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Photosynthesis

A New Approach for the Photosynthetic Antenna–Reaction Center Complex with a Model Organized Around an *s*-Triazine Linker

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Abstract: Two new artificial mimics of the photosynthetic antenna-reaction center complex have been designed and synthesized (BDP-H_2P-C_{60} and BDP-ZnP-C_{60}). The resulting electron-donor/acceptor conjugates contain a porphyrin (either in its free-base form (H_2P) or as Zn-metalated complex (ZnP)), a boron dipyrrin (BDP), and a fulleropyrrolidine possessing, as substituent of the pyrrolidine nitrogen, an ethylene glycol chain terminating in an amino group C_{60}-X-NH_2 (X = spacer). In both cases, the three different components were connected by *s*-triazine through stepwise substitution reactions of cyanuric chloride. In addition to the facile synthesis, the star-type arrangement of the three photo- and redox-active components around the central *s*-triazine unit permits direct interaction between one another, in contrast to reported examples in which the three components are arranged in a linear fashion. The energy- and electron-transfer properties of the resulting electron-donor/acceptor conjugates were investigated by using UV/Vis absorption and emission spectroscopy, cyclic voltammetry, and femtosecond transient absorption spectroscopy. Comparison of the absorption spectra and cyclic voltammograms of BDP-H_2P-C_{60} and BDP-ZnP-C_{60} with those of BDP-H_2P, BDP-ZnP and BDP-C_{60}, which were used as references, showed that the spectroscopic and electrochemical properties of the individual constituents are basically retained, although some appreciable shifts in terms of absorption indicate some interactions in the ground state. Fluorescence lifetime measurements and transient absorption experiments helped to elucidate the antenna function of BDP, which upon selective excitation undergoes a rapid and efficient energy transfer from BDP to H_2P or ZnP. This is then followed by an electron transfer to C_{60}, yielding the formation of the singlet charge-separated states, namely BDP-$H_2P^{\bullet+}$-$C_{60}^{\bullet-}$ and BDP-$ZnP^{\bullet+}$-$C_{60}^{\bullet-}$. As such, the sequence of energy transfer and electron transfer in the present models mimics the events of natural photosynthesis.

Introduction

Mimicking the photochemical process of natural photosynthesis by means of bioinspired synthetic models has been an area of great interest during the last decades.[1] The development of such molecular systems is important not only from a standpoint of mimicking photosynthesis to convert, for example, sunlight into energy, but also with respect to the construction of photonics, photocatalytic, and optoelectronic devices.[2] The complexity of artificial photosynthesis is the integration of light-harvesting, energy transfer, charge transfer, charge transport, and catalysis in a single system.[1a–c, 3]

As in natural photosynthesis, porphyrin-based reactions are key steps in artificial photosynthesis. Porphyrins and related tetrapyrrolic systems have widely been investigated as light-capturing antenna systems and/or as electron donors.[4–7] Notably, porphyrins feature rather moderate absorption cross section in the 430 to 500 nm region, and they allocate redox-active excited states.[8]

Fullerenes, which are well-known for their remarkable electron-acceptor properties, evolved as an interesting class of functional materials in the context of mimicking photosynthesis.[9] In particular, they feature low reduction potentials and small reorganization energies in charge-transfer reactions.[10–13] From these features, fast charge-separation and slow charge-recombination processes lead to long-lived charge-separated states.[14] The use of either noncovalent interactions, such as metal-to-ligand coordination or electrostatic interactions, or covalent bonds, provides easy means for constructing new electron-donor/acceptor ensembles and/or conjugates.[1f, 7, 15–17]

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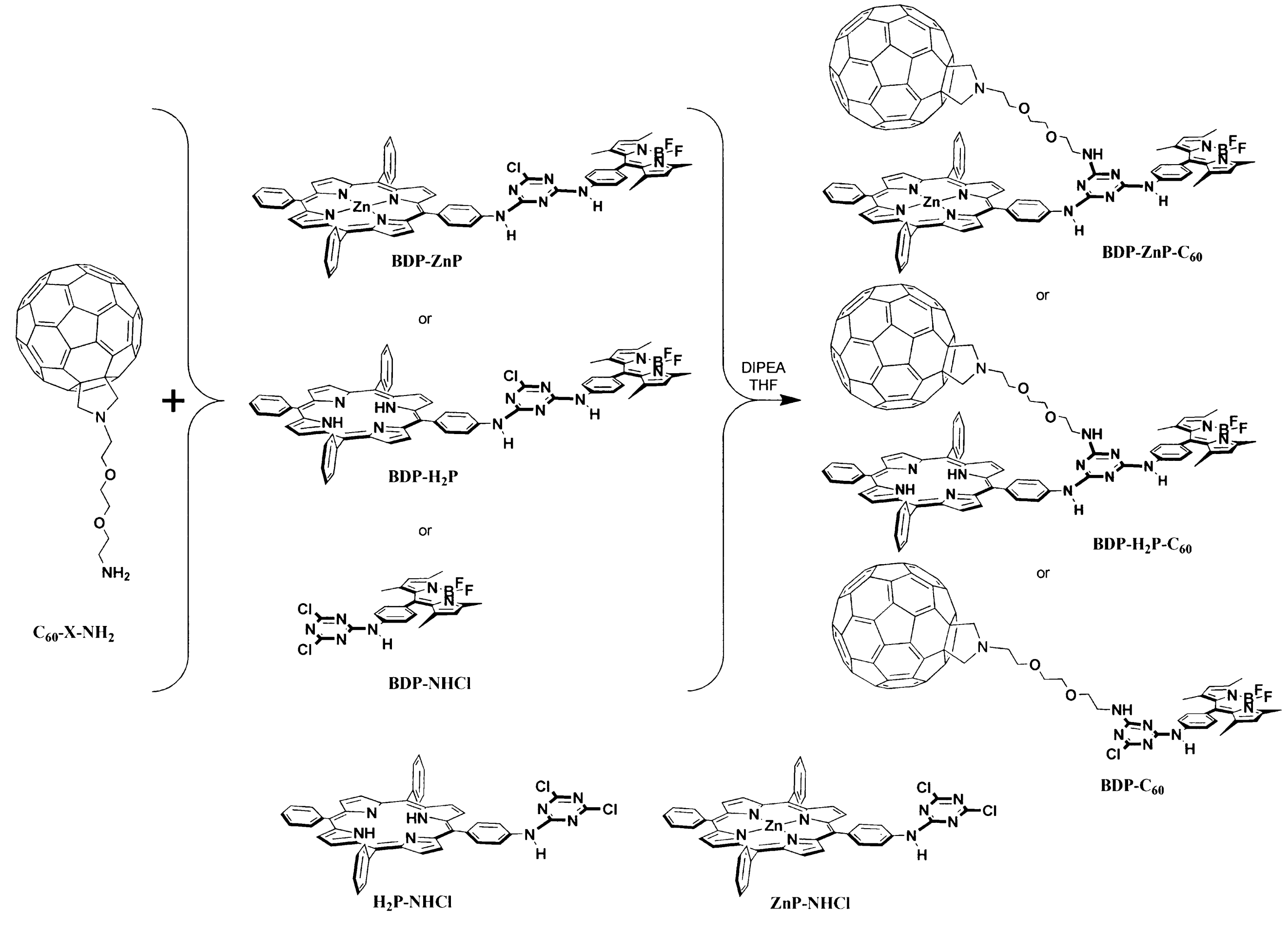
As a matter of fact, a wide variety of reaction center mimics based on fullerenes and porphyrins have been devised, synthesized, and examined.[7,18–22]

Furthermore, boron dipyrrins (BDP) are also of particular interest as light-harvesters.[23] BDPs are well-known for their high extinction coefficients, high fluorescence quantum yields, long-lived excited states, suitable excited-state energies, excellent photostability, and stability in many solvents.[24] Remarkable is also the ease of modification of the BDP core, which assists in tailoring the absorption and emission properties throughout the 450–680 nm range and, in turn, renders them complementary energy donors.[15e,25,26] In fact, several studies have demonstrated energy-transfer interactions between BDP, porphyrins, perylenediimides, and subphthalocyanines.[14,15b,e] Due to the good spectral overlap between fluorescence of BDP and absorption of porphyrins, an efficient transduction of singlet excited-state energy takes place.[15b,13c] Notably, only a few reports on the covalent linkage of BDP to a porphyrin and to a fullerene exist.[13c,14,15b,c,e,f] Among the latter, the one by Fukuzumi and co-workers, stands out due to its uniqueness.[27]

We recently described the facile synthesis of two BDP–porphyrin conjugates, that is, BDP-H_2P and BDP-ZnP, bridged by an *s*-triazine unit.[28] Fluorescence and transient absorption experiments showed that BDP excitation results in rapid BDP to porphyrin energy transfer. As a matter of fact, BDP increases the light-harvesting potential of the porphyrin chromophore. In the present work, we have further exploited these conjugates as precursors in reactions with an amino-functionalized electron-accepting fulleropyrrolidine possessing, as a substituent of the pyrrolidine nitrogen, an ethylene glycol chain terminating in an amino group C_{60}-X-NH_2 (X = spacer; Scheme 1). The new electron-donor/acceptor conjugates obtained in this way, namely BDP-H_2P-C_{60} and BDP-ZnP-C_{60}, feature three different components linked through *s*-triazine, and they were examined as artificial photosynthetic models in mimicking the energy- and electron-transfer processes of natural photosynthesis. The strategy followed in the synthesis of BDP-H_2P-C_{60} and BDP-ZnP-C_{60} represents a new and facile approach for the preparation of covalently linked multichromophoric systems with a star-type arrangement of three photo- and redox-active moieties around a central bridging unit. With such an assembly, the mutual structural arrangement of the chromophores is achieved, resulting in a triangular conformation, in which each chromophore interacts directly with the other two. It is believed that the latter would enhance electronic communication between the photoexcited electron donors and the fullerene derivative acceptor.



Scheme 1. Synthesis of BDP-H_2-C_{60}, BDP-ZnP-C_{60}, and BDP-C_{60}, and the structure of the reference compounds H_2P-NHCl and ZnP-NHCl.

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Experimental Section

Photophysical measurements

All measurements were performed in solvents of spectroscopic grade at room temperature in a 10×10 mm quartz glass cuvette. UV/Vis absorption spectra were recorded on a PerkinElmer Lambda2 UV/Vis two-beam spectrophotometer with a slit width of 2 nm and a scan rate of 240 nm min^{-1}. Emission spectra were recorded by using a Horiba Jobin Yvon FluoroMax-3 spectrometer with a slit width of 2 nm for excitation and emission and an integration time of 0.5 s in a wavelength range of 300–1000 nm. Quantum yields were determined from corrected emission spectra following the standard methods[29] using *meso*-tetraphenyl porphyrin (H_2P; $\Phi = 0.11$ in toluene)[30] and Zn-metalated *meso*-tetraphenyl porphyrin (ZnP; $\Phi = 0.03$ in toluene)[30] as standards. Emission lifetimes were determined by using time-correlated single-photon counting (TCSPC) on a Horiba Jobin Yvon FluoroLog3 emission spectrometer with a Hamamatsu MCP photomultiplier (R3809U-58). For excitation, a laser diode (NanoLED-405L, 403 nm, pulse width $\leq$200 ps, maximum of repetition rate 100 kHz) was used. Femtosecond transient absorption studies were performed with 420 and 490 nm laser pulses (1 kHz, 150 fs pulse width) from an amplified Ti:Sapphire laser system (Clark-MXR, Inc. CPA 2101), the laser energies were 120 and 200 nJ, respectively. Transient spectra were recorded with an analyzing solution in a 2 mm quartz glass cuvette.

Electrochemical data were obtained by cyclic voltammetry and square-wave voltammetry measurements, by using a conventional single-compartment three-electrode cell arrangement in combination with a potentiostat "AUTOLAB, eco chemie". Platinum and silver wires were used as the auxiliary and reference electrodes, respectively, whereas the working electrode was a glassy carbon electrode. Measurements were carried out in saturated toluene/acetonitrile (4:1, v/v) solutions, at room temperature, under argon. Tetrabutylammonium hexafluorophosphate ($TBAPF_6 = 0.1$ M) was used as the supporting electrolyte. All potentials are referenced to the ferrocene/ferrocenium couple ($Fc/Fc^+ = 0.33$ V).

Materials

H_2P-NHCl,[28] ZnP-NHCl,[28] BDP-H_2P,[28] BDP-ZnP,[28] BDP-NHCl,[28] and C_{60}-X-NH_2[31] were prepared according to published procedures. Tetrahydrofuran was freshly distilled from Na/benzophenone. All other chemicals and solvents were purchased from commercial sources and used as received.

NMR Spectra

^{1}H NMR spectra were recorded on Bruker AVANCE III-500 MHz and Bruker DPX-300 MHz spectrometers using solutions in deuterated solvents and the solvent peak was chosen as the internal standard.

Mass spectroscopy

High-resolution mass spectra were obtained on a Bruker UltrafleXtreme matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectrometer using *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix.

Results and Discussion

Synthesis and characterization

Cyanuric chloride is a very useful synthon, in view of the fact that the temperature-dependent stepwise substitution of its three chlorine atoms allows the sequential introduction of up to three different nucleophiles on the *s*-triazine unit. As a result, it provides an easy synthetic route to molecular architectures with different chromophores in good yields, avoiding multi-step and expensive preparation and purification methods. As shown in Scheme 1, BDP-H_2P-C_{60} and BDP-ZnP-C_{60} were prepared starting from BDP-H_2P and BDP-ZnP, respectively.[28] Nucleophilic substitution of the chlorine atoms of cyanuric chloride of BDP-H_2P-C_{60} and BDP-ZnP-C_{60} by the terminal amino group of C_{60}-X-NH_2, in THF heated at reflux and in the presence of *N*,*N*-diisopropylethylamine (DIPEA), produced the desired electron-donor/acceptor conjugates. BDP-C_{60} was synthesized in a similar way by treatment of BDP-NHCl with C_{60}-X-NH_2 and used as reference.[28] All compounds were fully characterized by ^{1}H NMR spectroscopy and MALDI-TOF mass spectrometry.

Physicochemical studies

Electrochemistry

The electrochemical behavior of BDP-H_2P-C_{60}, BDP-ZnP-C_{60}, and the corresponding references was investigated by cyclic and square-wave voltammetry. All redox potentials, which are reported versus the ferrocene/ferrocenium (Fc/Fc^+) couple, are summarized in Table 1. The cyclic voltammograms of BDP-H_2P-C_{60} and BDP-ZnP-C_{60} (Figure S1 in the Supporting Information) reveal reversible oxidations occurring at 0.6 V for ZnP and at 0.8 V for H_2P as well as at approximately 1.0 V for BDP. No C_{60}-centered oxidations were observed within the recorded potential window. Additionally, reversible processes corresponding to reductions were observed. In particular, C_{60}-centered reductions occur at −0.8 and −1.8 V, whereas BDP reductions are observed at −1.1 and −1.4 V. Reductions of ZnP and H_2P occur at −1.77 and −1.79 V, respectively. It should be noted that in BDP-H_2P-C_{60} and BDP-ZnP-C_{60} the reductions of H_2P/ZnP, and of C_{60} overlap.[32]

Table 1. Redox potentials of BDP-NHCl, BDP-C_{60}, BDP-H_2P, BDP-H_2P-C_{60}, BDP-ZnP, and BDP-ZnP-C_{60} versus Fc/Fc^+ (0.33 V) in toluene/acetonitrile (4:1, v/v) with tetrabutylammonium hexafluorophosphate 0.1 M as supporting electrolyte.

	$E_{1/2}$						
	Oxidation			Reduction			
	BDP/BPD$^{\bullet+}$	P/P$^{\bullet+}$	$C_{60}/C_{60}^{\bullet-}$	BDP/BDP$^{\bullet-}$	BDP/BDP$^{\bullet-}$	$C_{60}/C_{60}^{\bullet-}$	P/P$^{\bullet-}$
BDP-NHCl	1.015			−1.098	−1.46		
BDP-C_{60}	1.005		−0.81	−1.128	−1.45	−1.775	
BDP-H_2P	1.045	0.855		−1.115	−1.38		−1.77
BDP-H_2P-C_{60}	1.054	0.83	−0.845	−1.085	−1.4	−1.79	
BDP-ZnP	0.99	0.605		−1.08	−1.395		−1.775
BDP-ZnP-C_{60}	0.955	0.595	−0.805	−1.115		−1.775	

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Table 2.
Summary of spectroscopic data of BDP-NHCl, BDP-C_{60}, H_2P-NHCl, BDP-H_2P, BDP-H_2P-C_{60}, ZnP-NHCl, BDP-ZnP, and BDP-ZnP-C_{60} measured in pure toluene.

	Absorption	Fluorescence					
	λ_{max} [nm] (ε [$M^{-1}\,cm^{-1}$])	λ_{max} [nm]	φ (λ_{ex}=495 nm)		φ (λ_{ex}=418 nm)	τ [ns]	
			BDP	P	P	BDP	P
BDP-NHCl	504 (75 620)	514	0.58			3.25	
BDP-C_{60}	504 (75 580)	514	0.018			0.21	
H_2P-NHCl	420 (221 786)	651, 718		0.11	0.11		
BDP-H_2P	420 (473 980), 504 (98 679)	514, 651, 718	0.01	0.107	0.127	0.08[a]	9.26
BDP-H_2P-C_{60}	422 (251 268), 504 (74 222)	514, 653, 718	0.011	0.01	0.019	0.08[a]	9.63
ZnP-NHCl	423 (185 072)	596, 647		0.04	0.04		
BDP-ZnP	423 (460 960), 504 (81 767)	514, 596, 647	0.005	0.04	0.04	0.11	1.98
BDP-ZnP-C_{60}	426 (278 221), 504 (76 451)	514, 598, 649	0.011	0.003	0.006	0.12	0.76

[a] These values reflect the upper limits imposed by the time resolution of the laser diodes that have been employed to photoexcite the samples.

Absorption spectra

Absorption spectra of BDP-H_2P-C_{60} and BDP-ZnP-C_{60} as well as those of their references are shown in Figure 1 and a summary of their absorption characteristics is given in Table 2. The absorption spectrum of BDP-NHCl compares well with what is known from the literature, showing a dominant absorption with a maximum at 504 nm and a weak absorption in the 300–380 nm region (Figure 1, top).[28] Comparing the latter with BDP-C_{60}, again the characteristic feature at 504 nm is observed. Additionally, a broad absorption originating from C_{60} is discernible between 300 and 400 nm (Figure 1, top). Absorption spectra of BDP-H_2P-C_{60} and the corresponding references are shown in Figure 1 (central panel). H_2P-NHCl features the Soret band at 420 nm as well as Q-bands between 500 and 700 nm. For BDP-H_2P, in addition to the latter absorptions, the broad BDP absorption is observed at 504 nm; none of these peaks are, however, shifted. In the BDP-H_2P-C_{60} absorption spectrum all of the features of the single constituents are identified, that is, C_{60} between 300–380 nm, BDP at 504 nm, and H_2P at 422 nm as well as between 500–700 nm. Noticeably, a redshift of the Soret band to 422 nm is observed, which implies electronic communication between C_{60} and H_2P. The absorption spectrum of BDP-ZnP-C_{60} (Figure 1, bottom) also features a redshift of the Soret band from 423 to 426 nm, whereas all the remaining absorption characteristics of C_{60} (300–380 nm), BDP (504 nm), and ZnP (423, 550–600 nm) remain the same. Depending on the strength of electronic interactions, additional features in form of a charge transfer may arise between 800 and 900 nm, but no such features were observed.[9]

Emission spectra

With respect to the steady-state and time-resolved fluorescence assays with BDP-H_2P-C_{60} and BDP-ZnP-C_{60} and the corresponding references, the fluorescence maxima, quantum yields, and lifetimes are summarized in Table 2. In the top part of Figure 2, the fluorescence spectrum of BDP-NHCl is shown, which exhibits a maximum at 514 nm and a quantum yield of 58%. BDP-C_{60}, on the other hand, reveals a 96.9% quenching of the BDP fluorescence when excited at 495 nm. The BDP fluorescence lifetime in BPD-C_{60} is much shorter (0.21 ns) than that of BDP-NHCl (3.2 ns). This is taken as evidence of electronic communication, either in the form of energy or electron transfer, between the light-harvesting BDP and the electron-accepting C_{60} in the absence of either H_2P or ZnP. Exciting BDP-H_2P-C_{60} (Figure 2, middle panel) at 495 nm evokes again a rather strong quenching of the BDP fluorescence, namely 98.1%. Simultaneously, the H_2P related fluorescence evolves with 1%, which is in line with an earlier report[28] on an efficient energy-transfer from the singlet excited-state of BDP to H_2P in its ground state. This is confirmed by means of an excitation spectrum of the evolving H_2P fluorescence, which shows features of H_2P and BDP absorption (Figure S2 in the Supporting Information).[28] Similarly, in BDP-H_2P the BDP fluorescence is quenched by 98.3% and the H_2P fluorescence is activated with 15.5%. The H_2P fluorescence is notably quenched in BDP-H_2P-C_{60} relative to BDP-H_2P. Such quenching indicates deactivation of H_2P in the presence of C_{60}, probably through electron transfer. All of the aforementioned effects are even more pronounced when comparing BDP-ZnP with BDP-ZnP-C_{60} upon 495 nm excitation (Figure 2, bottom). The BDP fluorescence quenching in BDP-ZnP-C_{60} is 98.1% compared with BDP-NHCl, whereas BDP-ZnP gives rise to 99.1% quenching of the 514 nm fluorescence. In BDP-ZnP-C_{60}, ZnP fluorescence evolved, which was at the expense of BDP fluorescence quenching (as it was also observed in case of BDP-ZnP). Nevertheless, the presence of C_{60} causes appreciable quenching and a 2 to 3 nm redshift in the fluorescence pattern. Besides the BDP, ZnP, and H_2P quenching, no additional features are noted. In additional experiments all of the H_2P- and ZnP-containing systems were excited at 418 nm (Figure S3 in the Supporting Information). Clearly, in both scenarios the overall fluorescence intensity and, in turn, the corresponding quantum yields increase when comparing, for example, H_2P-NHCl/ZnP-NHCl with BDP-H_2P/BDP-ZnP and strongly decrease when comparing H_2P-NHCl/ZnP-NHCl and BDP-H_2P/BDP-ZnP with BDP-H_2P-C_{60}/BDP-ZnP-C_{60}.

Subjecting BDP-ZnP-C_{60} as well as the respective BDP-ZnP and ZnP-NHCl to strongly coordinating pyridine leads to marked shifts (Figure 3).[33] We assume that the pyridine coordination cancels the through space electronic communication with C_{60}. On the contrary, the H_2P analogues fail to reveal any noticeable shifts in the presence of similar concentrations of pyridine due to the lack of coordination (Figure S4 in the Supporting Information).

A closer inspection of the BDP fluorescence lifetimes further corroborates the quenching seen in the steady state measure-

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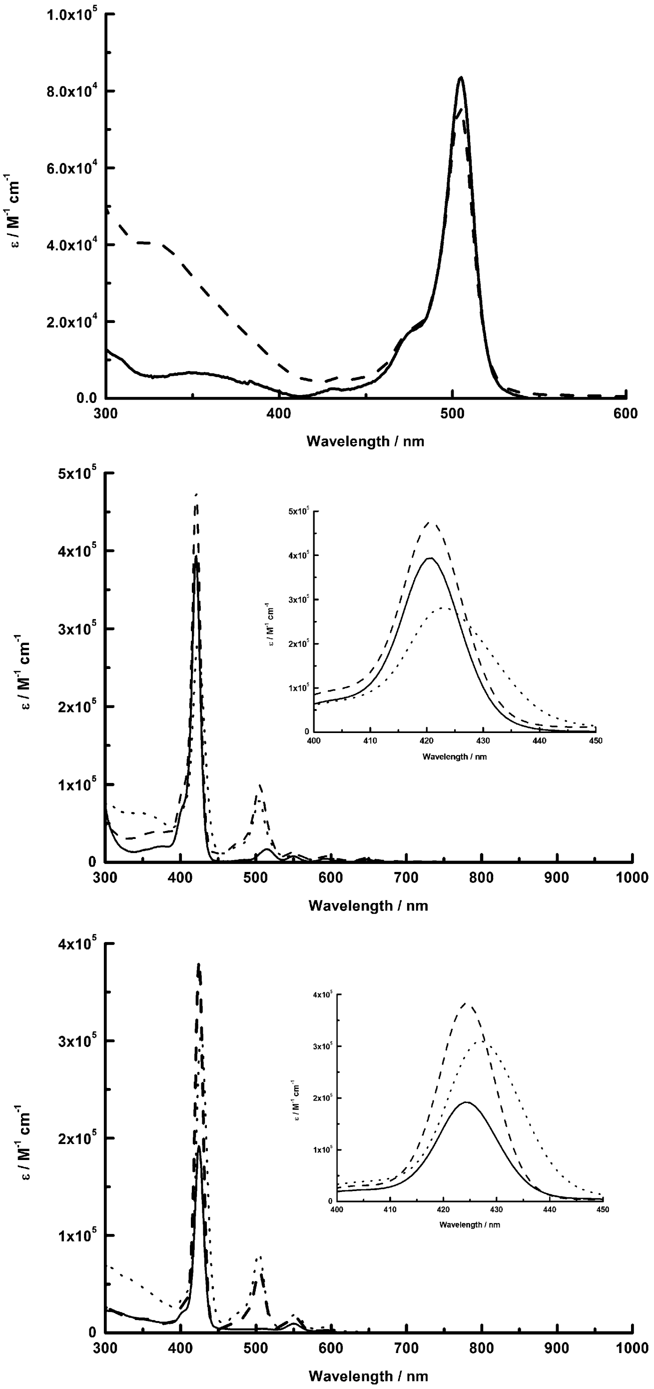

Figure 1. Absorption spectra of, top: BDP-NHCl (black solid line) and BDP-C_{60} (black dashed line); middle: H_2P-NHCl (black solid line), BDP-H_2P (black dashed line), and BDP-H_2P-C_{60} (black dotted line), inset: a zoom-in to illustrate the red shift in the Soret band; bottom: ZnP-NHCl (black solid line), BDP-ZnP (black dashed line), and BDP-ZnP-C_{60} (black dotted line), inset: a zoom-in to illustrate the red shift of the Soret band, at room temperature in toluene.

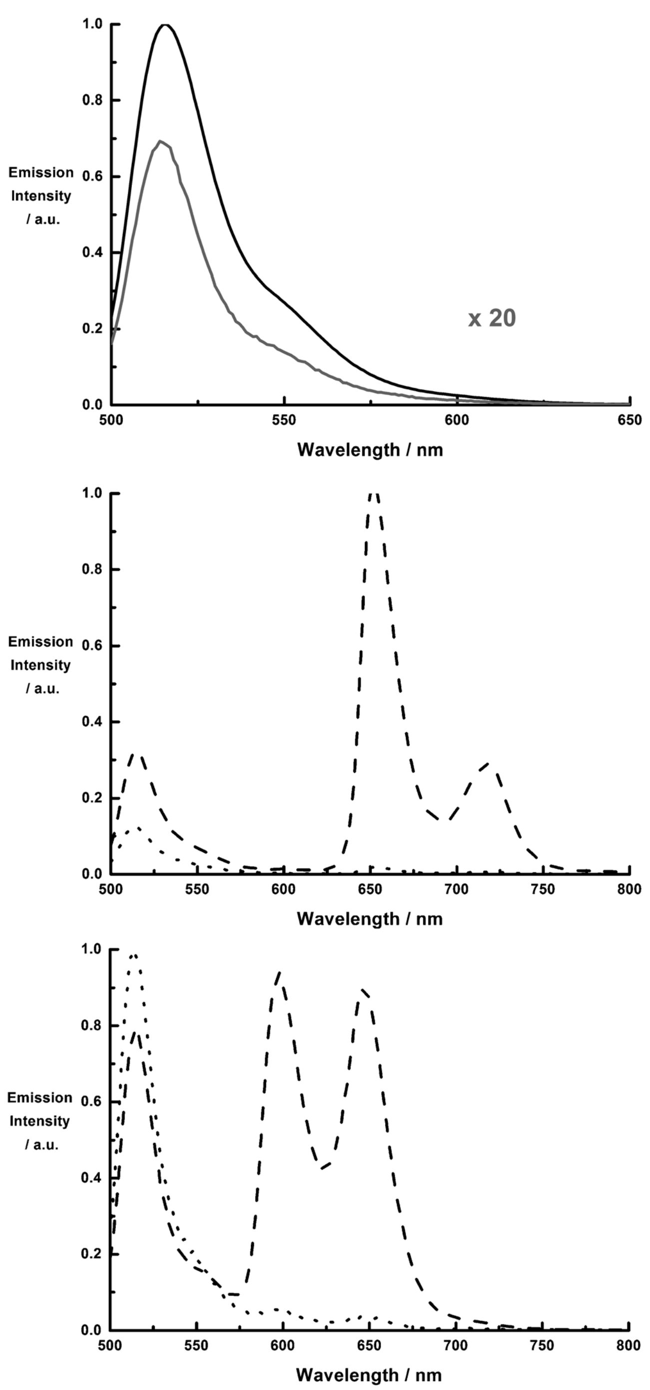

Figure 2. Fluorescence spectra (excited at 495 nm), top: BDP-NHCl (black solid line) and BDP-C_{60} (gray solid line); middle: BDP-H_2P (black dashed line) and BDP-H_2P-C_{60} (black dotted line); bottom: BDP-ZnP (black dashed line) and BDP-ZnP-C_{60} (black dotted line) at room temperature with an optical density (ΔOD) = 0.1 in toluene.

ments. For example, in BDP-H_2P/BDP-H_2P-C_{60} and BDP-ZnP/BDP-ZnP-C_{60} the values that relate to BDP are 0.08 and 0.11 ns, respectively. These results, compared with the intrinsic BDP-NHCl fluorescence lifetime of 3.25 ns, support the suggestion of a fast and efficient transduction of singlet excited-state energy from photoexcited BDP to either H_2P or ZnP. This is in accordance with H_2P or ZnP fluorescence lifetimes of 9.26 and 1.98 ns in BDP-H_2P and BDP-ZnP, respectively. Nevertheless, in the presence of C_{60}, in the case of BDP-ZnP-C_{60}, even these are quenched, as suggested by the lifetime of 0.76 ns. Obviously, the flexible linkers modulate the through space interactions between C_{60} and ZnP. Details about the fluorescence lifetimes as well as time fluorescence profiles are summarized in the Supporting Information (Figure S5 and Table S1 in the Supporting Information).

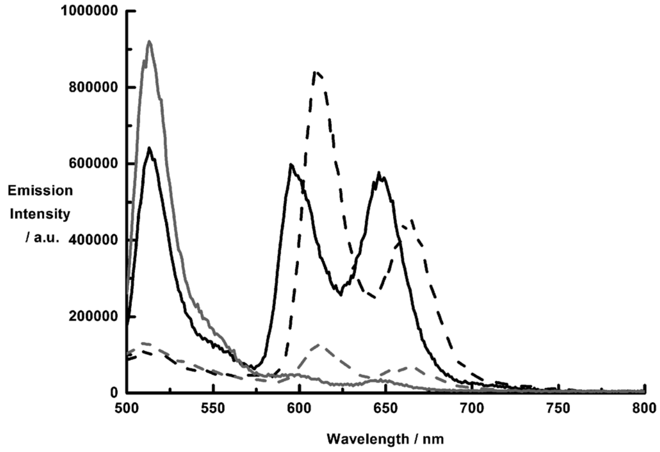

Figure 3. Fluorescence spectra (excited at 495 nm) of BDP-ZnP (black solid line) and BDP-ZnP-C_{60} (black dashed line) in comparison with BDP-ZnP (gray solid line) and BDP-ZnP-C_{60} (gray dashed line) in the presence of pyridine.

Transient absorption spectroscopy

To shed more light on the mutual interactions in the excited state, BDP-H_2P-C_{60}, BDP-ZnP-C_{60}, and their references were probed by using femtosecond transient absorption measurements. Here, excitation of H_2P/ZnP at 420 nm or excitation of BDP at 490 nm were chosen to be studied.

Excitation of H_2P-NHCl and ZnP-NHCl at 420 nm gives rise to the direct formation of the singlet excited state with maxima at 494, 535, 571, and 622 nm as well as minima at 515, 550, 592, and 648 nm for H_2P-NHCl, and maxima at 531, 575, and 623 nm as well as minima at 552, 595, and 652 nm for ZnP-NHCl. Due to intersystem crossing to the corresponding triplet manifolds, the latter decay with lifetimes of 9.8 and 2.1 ns for H_2P-NHCl and ZnP-NHCl, respectively, featuring maxima at 780 nm (H_2P-NHCl) as well as 840 nm (ZnP-NHCl).

Immediately after exciting BDP-NHCl at 490 nm, its singlet excited-state features (i.e., 1 ps) appear in the form of a bleaching at $\approx$500 nm (Figure S6 in the Supporting Information) featuring a lifetime of 3.2 ns. When exciting BDP-C_{60}, again the instantaneous formation of the BDP singlet excited state evolves $\approx$500 nm, followed by a 80 ps charge separation to afford $BDP^{\bullet+}$ and $C_{60}^{\bullet-}$, with characteristic major fingerprints at 415, 455, 480, 501, 523, 620, 679, and 1024 nm, respectively, in line with the spectroelectrochemical measurements (Figure S7 in the Supporting Information) and recently published values.[34] The metastable $BDP^{\bullet+}/C_{60}^{\bullet-}$ radical ion-pair state decays with a lifetime of 1600 ps (Figure S8 in the Supporting Information), to reinstate the singlet ground state. With the help of electrochemistry we have determined a thermodynamic driving force for converting the BDP singlet excited state (2.43 eV) into the $BDP^{\bullet+}/C_{60}^{\bullet-}$ radical ion-pair state (1.81 eV) of 0.62 eV.

Next, we turned to BDP-H_2P and BDP-ZnP, which were excited at 490 nm. Initially, the spectral features of the BDP singlet excited state (see above) are observed (i.e., 1 ps). The presence of the covalently attached H_2P/ZnP causes a significant shortening of the BDP singlet excited-state lifetimes, namely 32 ps for BDP-H_2P and 50 ps for BDP-ZnP (Figures S9 and S10 in the Supporting Information). Concomitant with the latter decay, we note the formation of a new transient. In the case of BDP-H_2P, the new transient features characteristic maxima at 500–700 nm, which resemble those seen for H_2P-NHCl. For BDP-ZnP, the corresponding minima at 550 and 600 nm agree well with the singlet excited-state absorptions of ZnP-NHCl. In other words, in BDP-H_2P and BDP-ZnP an intramolecular energy-transfer transduces singlet excited-state energy from the initially excited BDP (2.43 eV) to either ZnP (2.08 eV) or H_2P (1.9 eV). As a matter of fact, the current finding compares well with recent reports in the literature.[28]

Turning to BDP-H_2P-C_{60}, upon 490 nm excitation of the BDP its singlet excited state is formed as evidenced from the occurrence of ground-state bleaching at 500 nm. In analogy to the observation made with BDP-H_2P (see above) an intramolecular energy transfer sets in shortly after the formation of the BDP singlet excited state. The H_2P singlet excited maxima at 493, 538, 574, 624, and 685 nm and minima at 553, 595, and 654 nm grow in with 32 ps, which matches the decay of the BDP singlet excited state (Figure 4). Instead of seeing the slow

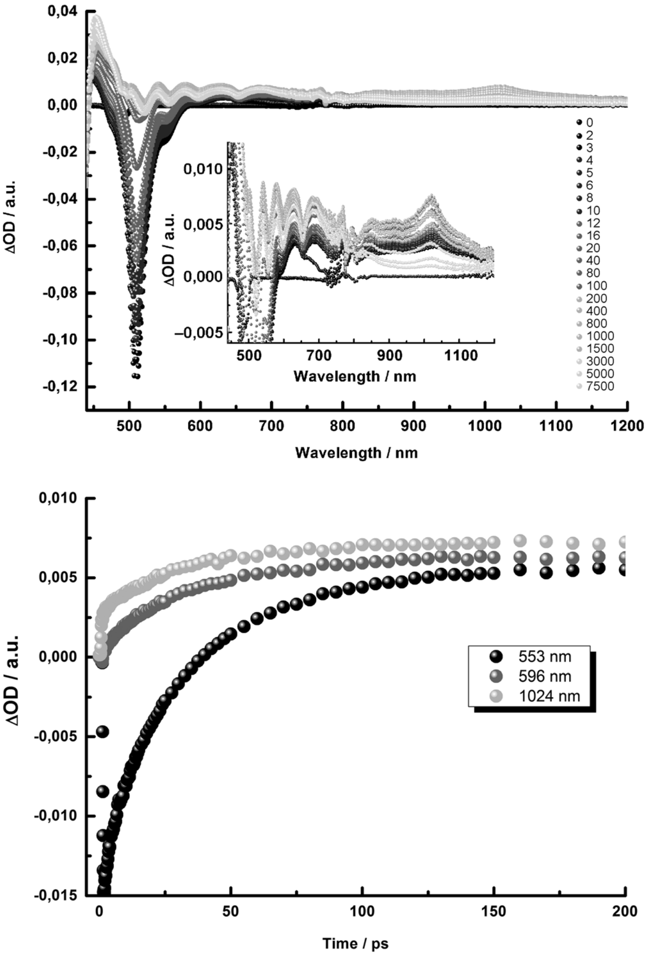

Figure 4. Top: differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (490 nm, 200 nJ) of BDP-H_2P-C_{60} in argon-saturated toluene with several time delays between 0 and 8000 ps at room temperature; inset: zoom-in to visualize the Q-band as well as the formation of the radical ion-pair. Bottom: time–absorption profiles of the spectra at 553 and 596 nm, monitoring the energy transfer (32 ps) as well as at 1024 nm, monitoring the charge separation (30 ps).

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intersystem crossing, which transforms the singlet excited state of H_2P and ZnP with 9.8 and 2.1 ns, respectively, to the corresponding long-lived triplet excited state, a rapid decay takes place with lifetimes of 30 and 26 ps for H_2P and ZnP, respectively. However, this rapid decay may be assigned to a direct electron-transfer from photoexcited BDP to C_{60}. Notably, this component reveals a very low pre-exponential factor and, in turn, we are inclined to neglect it in BDP-H_2P-C_{60} although it plays a major role in BDP-C_{60}. The latter correlates with an intramolecular charge separation to yield the one-electron-oxidized H_2P and the one-electron-reduced C_{60} within 30 ps. Spectroscopic evidence for the earlier involves maxima at 538, 574, 624, and 685 nm as well as minima at 553, 595, and 654 nm, whereas for the latter, maxima at 504 and 1024 nm are observed. The $H_2P^{\bullet+}/C_{60}^{\bullet-}$ radical ion-pair state is metastable and is subject to charge recombination with a lifetime of 3000 ps. The thermodynamic driving force of 0.22 eV results from a $H_2P^{\bullet+}/C_{60}^{\bullet-}$ radical ion-pair state of 1.67 eV and a singlet excited state of H_2P of 1.9 eV. Similarly, 490 nm excitation of BDP-ZnP-C_{60} leads to a cascade of energy transfer, charge-separation, and charge-recombination reactions (Figure 5). The BDP-centered singlet excited state has a lifetime of 35 ps and its features, that is, 500 nm ground-state bleaching, convert during energy transfer into those of the ZnP singlet excited state with maxima at 453, 581, and 617 nm as well as minima at 553 and 593 nm. Once formed, the singlet excited state of ZnP is subject to a charge separation with a lifetime of 26 ps to yield the metastable $ZnP^{\bullet+}/C_{60}^{\bullet-}$ radical ion-pair state. Again, the one-electron-reduced C_{60} was spectroscopically identified by its maximum at 1024 nm (see above), whereas a maximum at 532 nm relates to that of the one-electron-oxidized ZnP. The charge recombination, which reinstates the singlet ground state, occurs with a lifetime of 900 ps. Here, the thermodynamic driving force of charge separation (0.68 eV) is larger than that found in the case of BDP-H_2P-C_{60}. For both BDP-H_2P-C_{60} and BDP-ZnP-C_{60} the initial transduction of singlet excited-state energy is rate-determining with respect to the cascade of energy- and electron transfer as inferred from the lifetimes of singlet energy transfer in the reference compounds BDP-H_2P and BDP-ZnP (see above).

In complementary experiments involving 420 nm excitation of BDP-H_2P-C_{60} and BDP-ZnP-C_{60}, only the spectral features of H_2P and ZnP, respectively, were observed. No appreciable BDP-based features were seen at any time during the time evolution due to the dominating absorptions of H_2P/ZnP. Instead, absorption of H_2P and ZnP at around 400 nm and between 500 and 700 nm, respectively, was observed (Figures S11 and S12 in the Supporting Information). In line with the aforementioned experiments, in which the H_2P and/or ZnP are excited, charge separation to afford the $H_2P^{\bullet+}/C_{60}^{\bullet-}$ and $ZnP^{\bullet+}/C_{60}^{\bullet-}$ radical ion-pair states, respectively, and charge recombination to recover the singlet ground states sets in. For BDP-H_2P-C_{60}, the lifetimes of the formation and the decay of $H_2P^{\bullet+}/C_{60}^{\bullet-}$ are 5.7 and 3000 ps, respectively, whereas for BDP-ZnP-C_{60}, $ZnP^{\bullet+}/C_{60}^{\bullet-}$ is formed with a lifetime of 9.2 ps and decays with a lifetime of 2600 ps.

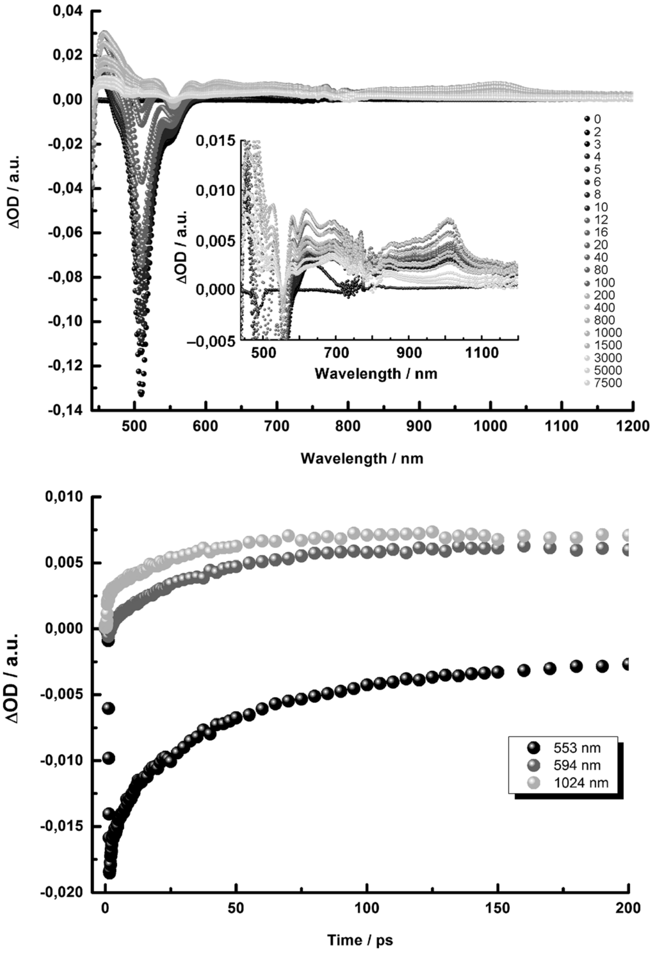

Figure 5. Top: differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (490 nm, 200 nJ) of BDP-ZnP-C_{60} in argon-saturated toluene with several time delays between 0 and 8000 ps at room temperature; inset: zoom-in to visualize the Q-band as well as the formation of the radical ion-pair. Bottom: time–absorption profiles of the spectra at 553 and 594 nm, monitoring the energy transfer (32 ps) as well as at 1024 nm, monitoring the charge separation (26 ps).

Conclusion

The sequence of events that follow excitation of BDP-H_2P-C_{60} and BDP-ZnP-C_{60} at 490 and 420 nm are sketched in the energy diagrams of Figure 6.

Excitation of BDP-H_2P-C_{60} and BDP-ZnP-C_{60} at 490 nm produces the first singlet excited state of BDP. A minor fraction decays through fluorescence to the ground state, whereas the major fraction (>99%) decays through photoinduced energy-transfer to afford the first singlet excited states of either H_2P or ZnP with lifetimes of 32 and 35 ps, respectively. In the next step, the H_2P/ZnP singlet excited states decay in part radiatively back to the ground state and in part by photoinduced electron-transfer, with lifetimes of 30 and 26 ps, to yield the BDP-$H_2P^{\bullet+}$-$C_{60}^{\bullet-}$ or BDP-$ZnP^{\bullet+}$-$C_{60}^{\bullet-}$ radical ion-pair states, respectively. Finally, the latter decay back to the ground state with lifetimes of 3000 ps for BDP-$H_2P^{\bullet+}$-$C_{60}^{\bullet-}$ and 900 ps for BDP-$ZnP^{\bullet+}$-$C_{60}^{\bullet-}$.

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Excitation of BDP-H_2P-C_{60} and BDP-ZnP-C_{60} at 420 nm leads to the second singlet excited state of either H_2P or ZnP, which rapidly decays to the first porphyrin singlet excited state through internal conversion. In the next step, the BDP-$H_2P^{\bullet+}$-$C_{60}^{\bullet-}$ and BDP-$ZnP^{\bullet+}$-$C_{60}^{\bullet-}$ radical ion-pair states are formed with lifetimes of 5.7 and 9.2 ps, respectively, which are shorter than those observed upon 490 nm excitation. Please note that in these particular cases the rate of electron transfer is not governed by the rate of BDP to H_2P/ZnP energy transfer. As in the case of the 490 nm excitation, the BDP-$H_2P^{\bullet+}$-$C_{60}^{\bullet-}$ and BDP-$ZnP^{\bullet+}$-$C_{60}^{\bullet-}$ radical ion-pair states decay back to the ground state with lifetimes of around 3000 ps.

It is worth noting that initial BDP excitation in BDP-H_2P-C_{60} and BDP-ZnP-C_{60} leads exclusively to an energy transfer to H_2P/ZnP and not to direct electron transfer to C_{60}, even though this is the case in BDP-C_{60} (see above). This is because the rate of BDP to C_{60} electron transfer (80 ps) is slower than that of the energy transfer of BDP to H_2P/ZnP (ca. 30–32 ps) rendering the latter the predominant decay pathway of the BDP singlet excited state in BDP-H_2P-C_{60} and BDP-ZnP-C_{60}.

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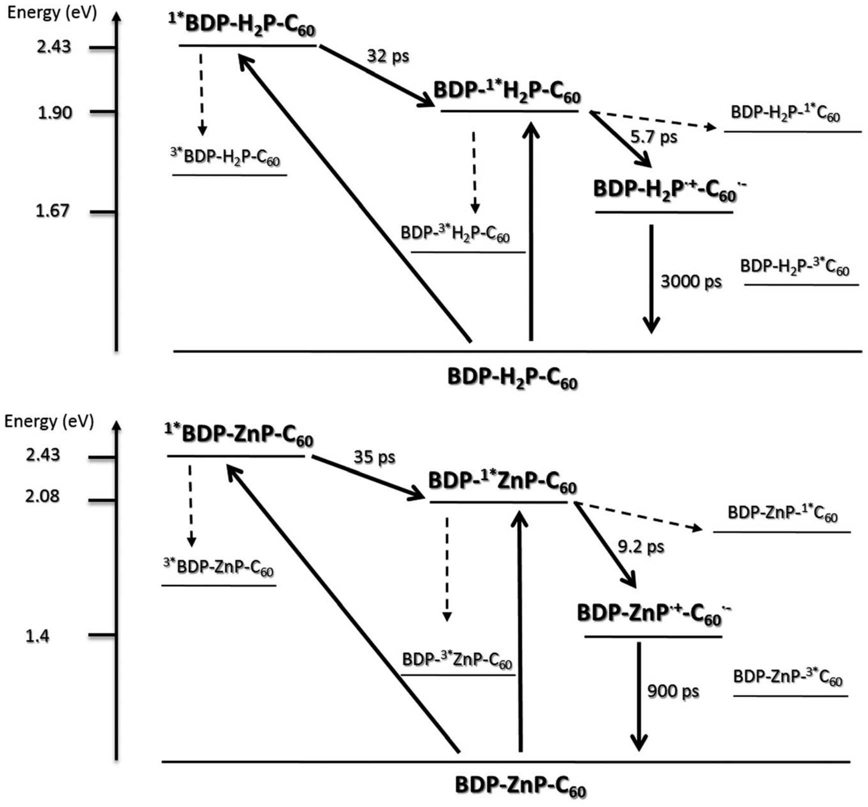

Figure 6. Jablonski diagrams illustrating the proposed sequence of events following excitation of BDP-H_2P-C_{60} (top) and BDP-ZnP-C_{60} (bottom) at 490 and 420 nm, respectively, see the main text for details.

Keywords: electron transfer · energy transfer · cyclic voltammetry · photosynthesis · synthetic methods

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