

#### Introduction 1.

One of the most important strategies to provide clean and affordable solar energy consists of mimicking nature, in which efficient harvesting and conversion of sunlight occurs. Conversion of light to chemical potential energy in photosynthesis involves two basic photophysical processes: sunlight is absorbed by ensembles of light-harvesting chromophores and then the excitation energy is transported to a reaction center where a charge-separated state is generated by charge transfer (CT).<sup>1</sup> The transport mechanism is a singlet-singlet excitation energy transfer (EET) among the chromophores within the antenna system. The antenna is efficiently coupled to the reaction center which converts electronic excitation energy to chemical energy in the form of long-lived transmembrane charge separation via multistep CT processes. The functionality of the light-harvesting chromophores is determined by their strong absorption throughout the visible spectrum (in order to maximize sun light absorption) as well as high fluorescence quantum yields (maximizing the probability of excitation energy transfer to a reaction center).

Naturally occurring photosystems consist of chlorophylls, carotenes and quinones.<sup>2</sup> In the past, great efforts have been made to synthesize artificial systems mimicking the arrangement of chlorophylls and quinones. Various classes of compounds exhibiting similar redox and photophysical properties have been studied extensively leading to an enormous variety of photosynthetic model compounds. Examples are porphyrinquinone, porphyrin-fullerene, phthalocyanine-quinone and phthalocyanine-fullerene systems.<sup>3</sup> Also chlorophylls, carotenes, perylenes, and viologens were used as parts of such molecular systems.

The design of artificial light harvesting and charge separation systems requires the components to have high chemical stability, tuneable electronic and electrochemical properties, and a facile synthetic route. Phthalocyanines (Pcs)<sup>4</sup> and boron dipyrromethenes (BDPs)<sup>5</sup> are two versatile classes of functional dyes exhibiting these desired qualities. Efficient strategies for synthesis of both chromophore classes are well established and the photophysical properties of these compounds can also be tuned readily through chemical modification of their structures. Another advantage is that many of these chromophores are characterized by large extinction coefficients, high fluorescence quantum yields, reasonably long first excited singlet state lifetimes, and good solubility and stability in many solvent systems. These properties have led to different applications of Pcs and BDPs, for example, in optoelectronic devices<sup>6</sup> and as photosensitizes for photodynamic therapy, molecular labels for proteins and DNA<sup>8</sup> and laser dyes.<sup>9</sup>

Pcs show strong absorptions in the UV-Vis region (at ca. 350 and 670 nm), whereas BDPs exhibit large extinction

<sup>&</sup>lt;sup>a</sup> Institut für Physik, Photobiophysik, Humboldt-Universität zu Berlin, Newtonstr. 15, D-12489 Berlin, Germany.

E-mail · eugenv ermilov@charite de

<sup>&</sup>lt;sup>b</sup> Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong, China <sup>c</sup> Institut für Physiologie, Campus Benjamin Franklin,

Charité – Universitätsmedizin Berlin, Arnimallee 22, D-14195 Berlin, Germany

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Fig. 1 Structural formulas of BDP-SiPc triads (4 and 5) and the reference compounds 1-3.

coefficients at *ca.* 500 nm. Thus, a broad range of the visible spectrum could be covered when these functional dyes are coupled together. While a substantial number of conjugates of these chromophores with other photo and redox-active units such as porphyrins, fullerenes, carotenoids, anthraquinones, perylenediimides and ruthenium polypyridine complexes have been studied extensively,<sup>4,5,10</sup> to our knowledge, covalently-linked BDP-Pc arrays have not been reported so far.

Recently, we have prepared two novel BDP-Pc hetero-triads in which a silicon(*iv*) phthalocyanine (SiPc) core is substituted axially with two BDP or mono-styryl BDP (MS-BDP) moieties.<sup>11</sup> The structures of these triads as well as the model compounds are shown in Fig. 1. By means of steady-state and time-resolved optical spectroscopy, it was found that the photophysical properties of these triads in toluene are strongly affected by two different types of interactions between their parts, namely photoinduced CT and EET, and it was shown that the probability of these transfer processes depends on the axial substituents.<sup>11</sup> In the present paper, we report our further photophysical study of these triads in polar and nonpolar environments.

### 2. Experimental

#### 2.1 General

All the reactions were performed under an atmosphere of nitrogen. Tetrahydrofuran (THF), toluene and pyridine were distilled from sodium benzophenone ketyl, sodium and KOH, respectively. Toluene and dimethylformamide (DMF) used for photophysical measurements were of spectroscopic grade (Aldrich) and used without prior purification. All other solvents and reagents were of reagent grade and used as received. Chromatographic purifications were performed on silica gel (Macherey-Nagel, 70-230 mesh) columns with the indicated eluents.

#### 2.2 Absorption and steady-state fluorescence

All photophysical measurements were performed in DMF and in toluene of spectroscopic grade (Aldrich), which were used without further purification. The ground state absorption spectra were recorded using a commercial spectrophotometer Shimadzu UV-2501PC. Steady-state fluorescence spectra were measured in 1 cm × 1 cm quartz cells using a combination of a cw-Xenon lamp (XBO 150) and a monochromator (Lot-Oriel, bandwidth 10 nm) for excitation and a polychromator with a cooled CCD matrix as detector system (Lot-Oriel, Instaspec IV).<sup>12</sup> To obtain fluorescence quantum yields of compounds under investigation, the following substances were used as standards solutions of tetraphenylporphyrin (H<sub>2</sub>TPP) in DMF, Rhodamine 110 and Rhodamine 6G both in ethanol ( $\Phi_{fl}^{H_2TPP} = 0.11$ ,<sup>13</sup>  $\Phi_{fl}^{R110} = 0.94^{14}$  and  $\Phi_{fl}^{R6G} = 0.95$ ,<sup>15</sup> respectively)—and values were calculated according following expression (1):

$$\Phi_{\rm fl}^{\rm x} = \Phi_{\rm fl}^{\rm ref} \frac{S_{\rm fl}^{\rm x}}{S_{\rm fl}^{\rm ref}} \frac{\rm OD_{\rm ref}(\lambda_{\rm exc})}{\rm OD_{\rm x}(\lambda_{\rm exc})} \left(\frac{n_{\rm x}}{n_{\rm ref}}\right)^2, \tag{1}$$

where  $\Phi_{\rm fl}^x$ ,  $S_{\rm fl}^x$ ,  $OD_x(\lambda_{\rm exc})$  and  $\Phi_{\rm fl}^{\rm ref}$ ,  $S_{\rm fl}^{\rm ref}$ ,  $OD_{\rm ref}$  ( $\lambda_{\rm exc}$ ) are the fluorescence quantum yield, the integrated fluorescence intensity and the optical density at the excitation wavelength,  $\lambda_{\rm exc}$ , of a sample and a reference substance, respectively,  $n_x$  and  $n_{\rm ref}$  are the refractive index of the solvent used for the sample and the reference, respectively.

#### 2.3 Time-resolved fluorescence spectroscopy

Time correlated single photon counting (TCSPC) technique in combination with scanning of the detection wavelength was used to acquire decay associated fluorescence (DAF) spectra.<sup>16</sup> The experimental setup was previously described.<sup>17</sup> A pulsed, frequency doubled, linear polarized radiation of a Nd:VO<sub>4</sub> laser (Cougar, Time Bandwidth Products) with a wavelength of 532 nm, a pulse width of 12 ps, and a repetition rate of 60 MHz was used directly for excitation of the samples or to synchronously pump a dye laser (Model 599, Coherent) tunable in the range from 610 to 670 nm. For excitation of the samples of a Ti:sapphire laser (Coherent Mira 900, 405 nm, FWHM 200 fs, a repetition rate of 76 MHz) were used. Optical

density (OD) of the samples was less than 0.15 at the absorption band of lowest energy. Fluorescence was detected under a "magic" polarization angle<sup>18</sup> relative to excitation with a thermo electrical cooled micro channel plate (R3809-01, Hamamatsu). Detection wavelength was chosen by a computercontrolled monochromator (77200, Lot-Oriel). Electrical signals were processed by a PCI TCSPC controller card (SPC630, Becker & Hickl). The instrument response function was 42 ps, as measured at an excitation wavelength with Ludox. Data were analyzed by a home-made program by applying a variable projection algorithm<sup>19</sup> to the global fitting problem. The Nelder-Mead simplex algorithm<sup>20</sup> was used for optimization of the nonlinear parameters, and the support plane approach<sup>18</sup> to compute error estimates of the decay times. Decay times and time shift were linked through all measurements of one scan sampled every 3 nm.

### 2.4 Picosecond transient absorption spectroscopy

To measure transient absorption spectra, a white light continuum was generated as a test beam in a cell with D<sub>2</sub>O/H<sub>2</sub>O mixture using intense 25 ps pulses from a Nd<sup>3+</sup>:YAG laser (PL 2143A, Ekspla) at 1064 nm. Before passing through the sample, the continuum radiation was split to get a reference spectrum. The transmitted as well as the reference beams were focused into two optical fibers and were recorded simultaneously at different traces on a CCD-matrix (Lot-Oriel, Instaspec IV). Tunable radiation from an OPG/OPA (Ekspla PG 401/SH, tuning range 200-2300 nm) pumped by third harmonic of the same laser was used as an excitation beam. The mechanical delay line allowed the measurement of light-induced changes of the absorption spectrum at different delays up to 15 ns after excitation. The OD of all samples was 1.0 at the maximum of the absorption band of lowest energy. Analysis of experimental data was performed using the compensation method.21

### 2.5 Electrochemical study

Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a platinum-sphere working electrode, a platinum-plate counter electrode, and a silver-wire pseudo-reference electrode. Typically, a 0.1 M solution of  $[Bu_4N][PF_6]$  in DMF containing the sample was purged with nitrogen for 15 min, then the voltammograms were recorded at ambient temperature. Potentials were referenced to saturated calomel electrode (SCE) using ferrocene as an internal standard ( $E_{1/2} = +0.38$  V vs. SCE).

## 3. Results

Treatment of the BDP-appended phenol  $2^{22}$  with the commercially available silicon(iv) phthalocyanine dichloride (SiPcCl<sub>2</sub>) in the presence of pyridine gave the bis(BDP) substituted phthalocyanine 4 in 34% yield. The MS-BDP analogue 5 was synthesized in a similar manner using phenol 3 as a starting material, which was prepared by Knoevenagel condensation of 2 with 3,4,5-trimethoxybenzaldehyde according to a previously described procedure.<sup>23</sup> The reference compound 1 was prepared by treating SiPcCl<sub>2</sub> with methyl

Table 1 Electrochemical properties of the reference compounds

Compound	$E^{ m oxd}/{ m V}$	$E^{ m red}/ m V$	
1	1.06 (irrev)	-0.57	
2	1.05 (irrev)	-1.21	
3	0.88 (irrev)	-1.05	

4-hydroxybenzoate in the presence of pyridine. The experimental details including full characterization data of these compounds are given in ref. 11.

The electrochemical properties of the reference compounds 1–3 were studied by cyclic voltammetry and differential pulse voltammetry in DMF. All of them exhibited a quasi-reversible reduction and an irreversible oxidation, of which the potentials are summarized in Table 1. The conjugates 4 and 5 had limited solubility in DMF. Hence, their electrochemical data were not measured.

Fig. 2 shows the ground state absorption spectra of compounds 1-5 in DMF. The corresponding spectra in toluene are shown in the ESI.<sup>†</sup> The absorption maxima for the triads 4 and 5 as well as the reference compounds 1, 2, and 3 in both DMF and toluene are given in Table 2. The absorption spectra of the triads are essentially the superposition of the absorption bands of the corresponding components and have three pronounced peaks: one with a maximum at 683 nm (belongs to Q-absorption band of SiPc 1), another one at 500 nm for the triad 4 (belongs to absorption of BDP 2) or 576 nm for the triad 5 (corresponds to the absorption of MS-BDP monomer 3), and the third band, located in the blue spectral region at around 350 nm, is a superposition of the B-band absorption of 1 and 2 (for the triad 4) or 1 and 3 (for the triad 5), respectively. Due to the absence of spectral shifts of the absorption bands of the triads compared with those of the corresponding reference compounds, the BDP and Pc parts of the triads in the ground state are considered as electronically decoupled.

Steady-state fluorescence spectra of the reference compounds **1–3** are shown in Fig. 3. The fluorescence maximum of **1** lies at 688 nm in toluene and undergoes a small bathochromic shift to 689 nm in polar DMF (Table 2). The fluorescence quantum yield of **1** has a value of 0.47 in DMF and 0.60 in toluene, as measured using a solution of H<sub>2</sub>TPP in DMF as the reference  $(\Phi_{\rm fl}^{\rm T2PP} = 0.11)^{13}$ . The fluorescence bands of compounds **2** and **3** are located at 510 and 580 nm in DMF and at 512 and 583 nm in toluene, respectively. The fluorescence quantum yield of **2** was calculated to be 0.32 (DMF) and 0.55 (toluene) using a solution of Rhodamine 110 in ethanol as the reference



Fig. 2 UV/Vis absorption spectra of 1, 2 and 4 (a), and 1, 3 and 5 (b) in DMF.

Compound	Solvent	$\lambda_{ m abs}/ m nm$	$\lambda_{\rm fl}/{ m nm}$		$\Phi_{ m fl}$	
			BDP-part excitation	Pc-part excitation	BDP-part excitation	Pc-part excitation
1	Toluene	358, 683	_	688	_	0.60
	DMF	355, 683		689		0.47
2	Toluene	503	512		0.55	_
	DMF	500	510	_	0.32	_
3	Toluene	572	583		0.78	_
	DMF	567	580		0.48	_
4	Toluene	358, 500, 683	N.d., <sup><i>a</i></sup> 687 <sup><i>b</i></sup>	687	N.d., $^{a}$ 0.35 $^{b}$	0.60
	DMF	354, 500, 683	$510,^{a} 689^{b}$	689	$0.005^{a}, 0.006^{b}$	0.016
5	Toluene	352, 570, 683	588, <sup>a</sup> 686 <sup>b</sup>	686	$0.003^{a}, 0.002^{b}$	0.003
	DMF	355, 570, 683	$580^{a}, 689^{b}$	689	$0.004,^{a} 0.003^{b}$	0.012
<sup><i>a</i></sup> BDP-part en	nission. <sup>b</sup> Pc-r	part emission.				

**Table 2** Absorption and fluorescence maxima,  $\lambda_{abs}$  and  $\lambda_{fl}$ , and fluorescence quantum yields,  $\Phi_{fl}$ , of 1–5 in DMF and in toluene



**Fig. 3** Steady-state fluorescence spectra: a—1, 2 and 4 in DMF, excitation at 500 nm; b—1 and 4 in toluene, excitation at 500 nm; c—1, 3 and 5 in DMF, excitation at 567 nm; d—1 and 5 in DMF, excitation at 670 nm.

 $(\Phi_{\rm fl}^{\rm R110} = 0.94).^{14}$  The values are lower than those of **3** (0.48 and 0.78, respectively, see Table 2), which were measured with respect to Rhodamine 6G in ethanol  $(\Phi_{\rm fl}^{\rm R6G} = 0.95).^{15}$ 

Due to the fact that the absorption bands of the Pcand BDP-parts of the triads are well separated, both the steady-state fluorescence spectra with selective excitation of the BDP or Pc moieties were recorded. Upon excitation of the triads 4 and 5 at the BDP-part absorption, two effects were observed in both solvents: fluorescence is strongly reduced compared to the reference compounds 2 and 3, respectively (for the triad 4 in toluene no fluorescence even of BDP was detected, Fig. 3b), and peak of SiPc fluorescence with maximum at around 689 nm appears (see Fig. 3a-c). The calculated fluorescence quantum yields are summarized in Table 2. It is seen that for both triads in polar DMF, the fluorescence quantum yields of the BDP- as well as Pc-part emission are much lower compared to those of the reference compounds. While in nonpolar toluene similar results were observed also for the triad 5 (see Table 2), a strong peak of the Pc-part fluorescence with a fluorescence quantum yield of 0.35 was detected upon excitation of the triad 4 at 500 nm.

With excitation at 670 nm, where only the Pc-part absorbs light, the fluorescence of the triads in both solvents has only one band similar to that of the reference SiPc 1 (as an example, the normalized fluorescence spectra of 1 and 5 in toluene are shown in Fig. 3d). In DMF, the fluorescence of both triads is much weaker compared to that of 1: the fluorescence quantum yields were estimated to be only 0.016 and 0.012 for the triads 4 and 5, respectively (see Table 2). It should be mentioned that these values are higher than those determined for the Pc-part fluorescence quantum yield of the fluorescence quantum of the fluorescence quantum yield of the triad 4 in toluene was observed when the Pc-part was selectively excited ( $\Phi_{\rm fl} = 0.60$ , similar to that of the reference 1), whereas a 200-times lower value was measured for the triad 5 ( $\Phi_{\rm fl} = 0.003$ , see Table 2) in the same solvent.

According to the above results, one can make the following preliminary conclusions: (i) the appearance of the Pc-part fluorescence with selective excitation of the BDP-part of the triads in both solvents is an indicator of EET from an initially photoexcited energy donor (BDP) to an energy acceptor (SiPc in its ground state). This conclusion is also supported by the strong quenching of the BDP-part fluorescence; (ii) the fluorescence quantum yield of the Pc-part emission was lower when the Pc moiety was excited indirectly (via energy transfer) compared to the case of direct excitation (see Table 2). This indicates a competition between energy transfer and an additional efficient deactivation process of the first excited singlet state of the BDP moieties in the triads; (iii) for both triads in DMF as well as the triad 5 in toluene, there is a quenching process of the first excited singlet state of the Pc moiety resulting in a strong reduction of its fluorescence quantum yield compared to that of the reference SiPc 1.

The time evolution of fluorescence was investigated by TCSPC technique. The fluorescence decays of all reference compounds 1–3 were found to be mono-exponential in both solvents and the estimated fluorescence lifetimes are summarized in Table 3. The solvent polarity has a negligible influence on the lifetimes of the first excited singlet state of compounds 1 and 3, whereas the fluorescence of 2 decays two times faster in DMF than in toluene.

The fluorescence decay of the triads was measured upon selective excitation of the BDP- or Pc-part. Excitation of the triad 4 in DMF at 400 nm and monitoring the fluorescence

		$ au_{ m fl}/ m ns$			
Compound	Solvent	For BDP-part emission	For Pc-part emission		
1	DMF	_	$5.35\pm0.01$		
	Toluene	_	$5.07\pm0.01$		
2	DMF	$1.69 \pm 0.01$	_		
	Toluene	$3.03\pm0.01$	_		
3	DMF	$3.55\pm0.01$	_		
	Toluene	$3.46 \pm 0.01$	_		
4	DMF	$(20 \pm 2) \times 10^{-3}$	$0.14\pm0.01$		
			$0.40\pm0.01$		
	Toluene	N.d.	$5.20\pm0.01$		
5	DMF	$(30 \pm 5) \times 10^{-3}$	$(65 \pm 5) \times 10^{-3}$		
			$0.54 \pm 0.02$		
	Toluene	$< 1 \times 10^{-2}$	$(15 \pm 2) \times 10^{-3}$		

Table 3Fluorescence lifetimes of the triads 4 and 5 as well as thereference compounds 1, 2 and 3 in DMF and toluene

signal at 510 nm (maximum of the BDP-part fluorescence, see Fig. 3a) resolves fast mono-exponential decay with a fluorescence lifetime,  $\tau_{\rm fl}$ , of 20  $\pm$  2 ps. At the same time fluorescence was detected at 690 nm, where the Pc-part gives dominant contribution (Fig. 3a) and decays bi-exponentially with decay times of 140 and 400 ps, both having practically equal amplitude. Similar decay times were resolved when the triad **4** was selectively excited at Pc-part absorption ( $\lambda_{\rm exc} = 614$  nm). It should be mentioned that both decay times belong to the fluorescence from the first excited singlet state of the Pc moiety, which was supported by the decay-associated fluorescence (DAF) spectra of the triad **4** in DMF (see Fig. 4a).

In good agreement with the results of steady-state measurements, no fluorescence signal due to BDP was detected when the triad **4** in nonpolar toluene was excited at the BDP-part absorption. However, an emission at 690 nm (maximum of the Pc-part fluorescence, see Fig. 3a) was seen which has a monoexponential decay with a lifetime of  $5.20 \pm 0.01$  ns. This decay time is similar to that of the reference compound **1**, supporting the conclusion that no quenching of the Pc-part of the triad **4** occurs in toluene. The same fluorescence decay time of  $5.20 \pm 0.01$  ns was resolved upon excitation of the triad **4** at 615 nm (Pc-part excitation) and monitoring at 690 nm.

The DAF spectra of the triad **5** in DMF excited at 532 nm (BDP-part excitation) are shown in Fig. 4b. Analysis of the fluorescence decay data reveals one decay component of the BDP-part with a decay time of  $30 \pm 5$  ps, whereas the population of the first excited singlet state of Pc moiety decays bi-exponentially: two DAF spectra with decay times of  $65 \pm 5$  ps and  $540 \pm 20$  ps were resolved, and the latter has a 2.5 times lower amplitude compared to that of the fast component (Fig. 4b). In the case of Pc-part selective excitation ( $\lambda_{exc} = 615$  nm), the bi-exponential character of the time-resolved fluorescence decay was measured with lifetimes of  $58 \pm 5$  ps and  $540 \pm 10$  ps (the corresponding DAF spectra are shown in the ESI†).

For the triad **5** in toluene, the decay of the BDP-part fluorescence was found to be very fast ( $\tau_{\rm fl} < 10$  ps, the exact value of the decay time was not determined due to the limited time resolution of the experimental setup). The fluorescence



Fig. 4 Decay-associated fluorescence spectra: a—triad 4 in DMF, excitation at 614 nm; b—triad 5 in DMF, excitation 532 nm. Normalized amplitudes are given in insert.

decay of the Pc-part (excited directly at 615 nm, or indirectly *via* EET from the BDP-part) was fitted monoexponentially with a decay time of  $15 \pm 5$  ps, contrary to the long decay time measured for the triad **4** in toluene (5.2 ns, Table 3).

To obtain information about the non-fluorescent intermediates and the recovery of the ground state population after photoexcitation, the transient absorption spectra of these compounds were also recorded. As expected, the recovery of the ground state for all the reference compounds was found to be monoexponential with characteristic times similar to the above measured fluorescence decay times. Using the compensation method,<sup>21</sup> the intersystem crossing (ISC)  $S_1 \rightarrow T_1$  quantum yields,  $\Phi_{\rm ISC}$ , were estimated to be  $0.34 \pm 0.03$  (in DMF) and  $0.32 \pm 0.03$  (in toluene) for SiPc 1, and 0 and 0.02 for 2 and 3, respectively, in both solvents.

The transient absorption spectra of the triads 4 and 5 in DMF at BDP- as well as Pc-part excitation are shown in Fig. 5. Both triads show strong ground state bleaching of the Pc moiety at around 690 nm independent of the excitation wavelength used. Furthermore, even at Pc-part excitation, the negative  $\Delta OD$  signal with maximum at 500 and 560 nm for 4 and 5, respectively, was observed (see Fig. 5). The ground state bleaching originates from the BDP-part of the triads, apparent from its spectral position and shape. It is worth noting, that EET from the initially excited Pc moiety to the BDP part of the triads is energetically unfavorable (the energy of  $S_1 \rightarrow S_0$ transition for SiPc is 1.81 eV, whereas S<sub>0</sub>-S<sub>1</sub> energy gap has a value of 2.45 and 2.16 eV for BDP-part of 4 and 5, respectively). Moreover, a newly induced absorption band appears at around 580 nm, which is assigned to the absorption of the radical anion SiPc<sup>•-</sup> of the charge separated state.<sup>17,24</sup>



Fig. 5 Transient absorption spectra of the triads 4 (a) and 5 (b) in DMF at BDP- (line) and Pc- (points) part excitation.

Control experiments verified that none of the reference compounds exhibits this feature alone.

For the triad 4, it was found that at BDP-part excitation the recovery of the ground state population of the BDP moiety occurs monoexponentially with a characteristic time of  $40 \pm 5$  ps. This value is two times longer compared to the lifetime of the BDP's first excited singlet state as found in time-resolved fluorescence measurements. The compensation of the  $\Delta$ OD signal in the spectral range of the Pc-part absorption shows biexponential decay of the ground state bleaching with characteristic times of  $40 \pm 5$  and  $500 \pm 100$  ps. The former, which has a higher contribution, is much faster than the fluorescence decay times for 4 being excited at 614 nm.

At Pc-part excitation, the recovery of the Pc ground state population is much slower compared to the above-discussed case of BDP-part excitation (see Fig. 6). It was fitted by a biexponential function with the characteristic times of  $130 \pm 20$  and  $410 \pm 100$  ps having practically equal amplitudes. Nevertheless, no remaining ground state bleaching signal was observed at delay time of 15 ns resulting in an ISC quantum yield value,  $\Phi_{\rm ISC} = 0$  (the same result was obtained at BDP-part excitation, too).

It was found that for the triad **5** in polar DMF, the recovery of BDP as well as Pc ground state population occurs monoexponentially with a characteristic time of  $35 \pm 5$  ps upon excitation at 530 nm. This value is close to the lifetime of the BDP-part fluorescence ( $\tau_{\rm fl} = 30 \pm 5$  ps, see Table 3), but shorter than the fast decay component of the Pc-part emission ( $65 \pm 5$  ps). With excitation at the Pc-part, the ground state population of BDP-part recovers monoexponentially with a lifetime of  $50 \pm 20$  ps. The same value was obtained when the



**Fig. 6** Ground state bleaching (Pc-part) of the triad **4** in DMF at BDP- and Pc-part excitation.

compensation of  $\Delta OD$  signal was done at the Pc-part absorption. Moreover, an additional component of 600  $\pm$  100 ps with a much lower contribution was also resolved for Pc-part ground state bleaching.

Upon excitation at 480 nm (BDP part), the ground state bleaching of both BDP- and Pc- parts of the triad **4** solved in nonpolar toluene was observed (Fig. 7a), but one should remember that depopulation of the first excited singlet state of the BDP moiety in the triad **4** occurs extremely fast (no fluorescence was seen from the initially excited BDP). At the same time, the bleaching of BDP ground state is visible even at a delay time of 4 ns after photoexcitation. Moreover, we should emphasize that only EET from the initially photoexcited BDP part to the SiPc moiety in its ground state will result in fast recovery of the BDP ground state. Thus one can conclude that before returning to the BDP ground state after photoexcitation, energy is "stored" in a long-lived dark state, which could be a charge-separated (CS) state.

Excitation of the triad **4** at 630 nm showed that no bleaching of the BDP ground state occurs (see Fig. 7b). The recovery of the Pc ground state as well as decay of the transient amplification signal (its intensity is proportional to the population of the first excited singlet state of the Pc moiety) follow a monoexponential manner with a characteristic time of 5.2 ns at BDP- as well as Pc-part excitation. The same decay time was found for the Pc-part fluorescence of the triad **4** in toluene in time-resolved fluorescence experiments.

The ISC quantum yield,  $\Phi_{ISC}$ , was calculated to be 0.32 at BDP- as well as at Pc-part excitation. The same value was estimated for the reference SiPc compound **1** in toluene.

The transient absorption spectra of the triad 5 in toluene are similar to those observed in DMF (the spectra are shown in the ESI<sup>†</sup>). Independent of the excitation spectral position, a strong induced absorption band with maximum at around 580 nm (this band belongs to the SiPc<sup>•–</sup> radical anion) as well as a negative  $\Delta$ OD signal with maximum at 560 nm (bleaching of the ground state absorption of the BDP moiety) were observed.

It was found that the ground state depletion of the SiPc moiety recovers monoexponentially with a characteristic time of  $1.7 \pm 0.1$  ns in both cases of excitation. At the same time, no transient amplification of probe light was observed in the spectral region of Pc-part. It means that depopulation of the Pc first excited singlet state occurs very fast (as it was found by time-resolved fluorescence measurements), but recovery of its ground state population is relatively slow due to the fact that excitation energy is stored in a "long-lived" intermediate state.



Fig. 7 Transient absorption spectra of the triad 4 in toluene at BDP- (a) and Pc- (b) part excitation at different delay times.

### 4. Discussion

The absorption and fluorescence spectra of both the triads **4** and **5** are well described as a superposition of the spectra of the corresponding components in polar as well as nonpolar solvents (see Fig. 2 and 3). These observations indicate that the BDP and Pc moieties within the triads do not couple in the ground state as well as in the first excited singlet state. The edge-to-face linkage also hinders planar stacking of the chromophores in the triads. Therefore, the solvent polarity only has a minor influence on the molecular geometry, thus allowing a better comparison of the transfer coupling coefficients.

To explain the results obtained, two different types of interaction between the BDP and Pc moieties should be taken into consideration, namely EET and photoinduced CT. It has been shown that upon excitation at the BDP-part of the triads, the fluorescence of the Pc-part appears. Hence, the existence of EET between the photoexcited BDP moiety and the Pc-part in its ground state is expected.

A Förster mechanism of EET between the initially photoexcited BDP-part and the Pc moiety in its ground state was assumed based on the following reasons: (i) it is well known that exchange mechanism of EET dominates over Förster one if the Coulomb part of the matrix element of perturbation to the Hamiltonian is much lower compared to the exchange term. This is possible, for example, when EET involves spin-flip transitions of the donor and acceptor molecules (one example is triplet-triplet EET). In case of BDP-Pc triads spin-allowed singlet-singlet EET takes place between BDPand Pc-parts. (ii) If the exchange mechanism of EET is dominant, there is usually a small spectral overlap between the donor's fluorescence emission and the acceptor's absorption. However, this is not the case for the triads. (iii) For efficient exchange energy transfer, an indispensable condition is an overlap of the electron clouds of the participating molecules. Otherwise, the probability of exchange EET falls rapidly with increasing distance between the donor and acceptor molecules. The separation between BDP and Pc moieties was found to be quite short (6 Å estimated by the HyperChem program package).<sup>25</sup> However, the covalent linkage prevents a close contact or staking of the planar chromophores within the triads, allowing them to orient in an almost orthogonal manner. Thus it is expected that the probability of exchange EET in the case of BDP-Pc triads is small. Of course, the exchange EET could also be an additional mechanism (besides Förster EET) involved in depopulation of the first excited

singlet state of the BDP-part and excitation of the Pc-part of the triads, but according to above arguments, we believe that the FRET is a major mechanism of energy transfer in BDP-Pc triads.

In order to estimate the probability of EET between the initially photoexcited BDP-part and the Pc moiety in its ground state, the Förster radii,  $R_0$ , for the triads were calculated using the well-known expression:<sup>26,27</sup>

$$R_0^6 = \frac{9000(\ln 10)\Phi_{\rm fl}}{128\pi^5 n^4 N_{\rm a}} \int I_{\rm fl}^n(\tilde{\nu})\varepsilon(\tilde{\nu})\frac{d\tilde{\nu}}{\tilde{\nu}^4}, \qquad (2)$$

where n is the refractive index of used solvent (1.43 for DMF and 1.49 for toluene);  $\Phi_{\rm fl}$  is the fluorescence quantum yield of a donor in absence of an acceptor (i.e. the value of the reference compound 2 in case of the triad 4 or the value of the reference compound 3 in case of the triad 5);  $N_a$  is the Avogadro's number;  $\varepsilon(\tilde{\nu})$  is the molar absorbance of the Pc-part at wavenumber  $\tilde{\nu}$  and  $I_{\rm fl}^n(\tilde{\nu})$  is the normalized fluorescence spectrum of the BDP-part. It is noted that the orientation factor was excluded from the Förster radius calculation. For the triad 4, the value of  $R_0$  was estimated to be 34 Å in DMF and 33 Å in toluene, whereas a better overlap between the fluorescence spectrum of an energy donor (MS-BDP) and the absorption spectrum of an energy acceptor (SiPc) results in much higher values of Förster radius for the triad 5 (67 Å and 65 Å in DMF and toluene, respectively). These values are much larger than the center-to-center distance between the donor and acceptor suggesting the presence of an efficient energy transfer channel from the BDP- to the Pc-part.

As it was shown above, a strong induced absorption band with maximum at around 580 nm appears during picosecond pump–probe investigations of the triads (see Fig. 5 and 7a). According to the data reported in literature,<sup>17,24</sup> this band could be assigned to the induced absorption of SiPc<sup>•–</sup> radical anion. In order to prove it, the free energy of charge separation was calculated using the Rehm–Weller<sup>28,29</sup> eqn (3):

$$\Delta G_{0}^{\mathrm{D}(\mathrm{A})} = e \left[ E^{\mathrm{oxd}}(\mathrm{D}/\mathrm{D}^{+}) - E^{\mathrm{red}}(\mathrm{A}/\mathrm{A}^{-}) \right] - E_{0,0}^{\mathrm{D}(\mathrm{A})} - \frac{e^{2}}{4\pi\varepsilon_{0}\varepsilon_{\mathrm{s}}R_{\mathrm{D}\mathrm{A}}} + \frac{e^{2}}{8\pi\varepsilon_{0}} \left[ \frac{1}{r_{\mathrm{D}^{+}}} + \frac{1}{r_{\mathrm{A}^{-}}} \right] \left[ \frac{1}{\varepsilon_{\mathrm{s}}} - \frac{1}{\varepsilon_{\mathrm{ec}}} \right],$$
(3)

where  $\Delta G_0^{D(A)}$  is the free energy of charge-separation (in electron volts) with selective excitation of an electron donor D (BDP), or an electron acceptor A (SiPc);  $E_{0,0}^{D(A)}$  is the energy

of  $S_0 \rightarrow S_1$  transition of the donor or acceptor;  $R_{DA}$  is the separation distance between the donor and acceptor moieties of a triad. Electrostatic interaction of the uprising ions is considered by the separation distance R of the ions, and  $\varepsilon_s$  is the dielectric constant of the solvent in which spectroscopic measurements were performed (37 for DMF and 2.4 for toluene). An additional term accounts for the different dielectric constant  $\varepsilon_{ec}$  of the solvent used for the electrochemical studies (DMF) compared to that for the spectroscopic measurements. It also accounts the effective radii of the cation  $(r_{D+})$  and the anion  $(r_{A-})$  radical. As usual,  $\varepsilon_0$  is the vacuum permittivity and *e* is the charge of the transferred electron.

#### Triad 4

a

BDP-SiPc-BDP\* (2.45 eV)

For the triad 4, the following parameters were used in the calculations:  $E^{\text{oxd}} = 1.05 \text{ V}, E^{\text{red}} = -0.57 \text{ V}, E^{\text{D}}_{0,0} = 2.45 \text{ eV},$  $E_{0,0}^{A} = 1.81 \text{ eV}, R_{DA} = 6 \text{ Å}, r_{D^+} = 3 \text{ Å}, r_{A^-} = 4.6 \text{ Å}.$  In polar DMF, the value of  $\Delta G_0^{\rm D}$  was found to be -0.83 eV for BDP-part excitation, whereas for Pc-part excitation  $\Delta G_0^A = -0.19$  eV. As  $\Delta G$  exhibits a negative value, electron transfer occurs when either the BDP- or Pc-part of the triad is excited. A chargeseparated state has energy of 1.62 eV and an energy diagram of the triad 4 in DMF is presented in Fig. 8a.

The recovery of the ground state population of the BDP-part after it was selectively excited occurs monoexponentially with a characteristic time of 40  $\pm$  5 ps, as found by picosecond

*k*<sub>EET</sub>

BDP-SiPc\*-BDP (1.81 eV)

 $k_0^{BDP}$ BDP-Pc\*-BDP\*+ (1.62 eV)  $k_0^{Pc}$  $k_{CR}$ BDP-SiPc-BDP BDP-SiPc-BDP\* (2.45 eV) h  $k_{CT}^{BDF}$  $k_{EET}$ BDP-Pc\*-BDP\*+ (2.16 eV) BDP-SiPc\*-BDP (1.81 eV)  $k_0^{BDF}$  $k_0^{Pc}$  $k_{CR}$ BDP-SiPc-BDP

Fig. 8 Scheme of energy levels and transitions between them for the triad 4 in DMF (a) and in toluene (b).

transient absorption spectroscopy (ps-TAS). It should be mentioned that this time is two times longer compared to the depopulation time of the BDP first excited singlet state, and was therefore associated with the lifetime of the created CS state (the rate of charge recombination,  $k_{CR}$ , was found to be  $2.5 \times 10^{10} \text{ s}^{-1}$ ).

At the same time, the decay of the ground state bleaching signal in the spectral range of the Pc-part absorption has a biexponential character with lifetimes of 40  $\pm$  5 ps and  $500 \pm 100$  ps, and the latter decay component has a much lower contribution. It is worth noting that the depopulation of the Pc first excited singlet state occurs much slower compared to the above mentioned 40 ps. It means that the ground state of the Pc-part is recovered mostly due to charge recombination (CR) followed by the photoinduced CT process:  $BDP^*-SiPc-BDP \rightarrow BDP^{\bullet^+}-SiPc^{\bullet^-}-BDP \rightarrow BDP-SiPc-BDP$ , without touching "long-lived" first excited singlet state of the Pc-part (e.g. BDP\*-SiPc-BDP  $\rightarrow$  BDP-SiPc\*-BDP  $\rightarrow$ BDP-SiPc-BDP, or BDP\*-SiPc-BDP  $\rightarrow$  BDP-SiPc\*-BDP  $\rightarrow$  $BDP^{\bullet^+}$ -SiPc $\bullet^-$ -BDP  $\rightarrow$  BDP-SiPc-BDP). Thus, the photoinduced CT is the dominant depopulation process of the first excited singlet state of the BDP-part of the triad 4 in polar DMF.

This conclusion is supported by steady-state fluorescence measurements. In fact, one can carry out simple estimations: at Pc-part excitation, the fluorescence quantum yield of the triad could be expressed as  $\Phi_{\mathrm{fl}}^{\mathrm{Pc}}(\mathrm{Pc}\text{-part excitation}) = \frac{k_{\mathrm{fl}}^{\mathrm{rc}}}{\sum_{i}k_{i}}$ where  $k_{\rm fl}^{\rm Pc}$  is the fluorescence rate,  $\sum_{i} k_i$  is the sum of all deactivation processes of the first excited singlet state of the Pc-part (one should remember that the BDP-part of the triad 4 does not have fluorescence when the Pc-part is selectively excited). The fluorescence quantum yield of the Pc-part emission at BDP-part excitation could be calculated as

$$\Phi_{\mathrm{fl}}^{\mathrm{Pc}}(\mathrm{BDP}\text{-part excitation}) = \Phi_{\mathrm{EET}} \frac{k_{\mathrm{fl}}^{\mathrm{Pc}}}{\sum_{i} k_{i}}$$
$$= \Phi_{\mathrm{EET}} \Phi_{\mathrm{fl}}^{\mathrm{Pc}}(\mathrm{Pc}\text{-part excitation}),$$
(4)

where  $\Phi_{\text{EET}} = \frac{k_{\text{EET}}}{k_{\text{EET}} + k_{\text{CT}}^{\text{BDP}} + 1/\tau_0^{\text{BDP}}}$  is the quantum yield of EET,  $k_{\text{EET}}$ ,  $k_{\text{CT}}^{\text{BDP}}$  are the rates of the energy and charge transfer,

respectively. Using the experimental data in Tables 2 and 3, it can be seen readily that  $\Phi_{\rm EET} \approx 0.38$ ,  $k_{\rm EET} \approx 0.6 k_{\rm CT}^{\rm BDP}$ , and  $k_{\rm CT}^{\rm BDP} = 3.1 \times 10^{10} \, {\rm s}^{-1}.$ 

Excitation of the triad 4 at Pc-part absorption and compensation of the ground state bleaching has shown that the recovery of the ground state population follows the kinetic of the Pc first excited singlet state depopulation. If one takes into account that the above estimated lifetime of the CS state is only 40 ps, and CT is a dominant deactivation process of  $S_1$  state population of the Pc moiety, this result is clearly understandable.

For the triad 4 in nonpolar toluene, the estimation of the free energy of charge separation gives negative value at BDP-part excitation ( $\Delta G_0^{\rm D} = -0.29$  eV), whereas for Pc-part excitation  $\Delta G_0^A = 0.35$  eV. Thus, photoinduced CT is an energetically favorable process only at BDP-part excitation.

A charge-separated state has energy of 2.16 eV, which lies high above the first excited singlet state of SiPc moiety, and an energy diagram of the triad **4** in toluene is presented in Fig. 8b. It should be mentioned that for nonpolar solvents, the influence of the radii of ions and the center-to-center distance of the electron donor and acceptor on a calculated value of  $\Delta G_0$ increases dramatically due to the small values of the dielectric constants. Since determination of  $r_{D+}$  and  $r_{A-}$  as well as  $R_{DA}$ is quite erroneous and contains a lot of insecurities, the values determined by eqn (3) are just a very rough estimation. Nevertheless, the experimental data support the above estimations, since no quenching of the first excited singlet state of the Pc moiety was observed, but SiPc<sup>•-</sup> induced absorption band appears upon BDP-part excitation (see Fig. 7).

Comparing the fluorescence quantum yield values of the Pc-part fluorescence at BDP- and Pc-part excitation, and carrying out similar calculations described above, it is easy to get that  $\Phi_{\text{EET}} \approx 0.57$ , and the rate of the photoinduced CT  $k_{\text{CT}}^{\text{BDP}} \approx 0.76k_{\text{EET}}$ . Interestingly, in nonpolar solvent the energy transfer becomes a dominant process in depopulation of the first excited singlet state of the BDP moiety, which is in contrast to the situation in polar DMF where probability of EET is lower compared to CT. Due to the fact that the time resolution of our experimental setups was not sufficient to resolve ultra fast decay of BDP-part fluorescence, the estimation of EET and CT rates was not done, but they are surely faster in DMF. The highest limit for EET rate could be obtained using the calculated Förster radius,  $R_0$ , value and the simple expression:

$$k_{\text{EET}} = \frac{1}{\tau_0^{\text{BDP}}} k^2 \left(\frac{R_0}{R_{\text{DA}}}\right)^6,\tag{5}$$

where  $\tau_0^{\text{BDP}}$  is the lifetime of the BDP moiety in the absence of an energy acceptor,  $R_{\rm DA}$  is the center-to-center distance between the donor (BDP) and the acceptor (Pc),  $k^2 = (\cos \vartheta_{DA} - 3 \cos \vartheta_{D} \cos \vartheta_{A})^2$  is the orientation factor,  $9_{DA}$  is the angle between the transition dipole moments of donor and acceptor,  $\vartheta_{\rm D}$  and  $\vartheta_{\rm A}$  are the angles between these respective vectors and the line joining the centers of the transitions. It should be emphasized that the accurate calculation of the orientation factor is a very difficult task lying far from the aims of the present manuscript. Nevertheless, we were able to do some reasonable assumptions of the  $k^2$  value. For a related metal-free porphyrin-(Si)-phthalocyanine triad, it was found that the orientation factor  $k^2 \approx 0.8^{17}$ . Hence, taking into account the difference between BDP and porphyrin chromophores and according to the results of molecular dynamic simulations, an orientation factor value of 1 was chosen for further analysis. With  $\tau_0^{\text{BDP}} = 3.03 \text{ ns}, R_{\text{DA}} = 6 \text{ Å},$ and  $R_0 = 33$  Å, the EET rate,  $k_{\text{EET}}$ , is estimated to be  $9 \times 10^{12}$  s<sup>-1</sup>. One should take into account that the orientation factor has a strong influence on the rate of EET (especially in covalently-linked donor-acceptor molecular systems, in which its value could strongly differ compared to commonly used 2/3 for homogeneous donor-acceptor mixtures in solution), and in turn its value is affected by the environment. Due to this reason the observed EET rate in the triad 4 in DMF is lower compared to the above estimated one.

Analysis of the ps-TAS data has shown that the recovery of the BDP-part ground state population of the triad **4** in nonpolar toluene occurs very slow compared to the extremely fast depopulation of its first excited singlet state due to the slow rate of charge recombination. The lifetime of the CS state formed was estimated to be 4.5 ns ( $k_{CR} = 2.2 \times 10^8 \text{ s}^{-1}$ ).

#### Triad 5

Using the Rehm-Weller approach with the following parameters:  $E^{\text{oxd}} = 0.88 \text{ V}, E^{\text{red}} = -0.57 \text{ V}, E^{\text{D}}_{0,0} = 2.16 \text{ eV},$  $E_{0.0}^{\rm A} = 1.81 \text{ eV}, R_{\rm DA} = 6 \text{ Å}, r_{\rm D+} = 4 \text{ Å}, r_{\rm A-} = 4.6 \text{ Å}, \text{ the}$ values of free energy of charge-separation at BDP- and Pc-part excitation,  $\Delta G_0^{\rm D}$  and  $\Delta G_0^{\rm A}$ , of **5** in DMF were estimated to be -0.71 and -0.36 eV, respectively, whereas in toluene these values were found to be -0.40 and -0.05 eV, respectively. As  $\Delta G_0$  exhibits a negative value, CT is energetically favorable process in both solvents when either the BDP- or Pc-part of the triad 5 is excited. A CS state has energy of 1.45 eV in DMF and 1.76 eV in toluene, which lies below the first excited singlet state of the Pc moiety in polar as well as nonpolar solvents. In general, the energy diagrams of the triad 5 in DMF and toluene are similar to those of the triad 4 in polar DMF (see Fig. 8a), and due to this reason they are given in the ESI.† It should be emphasized that these estimations are strongly supported by the experimental observations, since strong fluorescence quenching and fast depopulation of the first excited singlet state of the BDP- and Pc-parts of the triad 5 took place in both solvents.

Combining the experimental data obtained by steady-state and time-resolved fluorescence spectroscopy, the efficiency and rate of CT and EET processes were calculated to be  $\Phi_{\rm CT}^{\rm BDP} \approx 0.75$ ,  $\Phi_{\rm EET} \approx 0.25$ ,  $k_{\rm CT}^{\rm BDP} = 2.5 \times 10^{10} \text{ s}^{-1}$  and  $k_{\rm EET} = 8.3 \times 10^9 \text{ s}^{-1}$  for the **5** in DMF. It was found that photoinduced CT is a dominant deactivation process of the first excited singlet state of the BDP moiety. The same conclusion is valid for the Pc-part of the triad **5** as well.

The lifetime of the CS state generated is shorter than 30 ps, since the recovery of the ground state population of the BDP-part at 530 nm excitation follows the decay of its first excited singlet state as found in the ps-TAS experiments.

For both the triads in polar DMF, the decay of the first excited singlet state of Pc moiety has a biexponential character. The results of DAF spectroscopic study have shown that both decay components (fast and slow) belong to the same energetic state (both DAF spectra have the same spectral position of their maximum as well as shapes of the bands, see Fig. 4 and the ESI.<sup>†</sup>). One explanation could be that not only BDP-Pc-BDP triads, but BDP-Pc dyads with only one BDP chromophore also exist in solution. By comparing the extinction coefficients of the reference compounds 2 and 3 with those of the BDP-part absorption of the triads 4 and 5, it can be found that the latter are two times higher,<sup>11</sup> clearly showing that two BDP chromophores are covalently linked to one Pc moiety. Moreover, as shown by NMR spectroscopy, the samples are pure, and the signals due to the dyads were not seen.<sup>11</sup>

It is believed that there are two stable conformations for the triads, which are stabilized by the solvent. To prove this

hypothesis DAF experiments for triad **5** in acetonitrile (ACN), which has the same dielectric constant as DMF ( $\varepsilon = 37$ ), were carried out. The results are presented in Fig. S6 (ESI†). At Pc-part excitation, two DAF spectra were resolved, but the fast component has about two orders of magnitude higher in amplitude compared to the slow one. Thus, not only the polarity of the solvents, but also their chemical structure affects the photophysical properties of the triads. Each conformation could be characterized by its own orientation and center-to-center distance between BDP- and Pc-parts of the triads. As a result, the probability of charge transfer from the initially photoexcited Pc-part is different.

In nonpolar toluene, the behavior of the triad 5 after photoexcitation is greatly different from that of 4. The fluorescence of BDP- as well as Pc-part of the triad 5 is strongly quenched (see Table 2). The fast depopulation of the first excited singlet state of BDP moiety occurs via two competitive processes, namely EET and photoinduced CT. According to the results of steady-state fluorescence measurements, the efficiency of the EET,  $\Phi_{\text{EET}}$ , was calculated to be 0.67. Unfortunately, the decay time of BDP-part fluorescence was faster than the time-resolution of the TCSPC setup, thus a better estimation of  $k_{\text{EET}}$  and  $k_{\text{CT}}^{\text{BDP}}$  could not be made. The rough calculations could be done using the measured quantum yield of BDP-part fluorescence,  $\Phi_{\rm fl}^{\rm BDP}$ , (0.002, see Table 2), and taking into account the fluorescence lifetime,  $\tau_{\rm fl}$ , and the fluorescence quantum yield,  $\Phi_{\rm fl}$ , of the reference compound 3 in toluene (3.46 ns and 0.78, respectively, see Tables 2 and 3):  $k_{\text{EET}} + k_{\text{CT}}^{\text{BDP}} \approx \frac{1}{\tau_{\text{fl}}} \frac{\Phi_{\text{fl}}}{\Phi_{\text{BD}}^{\text{BDP}}} = 1.1 \times 10^{11} \text{ s}^{-1}.$ Then the rates of EET and CT were found to be  $7.4 \times 10^{11} \text{ s}^{-1}$ and  $3.6 \times 10^{10} \text{ s}^{-1}$ , respectively.

The photoinduced CT is a dominant process of the Pc first excited singlet state depopulation. Its rate was calculated to be  $3.2 \times 10^{10} \text{ s}^{-1}$  according to the results of fluorescence TCSPC spectroscopy. The lifetime of the CS state was determined by ps-TAS to be 1.7 ns, which is much longer compared to that determined in polar DMF solution, but shorter than the lifetime of the CS state in the triad **4** in toluene.

### 5. Conclusion

Phthalocyanine-boron dipyrromethene heteromers are good candidates for light-harvesting and charge separation complexes. We were able to demonstrate the potential of two non-sandwich-type heterotriads as both light-harvesting complex and charge separation unit in one molecule.

Upon BDP-part excitation, two types of transfer processes, namely energy and charge transfer, were found to be in competition for both triads independent of the solvent polarity. The first process delivers the excitation to the first excited singlet state of the Pc-part, whereas the latter one populates the CS state directly. It has been found that CT strongly supersedes EET for both triads in polar DMF. However, the probability of EET becomes higher than that of CT in nonpolar toluene.

For both triads in DMF, the direct or indirect (*via* EET) population of  $S_1$  state of the Pc-part is followed by hole transfer to the CS state. While the photophysical properties of both triads are similar in polar DMF, they differ strongly in

toluene upon Pc-part excitation. It was found that CT is energetically unfavorable for 4, whereas this process leads to efficient charge separation in the case of the triad 5.

The charge-recombination of the CS state generated occurs very fast directly to the ground state with a lifetime of 40 and 30 ps for the triad 4 and 5 in DMF, respectively. A lower polarity of the solvent stabilizes the CS state leading to a longer lifetime. The corresponding values in toluene were determined to be 4.5 and 1.7 ns for the triad 4 and 5, respectively. The triad 5 in toluene exhibits a broad absorption region and can effectively generate long-lived CS state *via* photoexcitation. This system is therefore a potentially useful artificial photosynthetic system.

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