Published in final edited form as:

J Phys Chem B. 2018 April 12; 122(14): 4131–4140. doi:10.1021/acs.jpcb.8b02123.

Excitonic Interactions in Bacteriochlorin Homo-Dyads Enable Charge Transfer: A New Approach to the Artificial Photosynthetic Special Pair

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Abstract

Excitonically coupled bacteriochlorin (BC) dimers constitute a primary electron donor (special pair) in bacterial photosynthesis and absorbing units in light-harvesting antenna. However, the exact nature of the excited state of these dyads is still not fully understood. Here, we report a detailed spectroscopic and computational investigation of a series of symmetrical bacteriochlorin dimers, where the bacteriochlorins are connected either directly or by a phenylene bridge of variable length. The excited state of these dyads is quenched in high-dielectric solvents, which we attribute to photoinduced charge transfer. The mixing of charge transfer with the excitonic state causes accelerated (within 41 ps) decay of the excited state for the directly linked dyad, which is reduced by orders of magnitude with each additional phenyl ring separating the bacteriochlorins. These results highlight the origins of the excited-state dynamics in symmetric BC dyads and provide a new model for studying the primary processes in photosynthesis and for the development of artificial, biomimetic systems for solar energy conversion.

Graphical Abstract

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.8b02123.

Fluorescence quantum yields, femtosecond transient absorption, rate constant determination, charge transfer rates as function of distance, fit of the BC1 fluorescence spectrum in DMF (PDF)

Notes

The authors declare no competing financial interest.

INTRODUCTION

Understanding the nature of the excited state in electronically interacting bacteriochlorin (BC) dimers is of great importance for understanding the key processes in photosynthesis, as well as for construction of biomimetic solar energy conversion systems. Photosynthetic reaction centers (RCs) from the purple bacteria contain a special pair, i.e., electronically coupled bacteriochlorophyll dimers that act as initial electron donors.^{1–3} Similarly, light-harvesting antenna in photosynthetic bacteria are composed of excitonically coupled bacteriochlorins, and it is assumed that this coupling facilitates an ultrafast energy migration through the antenna.^{4,5} In both cases (special pair and light-harvesting antenna), electronic interactions bath-ochromically shift the absorption band of the involved BCs and therefore make them more efficient in the collection of solar radiation.

The partial charge transfer (CT) character of the excited state of the special pairs has been postulated for a long time based on theoretical calculations,⁶ and results from Stark spectroscopy and hole burning experiments^{7–11} (see also literature cited in ref 12). Subsequently, it has been shown that the CT character has a pronounced impact on the directionality of the electron transfer. Specifically, the reaction center has two electron-cascade pathways branching from this bacteriochlor-ophyll dyad, each constituent BC with its specific electron-cascade pathway.^{3,12} It has been postulated that the partial CT character of the special pair excited state, additionally enhanced by an asymmetry of the protein environment,¹³ contributes profoundly to the direction and rate of the electron transfer.^{8,14} This influence becomes evident when the special pair is replaced by a heterodimer (composed of bacteriochlorophyll and metal-free bacteriopheophytin) and protein mutations, which collectively greatly enhance the CT contribution to the lowest electronically excited state.^{12,15–17}

The CT state also plays a role in the energy transfer within the light-harvesting antennas, both in photosynthetic bacteria¹⁸ and in plants.^{19–21} In addition, the CT state may play a role in energy dissipation in light-harvesting antenna.^{22,23}

The direct investigation of the special pair in RCs and photosynthetic antenna is difficult due to the complexity of the natural system, which causes difficulties in studying and manipulating individual photoinduced steps.³ Therefore, utilizing synthetic models can greatly improve our understanding of the nature of the special-pair excited-state dynamics, specifically the role of interpigment electronic coupling and the specific environment

provided by the protein matrix on the nature of the excited state. These models also help to narrow down the role of the special pair without the additional convolution of other surrounding molecules. Moreover, synthetic compounds, mimicking the function of photosynthetic apparatus, are potentially useful for developing artificial solar energy conversion systems.^{24–30} For these purposes, several types of porphyrin arrays have been developed, where an excitonic interaction between individual porphyrins occurs, such as directly linked,^{24,31,32} co-facial,³³ and slipped co-facial^{25,34} dyads. These systems can efficiently mimic the light-harvesting, energy-transfer, and charge-separation functions of natural light-harvesting antennas and RCs. However, it is unclear whether all important aspects of natural systems are reproduced by porphyrin arrays. For example, although the CT state has been proposed to be coupled to the excitonic state in certain dyads,^{32,35} the majority of work, specifically the ones where such arrays are employed as models of natural light-harvesting antennas or special pairs, do not determine nor discuss the contribution of CT to their excited states.

Nature utilizes chlorophylls and bacteriochlorophylls as the key light-harvesting and redox-active units for light-harvesting antennas and RCs.^{1,4,5} The key structural difference between these pigments and porphyrins is the partial saturation of the core tetrapyrrolic macrocycles, either in one pyrrolic ring (i.e., chlorins in chlorophylls *a* and *b*) or in two opposite pyrrolic rings (i.e., bacteriochlorin in bacteriochlorophylls *a*, *b*, and *g*; see Figure 1).^{1,2,36,37} There are few model systems utilizing actual chlorins or bacteriochlorins as functional units. In the 1970s–1980s, Wasielewski,^{38–43} Boxer,^{44,45} and others^{46,47} developed models in which (bacterio)chlorins co-facial dyads show a solvent-dependent fluorescence quenching, which indicates a contribution of the CT state to S_1 . However, the degree of fluorescence reduction in polar solvents (and thus the degree of CT mixing) is much higher in nonsymmetrical dyads, with an inherent redox asymmetry, and much less for symmetrical ones.^{41,43} Moreover, in some of these dyads, there is no evidence for excitonic interactions between the macrocycles,⁴³ whereas other exhibit a conformational flexibility, which complicates the analysis of the spectroscopic data.^{45,46} Recently, a semisynthetic bacteriochlorophyll dyad has been reported, where two Zn(II) electronic coupling of both states. Both factors seem to be tuned by the specific protein environment) bacteriochlorins were relative energies of the CT and excitonic states and (2) the covalently held in close contact within a synthetic protein.^{48,49} Exciton coupling in dyads was confirmed by absorption spectroscopy and the CT character of the excited state was confirmed by Stark spectroscopy. The degree to which CT mixes with the excitonic state depends on (1) the relative energies of the CT and excitonic states and (2) the electronic coupling of both states. Both factors seem to be tuned by the specific protein environment.⁴⁹ The mixing of CT and S_1 states has been also proposed for symmetrical synthetic conjugated chlorin—chlorin⁵⁰ and directly linked chlorin—porphyrin dyads.⁵¹ In all of the later cases, it has been proposed that the mixing of CT with S_1 results in very fast nonradiative deactivation of the excited state in polar solvents, whereas actual charge-separated state is not observed.

Bacteriochlorins (BCs) are attractive candidates for solar energy conversion due to their multiple absorption bands in the ultraviolet, visible, and near-IR spectral ranges that overlap well with the sun's spectrum.^{1,36,37} There are crucial electronic differences between fully conjugated porphyrins and the partially saturated BCs (Figure 1). The partial saturation in

BCs results in significant changes in their electronic structure,⁵² making BCs more efficient in absorbing near-IR light, easier to oxidize, and harder to reduce than their porphyrin analogues.⁵³ Overall, the electronic, optical, and redox properties of natural bacteriochlorophylls are more closely mimicked by synthetic bacteriochlorins than by porphyrins.³⁷ Moreover, a recent computational study on the charge transfer (CT) in a series of porphyrin, chlorin, and BC dyads has shown that BC dyads are associated with the highest rate for photoinduced charge separation process and with the lowest rate for charge recombination of the three dyads in the series.⁵⁴ Taken together, the BC arrays can serve as a reliable model of natural bacteriochlorophyll-containing photosynthetic systems.

Contrary to the widely investigated porphyrins,⁵⁵ only a handful of studies on synthetic BC arrays have been reported so far.^{36,38,48,49,56–61} We recently reported a series of symmetrical strongly conjugated^{56,58} and directly linked^{59,60} BC—BC dyads. In these derivatives, a significant quenching of fluorescence in solvents of high dielectric constant was observed, which suggests a contribution of CT to the excited state. The quenching of fluorescence in strongly conjugated BC dyads has been attributed to the enhanced $S_1 \rightarrow S_0$ internal conversion caused by a contribution of charge-resonance configuration to the excited state in polar solvents.⁵⁸ However, the dynamics of the excited state in symmetrical, meso-meso directly linked, and weakly coupled BC dyads and the reason for the significant reduction in fluorescence in polar solvents have not yet been investigated.

Here, femtosecond time-resolved spectroscopy and computation are utilized to investigate the photophysical properties of synthetic, structurally symmetric bacteriochlorin homo-dyads, exhibiting a different degree of electronic conjugation, **BC1** — **BC3**,⁵⁹ and a monomer, **BC4**^{37,62} (Figure 1B). The monomer **BC4** was used to compare how the dyad's excited-state behavior deviates from that of the constituent monomers. The effect of the linker length and solvent on the excited-state dynamics is determined using time-resolved absorption, fluorescence, and computational analysis. In the low-dielectric-constant solvent toluene ($\epsilon = 2.38$), the excited-state dynamics of the dyads are invariant of linker length and similar to that observed for the monomer (**BC4**). However, in the high-dielectric solvent *N,N*-dimethylformamide (DMF, $\epsilon = 36.7$), the excited state of the dyads is strongly quenched relative to the monomer **BC4** or weakly coupled **BC3**. This quenching is attributed to charge transfer (CT) between the BC rings supported by computational studies, which confirm the relevance of the CT states in a solvent with high ϵ . These results provide an essential perspective to improve our ability in designing molecular systems that are effective in harvesting solar radiation for charge separation and give an insight into the excited-state properties of the bacteriochlorophyll special pair.

EXPERIMENTAL SECTION

The synthesis and basic spectral characterization of the target dyads **BC1-BC3**⁵⁹ and monomer **BC4**^{37,62} were performed as described previously.

Femtosecond-TA (fs-TA) measurements were performed using a Clark MXR CPA-2001 laser that outputs 150 fs pulses of 780 nm light at a repetition rate of 1 kHz. The fundamental 780 nm light was split with 95% of the light sent through a TOPAS (Light

Conversion) to generate the pump pulses at the desired wavelength and 5% was directed toward a motorized optical delay stage and then focused into a sapphire crystal to generate the white-light-continuum probe beam measuring the spectral range from 450–780 nm. The maximum time window of the experiment was instrument-limited to 3 ns. The time-resolved fluorescence measurements were performed using the same laser source as in the transient absorption measurements. The contour plots and kinetics were collected using an Optronis streak camera. The ground-state UV-vis absorption measurements were performed before and after each time-resolved measurement to ensure the samples were not degraded upon laser excitation.

Computations were performed following the previously reported protocol,^{63,64} which was used for a study of similar systems⁶³ and has been benchmarked extensively. The applied approach implements the Fermi golden rule, which employs density functional theory with environment effects taken into account through polarizable continuum models. The dispersion-corrected range-separated hybrid ω B97XD functional and fragment-charge difference method were used for the calculation of the excited states and electronic coupling. DFT calculations of MOs, presented in Table S2, were performed in vacuum using Spartan 10 for Windows (Wavefunction, Inc., Irvine, CA) employing the B3LYP functional and 6–31G* basis set.

RESULTS AND DISCUSSION

The optical properties of these dyads were characterized by first measuring the ground-state absorption (Figure 2). Comparing the position of the Q_y peaks of each sample listed in Table 1, it is found that there are no major shifts when switching solvents, which demonstrates that the solvent polarity does not have an impact on the ground-state absorption properties. However, sequential addition of phenylene rings in the bridge position (**BC1-BC3**) shifts the absorption maxima closer to that of the monomer BC4. Increasing the number of phenylene bridge units lessens the electronic coupling between the BCs, leading to a blue-shift of the Q_y absorption.

The directly linked **BC1** shows the largest dyad-induced shift, with the Q_y peak centered at 731 nm, compared to the weakest coupled dyad, **BC3**, which absorbs at 717 nm. The slight bathochromic shift in the Q_y band of **BC2** and **BC3** is ascribed to the substitution with a phenyl ring at the 15 position of the BC, a similar shift has been observed for an analogous 15-tolyl-substituted BC, for which $\lambda_Q = 712$ nm.⁵⁹ The Q_y peak of **BC1** is also split, with its weaker second absorption centered at 706 nm. This splitting can be attributed to the excitonic coupling between BC macrocycles.⁶⁵ Overall, the bathochromic shift of Q_y band is caused by two factors— substitution by a large aromatic BC system at the 15-position of BC and the excitonic BC-BC interactions. The lower-energy transition at 730 nm is labeled Ψ_{BC1}^+ and the higher-energy transition at 706 nm is labeled Ψ_{BCr} (Figure 3). The electronic coupling (V) between the monomer subunits in **BC1** can be calculated as one-half of the energy splitting (observed or calculated) between both lowest-lying energy transitions, which we determine to be $V = 242.2 \text{ cm}^{-1}$. This V value indicates an electronic coupling of the BC units lower than that in bacteriochlorophyll special pairs (e.g., $V = 550 \text{ cm}^{-1}$ for

P870 and $V = 950 \text{ cm}^{-1}$ for P960).⁶⁶ However, V for **BC1** is comparable to that reported for light-harvesting antennas ($V = 300 \text{ cm}^{-1}$ for B850⁶⁶).

Based on the relative intensities of the split Q_y peaks at 706 and 730 nm, the dihedral angle of the BC transition dipoles in **BC1** was determined to be 57.5° . To determine the angle between the transition dipole of the two BC monomer constituents in the dyad, eq 165 can be applied, where $I_{\text{BCI}^\pm}$ is the intensity of the two Q_y absorption peaks of **BC1**, I_{BC4} is the intensity of the monomer, and θ is the angle between the two BC constituents. For **BC1**, the intensity of the 706 nm peak (Ψ_{BCI^-}) is 0.3, whereas the peak at 730 nm is 1. However, there are two unknown variables in eq 1, I_{BC4} and θ .

$$I_{\text{BCI}^\pm} = I_{\text{BC4}}(1 \pm \cos\theta) \quad (1)$$

Equation 1 can be separated to solve for both the plus and minus terms and rearranged to solve for I_{BC4} , as shown in eqs 2a and 2b. Setting these two equations equal to one another allows to solve for θ , which gives 57.5° .

$$I_{\text{BC4}} = \frac{I_{\text{BCI}^+}}{(1 + \cos\theta)} \quad (2a)$$

$$I_{\text{BC4}} = \frac{I_{\text{BCI}^-}}{(1 - \cos\theta)} \quad (2b)$$

Additional support for strong electronic interaction in **BC1** is provided by density functional theory calculations (Table S2). The calculations have revealed a splitting of the each relevant orbital (highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital, HOMO-1, etc) into two new orbitals, with the same symmetries as the relevant orbitals in each monomer. This splitting can be interpreted as arising from linear combination of the relevant orbitals of each monomer, leading to the formation of “bonding” and “antibonding” excitonic orbitals. Such a splitting has been previously observed for strongly conjugated BC dyads, and it has been considered as a signature of a strong electronic interaction between macrocycles.^{58,60,61} As expected, such a splitting is observed only for **BC1**, whereas pairs of degenerated orbitals are present for **BC2-BC3**.

The shifts in the absorption spectra of **BC1-BC3** show that the directly linked **BC1** exhibits the strongest electronic coupling between the rings, which leads to its Q_y transition appearing at a lower energy due to spatial proximity of the molecular orbitals of the BC macrocycles. The exciton interactions are due to the close distance of the BCs in the dyad and, because the relative intensities of these peaks are the same in both toluene and DMF, the exciton interactions are solvent-independent. The insertion of phenyl (**BC2**) or biphenyl

(**BC3**) bridge between BC macrocycles causes a smaller bathochromic shift of the Q_y band, and splitting is no longer visible, which collectively indicate that interpigment electronic coupling is much weaker than in **BC1**.

fs-TA spectroscopy^{67–72} was carried out to determine the excited-state relaxation dynamics of **BC1-BC4**. The fs-TA spectra of **BC1** in DMF are shown in Figure 4A and the spectra for all BCs in both solvents can be found in Figure S2. All BCs show two bleach features that align with the Q_x and Q_y bands in the ground-state absorption spectra. **BC1** has a transient absorption at 700 nm, which is not seen in the other dyads.

The normalized kinetic traces of the Q_y bleaching in toluene and DMF are shown in Figure 4B,C, respectively. In toluene, all BCs show similar decay kinetics with a lifetime of approximately 5 ns (Table 1). These decay dynamics reveal that relaxation from the excited state to the ground state in toluene is invariant to the linker substitution or linker length.

In DMF, however, the longer time component of **BC1** and **BC2** was quenched, and instead, a new, fast relaxation component was observed, whereas **BC3** exhibits minimal quenching and behaves more like the monomer (Table 1). Because quenching is only observed in solvents of high ϵ , this implies the accelerated relaxation results from intramolecular charge transfer (CT) between the BC rings. The CT would either produce nonemissive cation/anion radical pairs, which are only stabilized in solvents of high ϵ , or cause a very fast internal conversion, which is manifested by a significant reduction in fluorescence.^{49,51}

To understand the fluorescence properties, the steady-state fluorescence of these dyads were measured (Figure 5). In toluene, a blue-shift in the fluorescence wavelength maximum is observed as the distance between BCs in the dyads increased, in agreement with the ground-state absorption spectra. The fluorescence maximum changes by 9 nm for **BC1** from toluene to DMF and all other dyads show smaller shifts of 2 nm. It is worth noting that for **BC1** a weak fluorescence was observed at longer wavelengths ~770 nm in DMF (i.e., possibly from low-lying CT states). To the best of our knowledge, emissive CT states involving tetrapyrrolic macrocycles have not been reported to date. A convolution of three Gaussian fluorescence curves is presented in Figure S4, which reproduces the measured fluorescence spectrum of **BC1** in DMF.

The fluorescence quantum yield (Φ_f) of **BC1** in DMF is reduced by 99% and that of **BC2** by 70% compared to their quantum yields in toluene. The **BC3** dyad shows 27% quenching when in DMF compared to when in toluene. As expected, the monomer **BC4** shows little quenching of 9% when in DMF compared to the fluorescence in toluene. This quenching of Φ_f indicates that in DMF, BC dyads exhibit a competing nonradiative deactivation mechanism, which depends on the distance between the BCs and the solvent dielectric constant.

For **BC1** in DMF, two sharp emission peaks are observed, one at 711 nm and another at 749 nm. These two emission features are also observed for **BC1** in toluene; however, due to large fluorescence quantum yield (Φ_f) of the 749 nm peak of **BC1** in toluene (0.28) versus that in

DMF (0.003), the 711 nm peak appears as a small shoulder when **BC1** is dissolved in toluene.

Figure 6 shows the fluorescence kinetic traces of the BCs in DMF and toluene, and the corresponding time-resolved fluorescence contour plots recorded with a high-speed streak camera are presented in Figures 7 and 8. Similar to the fs-TA kinetics, the fluorescence lifetimes of BCs in toluene are invariant of linker length and all dyads and the monomer have a relaxation time constant τ_{rel} of 5 ns (Table 1).

In DMF, τ_{rel} is drastically reduced for **BC1** ($\tau_{\text{rel}} < 50$ ps). The fluorescence quantum yields Φ_{fl} corroborate the observed quenching of the fluorescence, which for **BC1** is reduced nearly 100-fold in DMF compared to that in toluene (Table 1). The origin of this quenching is in the nonradiative relaxation from the S_1 state to the CT state followed by electron–hole recombination and ultimately repopulation of the S_0 ground state.

These CT properties are reduced upon the addition of the phenylene bridge due to the increased BC separation leading to nearly negligible electronic coupling between the macrocycles; therefore, the observed fluorescence occurs from the excited state localized on one macrocycle (i.e., fully decoupled state).

For **BC1**, the same emission peaks observed in the steady-state fluorescence measurements are found in the time-resolved data set too. However, τ_{rel} for the high-energy emission at 711 nm is solvent-independent. The minimal quenching of the emission at 711 nm, contrasted with the relatively short lifetime at 749 nm, indicates that the CT state primarily mixes with the lower-energy Ψ_{BC1}^+ state.

The origin of the higher-energy emission is not 100% clear at this point. We can rule out the possibility that this is an impurity. The presence of similar peak in other directly linked BC dyads reported previously⁶⁰ suggests that this is an inherent feature of this class of compounds. This emission is also rather unlikely from the higher-excitation state, given that typically a very fast (<1 ps) relaxation from the upper to the lower exciton state occurs.⁷³ The presence of weakly fluorescent H-aggregates is also unlikely. The absorption spectra in the broad range of solvent are very similar and independent of the **BC1** concentration. The presence of the long-wavelength emission band is also observed in a broad range of solvents, including one in which **BC1** shows good solubility. Thus, the aggregation seems not to underlie any of the observed emission.

The key energetic parameters that control the CT process, i.e., the electronic coupling (V_{el}), reorganization energy (E_{reorg}), activation energy (E_{A}), and driving force (E), were also computed (Table 3). As the distance between BCs in the dyads increases, the calculated V_{el} decreases from 125.8 cm⁻¹ in **BC1**, to 42.7 cm⁻¹ in **BC2**, and 9.7 cm⁻¹ in **BC3**. Furthermore, the E_{A} for BC1 and BC2 are approximately 300 meV (2420 cm⁻¹) and for **BC3** is 463 meV (3734 cm⁻¹). It is also found that the E_{A} for CT increases from 88 to 127 meV with increasing distance. All of these factors contribute to the decrease in k_{CT} upon the introduction of phenyl ring spacers (Table 3), in agreement with the experimental results.

To further support the hypothesis of photoinduced CT within **BC1-BC3**, computational analysis was performed. The calculated solvated CT state energies are given in Table 2. In toluene, the CT state remains higher in energy than S_1 because the solvation energy is insufficient to stabilize the CT states. On the other hand, in DMF, the CT state energy becomes approximately (within 0.1 eV) the same as the S_1 state energy and mixing of these states can occur, leading to the quenching of fluorescence.

The lifetime of S_1 for the native special pairs has been estimated to be 180–350 ps,¹² which is an order of magnitude shorter than those observed for **BC1** in toluene (5 ns) but five times longer than that in DMF (41 ps). The lifetimes of S_1 for both **BC2** and **BC3**, either in toluene or in DMF, are an order of magnitude longer than those of the native special pair.⁵ It should be pointed out that the dielectric constant ϵ in the close vicinity of the native RC was found to be $\epsilon = 1.5$ –9, which is on average higher than that for toluene (2.38), but significantly lower than that for DMF (36.7). The dielectric constant has a pronounced impact on the mixing of the CT with the excitonic state by modulating the energy of CT and affecting the electronic coupling between both states.^{16,17,49} Reduction in the Φ_f for **BC1** parallels the increase in ϵ of the solvent (Table S1), thus it is reasonable to assume that the degree of CT mixing with the excitonic state strongly depends on ϵ as well. This result emphasizes the importance of the local dielectric constant on the photophysical properties of the excited state of the investigated BC dyads (Table 3).

CONCLUSIONS

In summary, we have shown that there is a substantial contribution of CT to the deactivation of the excited state in fully symmetrically arranged, electronically coupled BC dyads. k_{CT} strongly depends on the distance and electronic coupling between the BC, i.e., k_{CT} is reduced by nearly an order of magnitude with each phenyl ring inserted between the BC rings. Most importantly, the kinetics of the excited state of BC dyads strongly depend on the solvent dielectric constant ϵ , which emphasizes the importance of amino acid composition in the special pair protein matrix on the pair's properties. Although there are important differences between **BC1-BC3** and natural special pairs (e.g., utilization of free-base BC versus Mg chelates, linear vs slipped co-facial arrangement of chromophores), it is hoped that the reported dyads represent models for naturally occurring special pairs, help to narrow down the role of the special pairs without additional surrounding molecules, and offer the opportunity for fundamental studies on the primary processes in natural photosynthesis, leveraging these systems for bioinspired solar energy conversion systems.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENTS

This work was supported by the Center for Chemical Dynamics at Case Western Reserve University, NSF (CHE-1301109 to MP and CHE-1362504 to BDD). We are also grateful to generous resource allocations on the Ohio Supercomputer Center and the Kent State University, College of Arts and Sciences Computing Cluster. N.N.E. is a member of CBI Program at UMBC, supported by the NIH (Grant No. 5T32GM066706) and a member of the

Meyerhoff Scholars Program at UMBC, supported by the NIGMS Initiative for Maximizing Students Development Grant (Grant No. 2 R25-GM55036).

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Figure 1.
(a) Structure of porphyrin, chlorin, and bacteriochlorin. (b) Dyads and monomer investigated in this work.

Figure 2.

UV-vis absorption of BCs in (A) toluene and (B) DMF. The directly linked **BC1** (black) shows a red-shifted Q_y band relative to the other dyads. As the number of phenylene bridge units are increased, the Q_y band of the dyads blue-shifts toward that of the monomer **BC4** (blue).

Figure 3.

(A) Comparison of the UV-vis absorption spectrum of **BC1** dyad (black) and the most distant dyad **BC3** (green). The dashed lines indicate the maxima of the absorption peaks. (B) Illustration of the excited-state energies of two BC monomers ($\Psi_{BC,mono}$) interacting to form the split **BC1** Ψ_{BC1^-} (green) and Ψ_{BC1^+} (red) excitonic states.

Figure 4.

(A) fs-TA spectra of **BC1** in DMF at indicated delay times (noted in legend) after 500 nm laser pulse excitation. (B) Kinetic traces of the transient bleaching of the dyads **BC1-BC4** in toluene and in (C) DMF, monitored at the Q_y band transition.

Figure 5. Steady-state fluorescence spectra of the dyads **BC1-BC3** and the monomer **BC4** in (A) toluene and (B) DMF excited at 500 nm. All BCs have similar fluorescence in either solvent, except for **BC1**, which has a split peak in DMF, whose higher energy is similar to the monomer's (**BC4**) fluorescence.

Figure 6. Time-resolved fluorescence decay kinetics of BCs in (A) toluene and (B) DMF. Data were fit with single exponential decay equations and the obtained lifetimes are summarized in Table 1.

Figure 7.

Time-resolved fluorescence contour plots of BCs in (A-D) toluene and in (E-H) in DMF measured on a high-speed streak camera. From these plots, it is easy to notice trends in fluorescence decay. In DMF, fluorescence is quenched compared to that in toluene, with **BC1** showing the largest decrease in fluorescence lifetime. In DMF, the shorter wavelength peak is hypothesized to be due a local excited-state emission and the longer wavelength emission due to the lower-energy excitonic state Ψ_{BC+} , which is strongly coupled to the

charge-transfer (CT) state and as such quenched, owing to the additional relaxation pathway through the CT state.

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Figure 8.

Illustration of the relaxation pathways for **BC1** in DMF. Following excitation (blue) from the ground state to the excited state, **BC1** relaxes to Ψ_{BC1^-} (green) and then Ψ_{BC1^+} (red) states. From these states, radiative (solid arrow) and nonradiative (not shown) relaxations occur. The CT state (blue) primarily mixes with the Ψ_{BC1^+} state, which leads to accelerated nonradiative relaxation in high-dielectric solvents and possibly to the red-shifted, broad emission centered at 770 nm (see Figure S4).

Table 1.

Absorption Maxima of the Q_y Bands, Decay Dynamics of the Transient Q_y Bleaching, Fluorescence Wavelength, Fluorescence Quantum Yield, Relaxation Lifetime, Relaxation Rate Constant, Fluorescence Rate Constant, Nonradiative Rate Constant, CT Rate Constant, and Back Electron Transfer Rate Constant of BCs in Toluene and DMF

compound	λ_{Q_y} (nm)	τ_1^{decay} (ps) ^a	τ_2^{decay} (ps) ^a	λ_n (nm)	Φ_n^b	τ_{rel} (ns) ^b	k_{rel} ($\times 10^8 \text{ s}^{-1}$)	k_n ($\times 10^8 \text{ s}^{-1}$)	k_{nr} ($\times 10^8 \text{ s}^{-1}$)	k_{CT} ($\times 10^8 \text{ s}^{-1}$)	k_{het} ($\times 10^8 \text{ s}^{-1}$)
Toluene											
BC1	731	4556		738	0.28	5.01 ± 0.03	2.0	0.52	1.5		
BC2	718	5633		725	0.22	5.10 ± 0.03	2.0	0.43	1.5		
BC3	717	6264		726	0.22	5.10 ± 0.04	2.0	0.43	1.5		
BC4	710	6419		712	0.19	4.94 ± 0.05	2.0	0.45	1.6		
DMF											
BC1	730	41 ± 0.05		749	0.003	c_{240}^d	0.73		2.1	240	240
BC2	718	12 ± 1	1829 ± 30	727	0.07	1.88 ± 0.03	5.3	0.37	1.3	3.6	5.4
BC3	716	33 ± 2	4731	725	0.16	4.84 ± 0.05	2.1	0.33	1.2	0.56	1.5
BC4	708	45 ± 9	6549	714	0.17	4.98 ± 0.04	2.0	0.40	1.6		

^aExtrapolated lifetimes were determined by fitting the exponential decay equation to a final y_0 value of 0.

^b Φ_{fl} and τ_{rel} were determined in air-equilibrated solvents exciting at the maximum of the Q_x band. Φ_{fl} was established using tetraphenylporphyrin in nondegassed toluene ($\Phi_{\text{fl}} = 0.07$) as a standard.

^c τ_{rel} was instrument-limited at 50 ps; therefore, τ_{rel} obtained from fs-TA was used.

^dFor BC1, k_{rel} was calculated using the lifetime of the Q_y bleach from the fs-TA measurements.

Table 2.

Calculated Gas-Phase Charge-Transfer State ($E_{\text{gas}}^{\text{CT}}$), DMF Solvation Energy (E_{sol} ; Toluene Solvation Energy in Parenthesis), DMF-Solvated CT State Energy at the Equilibrium Ground-State Geometry ($E_{\text{sol}}^{\text{CT}}$) and CT State Geometry ($E_{\text{sol}}^{\text{CT}*}$), and Calculated S_1 Energy Level

compound	$E_{\text{gas}}^{\text{CT}}$ (eV)	E_{sol} (eV)	$E_{\text{sol}}^{\text{CT}}$ (eV)	$E_{\text{sol}}^{\text{CT}*}$ (eV)	E_{s1} (eV)
BC1	3.07	1.01 (0.52)	2.06	1.72	1.72
BC2	3.72	1.62 (0.89)	2.10	1.82	1.76
BC3	4.08	1.83 (1.01)	2.25	1.79	1.76

Table 3.

Calculated Dyad Spacing (R), Electronic Coupling (V_{el}), Reorganization Energy (E_{reorg}), Activation Energy (E_A), CT Driving Force (E), Marcus CT Rate (k_m), and Fermi Golden Rule CT Rate (k_{FGR})

compound	R (Å)	V_{el} (cm-1)	E_{reorg} (meV)	E_A (meV)	E (meV)	k_{Marcus} (s ⁻¹)	k_{FGR} (s ⁻¹)
BC1	9.27	125.8	337	88	-7	2.2×10^{11}	6.2×10^{11}
BC2	13.60	42.7	282	93	-42	2.2×10^{10}	6.4×10^{10}
BC3	17.92	9.7	463	127	-23	2.3×10^8	7.3×10^9