Photoisomerization of Enediynyl Linker Leads to Slipped Cofacial Hydroporphyrin Dyads with Strong Through-Bond and Through-Space Electronic Interactions

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Supporting Information



ABSTRACT: Photoisomerization of 3,4-di(methoxycarbonyl)-enediyne linker in hydroporphyrin (chlorin or bacteriochlorin) dyads leads to thermally stable cis isomers, where macrocycles adopt a slipped cofacial mutual geometry with an edge-to-edge distance of ~3.6 Å (determined by density functional theory (DFT) calculations). Absorption spectra exhibit a significant splitting of the long-wavelength Q_y band, which indicates a strong electronic coupling with a strength of $V = \sim 477 \text{ cm}^{-1}$ that increases to 725 cm⁻¹ upon metalation of hydroporphyrins. Each dyad features a broad, structureless emission band, with large Stokes shift, which is indicative of excimer formation. DFT calculations for dyads show both strong through-bond electronic coupling and through-space electronic interactions, due to the overlap of π -orbitals. Overall, geometry, electronic structure, strength of electronic interactions, and optical properties of reported dyads closely resemble those observed for photosynthetic special pairs. Dyads reported here represent a novel type of photoactive arrays with various modes of electronic interactions between chromophores. Combining through-bond and through-space coupling appears to be a viable strategy to engineer novel optical and photochemical properties in organic conjugated materials.

■ INTRODUCTION

Excitonically coupled chromophores¹ are key components of light-harvesting antennae and photosynthetic reaction centers; as such, they are crucial for initial processes in photosynthesis, that is, light harvesting and charge separation.^{2,3} Bacterial photosynthetic light-harvesting antenna are constructed from bacteriochlorophyll a clusters with increasing interpigment excitonic coupling, which leads to a shift of the longwavelength Q_v absorption band from 800 nm in the nearly noninteracting pigments found in B800 to 850 and 875 nm, in B850 and B875, respectively.^{2,3} This shift is, at least in a large part, due to the excitonic interactions between bacteriochlorophylls.^{2,3} Chlorosomes, i.e., light-harvesting antennae found in green sulfur bacteria, are composed of self-assembled bacteriochlorin *c* molecules, where strong interpigment interactions lead to ~ 100 nm bathochromic shift in the Q_y absorption band.⁴ Excitonic coupling is also evident in plant² and bacterial⁶⁻⁹ photosynthetic reaction centers between closely positioned chlorophylls and bacteriochlorophylls, respectively. Thus, the reaction center from purple photosynthetic bacteria Rhodobacter sphaeroides contains a special pair (P867) of two excitonically coupled bacteriochlorophyll a, absorbing at 867 nm,^{3,10} whereas P960, a special pair from

Rhodopseudomonas viridis, contains a pair of bacteriochlorophyll b_{1}^{11} which absorbs at 960 nm.⁷ The strength of excitonic coupling varies from $\sim 200 \text{ cm}^{-1}$ in B850¹² to 550 cm^{-1} in P867, up to ~900 cm^{-1} in P960. Thus, the extent of excitonic interaction tunes the absorption properties of photosynthetic pigments and, in turn, the energy of the excited states, which collectively allows for a more efficient harvesting of solar photons and assures the flow of the excitation energy to the reaction centers.² Moreover, excitonic coupling is proposed to play a crucial rule in the ultrafast and essentially quantitative energy transfer between light-harvesting antenna and reaction center,^{2,9} as well as in ultrafast charge separation, for example, through vibronic coherence.^{13–16}

Excitonic coupling is currently viewed as the consequence of two phenomena: (a) electrostatic interaction between transition dipole moments of chromophores, as described in Kasha's model (aka long-range coupling)^{1,17} and (b) shortrange excitonic coupling, which resulted from the throughspace overlap of π -orbitals of interacting chromophores.¹⁷ For chromophores separated by a close distance, like bacterio-

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chlorophylls in light-harvesting antenna and special pairs, short-range excitonic coupling seems to play a dominant role.¹⁸

To mimic coupled systems observed in the natural photosynthetic apparatus, a large number of excitonically coupled or strongly conjugated porphyrin arrays have been studied, including directly linked,^{19,20} cofacial,^{21–23} slipped cofacial,²⁴ and ethynyl- or butadienyl-linked arrays.²⁵ However, nature utilizes hydroporphyrins, which are partially saturated porphyrin congeners (chlorins and bacteriochlorins) as key photo- and redox-active components in the photosynthetic apparatus.² Hydroporphyrins possess a much more intensive $S_0 \rightarrow S_1$ transition (Q_y band) relative to porphyrin.²⁶⁻²⁸ Moreover, hydroporphyrins feature a lower magnitude of $E_{1/2}^{0/+}$ and $E_{1/2}^{-/0}$ values (i.e., they are easier to oxidize and harder to reduce) compared to corresponding porphyrins.² Therefore, it is expected that the structure-excitonic coupling relationship and properties of excitonically coupled hydroporphyrins will be different from that of porphyrins. Synthetic hydroporphyrin arrays with excitonic coupling have been studied to a much lesser degree than porphyrinic architectures. There have been extensive studies performed on chlorosome models, in which semisynthetic chlorins or bacteriochlorins self-assemble into oligomers,^{25,30} where individual hydroporphyrins strongly interact with one another. There are also several examples of synthetic, covalently linked cofacial $^{31-52}$ or directly linked^{53,54} arrays. For some of such arrays, evidence for excitonic coupling is observed; however, hydroporphyrin arrays have been investigated much less extensively than corresponding porphyrinic systems.

We recently reported arrays composed of hydroporphyrins with varying degree of electronic interaction. These dyads include strongly conjugated arrays, where hydroporphyrins are connected by ethynyl, butadiynyl, or vinyl linkers, $^{55-57}$ mesomeso directly linked hydroporphyrin dyads, $^{58-60}$ and weakly conjugated arrays, where hydroporphyrins are connected by phenylene linkers. 58,60 In strongly conjugated dyads, we observed a significant bathochromic shift and splitting of the Q_y band, which is a result of through-bond π -conjugation. In directly linked arrays, splitting of the Q_y band is most likely due to short-range excitonic coupling only, since the perpendicular mutual arrangement of macrocycles effectively prevents direct π -electronic coupling. ⁵⁹

Continuing our studies on the dependence of photophysical properties of strongly conjugated hydroporphyrin dyads on the linking moiety, we intended to prepare a series of arrays where chlorins and bacteriochlorins are connected by a linker comprising alternating carbon-carbon triple and double bonds, i.e., hexa-3-en-1,5-diyne (enediyne) unit. Conjugated chromophores containing this unit possess unusual optical and electrochemical properties, as was demonstrated by Diederich⁶¹⁻⁶⁶ and others.^{61,67} The Diederich group also reported a conjugated porphyrin dimer, connected by an enediyne unit.⁶⁸ Moreover, conjugated enediynes undergo trans-cis photoisomerization, a trait that has been utilized for the development of photochromic and redox-active molecules.^{69–73} Overall, we have anticipated that the combination of enediynes with hydroporphyrins will lead to molecules with interesting and useful optical and photochemical properties.

Here, we report the synthesis and properties of dyads composed of two identical hydroporphyrins: chlorin (cis-2C, cis-2ZnC, and trans-2C) or bacteriochlorin (cis-2BC, Chart 1), connected through their respective 13-positions by 3,4-

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dimethoxycarbonyl-hexa-3-en-1,5-diynyl motif. We selected this particular diester-substituted enediyne linker primarily due to the anticipated straightforward synthesis through the Sonogashira reaction, which utilizes dimethyl dibromofumarate.^{69–71} It is also known that diester-substituted enediynes undergo trans–cis photoisomerization.^{69–71} As a reference, we also prepared dyad **phen-2C**, where two chlorins are connected by *o*-diethynylphenylene linker. As benchmarks, we included known monomers: C-PE⁵⁷ and BC-2PE^{55,56} (Chart 1). We found that enediyne-linked hydroporphyrin dyads exhibit trans–cis photoisomerization, leading to thermally stable cis isomers, with a slipped cofacial arrangement of macrocycles, in which both strong through-bond and through-space interactions occur.

RESULTS AND DISCUSSION

Our synthetic approach is outlined in Scheme 1. Dimethyl 2,3dibromofumarate 1 was prepared by bromination of dimethyl acetylene dicarboxylate with pyridinium perbromide, according to the previously reported procedure.^{74,75} Initially, we intended to perform synthesis via enediyne 3 (Scheme S1); however, attempted deprotection of 2 leads to complete decomposition

Scheme 1. Synthesis of trans-2C and cis-2C



of starting material, and no 3 could be isolated; apparently, 3 is unstable at room temperature, similar to analogous enediynes reported previously.⁷⁶ Therefore, we pursued the syntheses of dyads through the Sonogashira reaction of 1 with ethynylsubstituted chlorin $Ch-E^{57}$ and bacteriochlorin BC-E,⁵⁵ which syntheses were reported previously.

The Sonogashira reaction between Ch-E and 1 in the presence of $Pd_2(dba)_3/P(o-tol)_3$ in toluene/triethylamine (5:1) at 60 °C for 2 h, performed without any protection from ambient light, afforded two dyads, which were identified as cis-2C (28% yield) and trans-2C (minor product, <5% yield, Scheme 1). The low combined yield of both products is attributed to the formation of a large amount of butadiynyllinked b-2C as a side product (~30%, yield refers to a semipurified sample). The analogous Sonogashira reaction, when performed in the dark (reaction mixture was rigorously protected from light at each stage: reaction, workup, purification, and analysis of products), leads to isolation of trans-2C (21% yield) and cis-2C (trace). As observed for reaction performed in the presence of light, a large amount of butadiyne-linked dyad b-2C was also isolated. cis-2C and trans-2C can be separated by column chromatography in the dark; however, when exposed to ambient light, either dyad equilibrates within a few hours to the mixture of cis-trans isomers in approximately 10:1 ratio of cis-2C to trans-2C. cis-**2ZnC** was obtained in the reaction of cis-2C with $Zn(OAc)_2$ in CHCl₃/MeOH in 67% yield. The Sonogashira reaction of bacteriochlorin BC-E with 1, conducted in the presence of ambient light, leads to the formation of a mixture of cis-2BC as the major product (35% yield, Scheme 2) and other product (presumably trans-2BC) in >10:1 ratio; however, attempts to separate both products using chromatography were unsuccessful. A large amount of homodimer $b-2BC^{55}$ was also isolated in this case (20-30%).

Dyad phen-2C was synthesized in the Sonogashira reaction of Ch-E with 1,2-dibromobenzene in 38% yield (Scheme 3). Analogously to reactions described above, some amount of dyad b-2C was also isolated (the yield of b-2C was not determined).

The structures of the final dyads were confirmed by the detailed analysis of their NMR spectra. The ¹H NMR spectrum of cis-2C exhibits significant shifts of the resonances of methylene protons at the 17-position of chlorin macrocycle (H-17 to 2.11 ppm, compared to δ 4.67 in the Ch-E) and geminal methyl groups at the 18-positions (Me-18 to -0.48 ppm, compared to 2.01 ppm in Ch-E). Similarly, the spectrum of cis-2BC exhibits a significant shift of the H-17 (to 2.81 ppm, compared to 4.10 ppm in BC-E) and Me-18 (to 0.55 ppm, compared to 1.93 ppm in BC-E) in bacteriochlorins. Resonances of 7-methylene protons and geminal 8-methyl substituents appear at 4.41 ppm and 1.88 ppm, respectively, which is comparable to that observed for monomer BC-E. ¹H NMR spectrum of trans-2C shows resonances of H-17 and Me-18 at 4.73 ppm and 2.10 ppm, respectively, which is comparable to that observed for Ch-E. The detailed assignment of chemical shifts in chlorin dyads and monomers is presented in Table S1.

The observed significant changes in chemical shift of certain protons between monomers and dyads are consistent with cis stereochemistry of the enediyne linker, which forces macrocycles to adopt a slipped cofacial geometry so that some protons of one macrocycle are placed in the shielding cone of the aromatic system of the other macrocycle (Figure 1). To



Scheme 3. Synthesis of phen-2C





Figure 1. DFT energy-minimized structures of **cis-2C** and **cis-2BC**. Hydrogen atoms are omitted for clarity. The green spheres represent centroids for the macrocycles.

further confirm this hypothesis, we analyzed dyad **phen-2C**, where two chlorins are connected by *o*-diethynylphenylene linker. In **phen-2C**, macrocycles should adopt a similar geometrical arrangement as in **cis-2C**; thus, the similarity of ¹H NMR spectra of both **cis-2C** and **phen-2C** will be further indirect confirmation of the structure of the former. ¹H NMR spectrum of **phen-2C** shows similar features as for **cis-2C**, e.g., resonances of H-17 and Me-18 appear at 2.25 and -0.37 ppm, respectively. Detailed analysis of NMR spectra and density functional theory (DFT) calculations lead to the conclusion that the most likely conformation of **cis-2C**, **cis-2BC**, and **phen-2C** is that with a slipped antiparallel arrangement of macrocycles (Figure 1). Such a structure is supported by a

significant upfield shift of H-17 and Me-18, and a smaller upfield shift for H-20, H-2, and H-3 resonances for dyads versus monomer. Furthermore, there are no notable shifts of methyl groups of mesityl substituents at the 10-position of chlorin nor for H-7 and H-8 for dyads versus monomer (see Table S1, Supporting Information). DFT calculations support this structure, showing that such an antiparallel slipped cofacial geometry is associated with the lowest energy for cis configuration of the linker. The center-to-center distance between chlorin macrocycles in such an arrangement is 7.17 Å, while the edge-to-edge distance (measured as the distance between carbon atoms C-15) is 3.64 Å. Similarly, for cis-2BC, the center-to-center distance is 7.20 Å and the edge-to-edge distance is 3.58 Å. In cis-2ZnC, these distances are shorter, i.e., 6.59 and 3.55 Å, respectively. For phen-2C, the corresponding distances are 7.22 and 3.65 Å, respectively (all distances above are obtained from DFT calculations for energy-minimized structures).

The ¹H NMR spectra also suggest that the structures presented in Figure 1 undergo fast conformational interconversion on the NMR time scale since no differentiation between the "inner" and "outer" Me-18 and H-17 positions of macrocycles was observed. Such an interconversion would involve simultaneous rotation of both macrocycles along respective ethyne linker back and forth and "inverting" the stacking arrangement of macrocycles in dyads. Note that the proposed structures are axially chiral and such an interconversion transforms one enantiomer into the other.

Photoisomerization of Enediyne-Linked Chlorin Dyads. The results discussed above indicate that the enediyne-linked hydroporphyrin arrays undergo fast trans-cis photoisomerization. Both cis-2C and trans-2C isomers are stable in the solid state in the dark at room temperature (no changes observed for months). In solution, pure cis-2C and pure trans-2C, when exposed to ambient light, undergo equilibration within a few hours to the mixture containing cis-2C and trans-2C in 10:1 ratio. In a more controlled experiment, we irradiated solutions of cis-2C and trans-2C in toluene at the maxima of their B bands. This resulted in the equilibration of each solution to cis/trans ratio of 10:1 within 23 min (Figures 2 and 3). The isomerization time scale was much the same upon irradiation of trans-2C at the maximum of the Q_v band (700 nm). ¹H NMR spectroscopy further confirmed a trans-cis isomerization, as exposure to ambient



Figure 2. Changes in the absorption spectrum of trans-2C upon irradiation at the maximum of the B band absorption in toluene (absorption spectra were taken in 1 min intervals).



Figure 3. Changes in the absorption spectrum of **cis-2C** upon irradiation at the maximum of the B band absorption in toluene (absorption spectra were taken in 1 min intervals).

light of **cis-2C** in NMR tube results in ¹H NMR spectrum consistent with that observed for a cis/trans mixture of 10:1 ratio. Both **cis-2C** and **trans-2C** are stable in the dark since no changes in their absorption spectra were observed (see Supporting Information).

The photochemical trans-cis isomerization of compounds possessing an enediyne moiety is well known;⁶⁹⁻⁷³ however, the nearly quantitative and rapid conversion of **trans-2C** to **cis-2C** is rather unexpected, since DFT calculations show that **trans-2C** is more stable than **cis-2C** by 13.8 kJ/mol. We hypothesize that the $\pi-\pi$ interactions⁷⁷ between large aromatic systems of the two hydroporphyrins might stabilize cis isomer and facilitate trans-cis isomerization. It is generally accepted that $\pi-\pi$ aromatic interactions are not well reproduced by a simple DFT method, and dispersion-corrected DFT are required for an accurate account for these interactions.⁷⁸

Absorption and Emission Properties. Absorption spectra of cis-2C and trans-2C and equilibrated mixture of cis-2BC, as well as spectra of phen-2C, are presented in Figure 4. The Q_y-type band in trans-2C ($\lambda_{Q_y} = 701 \text{ nm}$) is broadened and significantly shifted bathochromically, compared to that in **C-PE** (λ_{Q_y} = 656 nm).⁵⁷ The maximum of Q_y band in trans-**2C** is located between ethynyl-linked dyad ($\lambda_{Q_v} = 689 \text{ nm}$) and vinyl-linked dyad (λ_{Q_y} = 707 nm) reported previously.^{56,57} Absorption spectrum of cis-2C contains a split Q_v-type band, with the maximum of the more intensive band centered at 659 nm and a second maximum centered at 704 nm (the second maximum coincidentally overlaps with the maximum of Q_y band in trans-2C; therefore, we cannot rule out that a trace amount of trans-2C is present even in a sample purified under rigorous exclusion of light). Similar splitting is observed for cis-2BC, where corresponding maxima are centered at 752 and 811 nm. Observed splitting of the $Q_{\rm y}$ bands in dyads is consistent with the excitonic interaction between closely positioned macrocycles in the "oblique" orientation of transition dipole moments,¹ which is consistent with a slipped cofacial geometry of dyads, as discussed above. Such excitonic interaction results in the formation of two new states, P_ with lower energy and P+ with higher energy, compared to the excited state of monomers. In a slipped cofacial geometry, both transitions $(S_0 \rightarrow P_- \text{ and } S_0 \rightarrow P_+)$ are allowed. The electronic coupling between macrocycles (V, calculated as one-half of the splitting energy of Q-like band) is $V = 474 \text{ cm}^{-1}$ for cis-2C and



Figure 4. Normalized absorption spectra of dyads in toluene at room temperature: phen-2C (black), cis-2ZnC (blue), cis-2C (green), trans-2C (purple), cis-2BC (red). The lower panel presents the expanded region of Q_y bands.

 $V = 483.7 \text{ cm}^{-1}$ for **cis-2BC**. The excitonic coupling for **cis-2ZnC** $V = 724 \text{ cm}^{-1}$ is much larger than that observed for the free base, despite nearly identical geometry of both dyads. The absorption spectrum of **phen-2C** does not show a distinct splitting but a shoulder at the long-wavelength side of the Q_y band. The fitting of Gaussian curves gave two peaks with maxima at 653 and 671 nm, which indicates a $V = 205 \text{ cm}^{-1}$.

The coupling strength between hydroporphyrins in **cis-2C** and **cis-2BC** is thus comparable to that observed in the purple bacteria special pair P867 ($V = 550 \text{ cm}^{-1}$). For **cis-2ZnC**, the coupling is slightly lower than that observed for P960 ($V = 900 \text{ cm}^{-1}$).

Emission Properties. Emission properties of dyads in toluene are given in Figure 5 and Table 1. Dyads cis-2C, cis-2ZnC, and cis-2BC feature structureless, broad (full width at half-maximum (FWHM) > 900 cm^{-1}) emission, with a relatively large Stokes shift (i.e., 449, 832, and 311 cm^{-1} for cis-2C, cis-2ZnC, and cis-2BC, respectively). These emission features differ significantly from those observed for monomers or previously reported ethynyl-, butadienyl-, or vinyl-linked, strongly conjugated hydroporphyrin arrays, which all exhibit relatively narrow (FWHM $< 400 \text{ cm}^{-1}$) emission with Stokes shift of $< 200 \text{ cm}^{-1}$.^{55,57} In addition, the fluorescence quantum yield (Φ_f) is substantially reduced in comparison to respective monomers (4-fold for cis-2C compared to that of C-PE and 6fold for cis-2BC compared to that of BC-2PE), which also differs from that observed for previously reported strongly conjugated hydroporphyrin dyads, which typically exhibit enhanced $\Phi_{\rm fr}$ compared to the corresponding monomers.^{55,57} Broad emission spectra with a relatively large Stokes shift and



Figure 5. Emission spectra of dyads in toluene at room temperature: phen-2C (black), cis-2ZnC (blue), cis-2C (green), cis-2BC (red). Emission spectrum of trans-2C is identical with that of cis-2C and it is not shown.

low Φ_f observed for cis-2C, cis-2ZnC, and cis-2BC are characteristic for excimers.^{79–84} Excimer is formally formed by the mixing of localized excited states and charge-resonance transfer states,^{83,85} and its formation, which is often also accompanied by large geometrical relaxation, leads to the reduction of the excited-state energy.^{86,87} It is characteristic that both Stokes shift and FWHM of the emission band parallel the degree of electronic coupling calculated from splitting of the Q_y-type band. It is interesting to note that a large Stokes shift and broad emission band were also reported for P867, for which the primary electron acceptor (bacterio-chlorophyll *a* monomer) was reduced.⁸⁸ The weak shoulder on the short wavelength side of the emission bands of dyads is attributed either to the emission from the localized, monomer-like excited state or to the trace amount of strongly fluorescent monomeric impurities. Further research is being performed to clarify this issue.

Emission spectrum of trans-2C is identical with that for cis-2C. Excitation spectrum for trans-2C overlaps very well with the absorption spectrum of cis-2C. These suggest that the excitation of trans-2C leads first to isomerization of trans-2C* to cis-2C* followed by emission from the excited state corresponding to the latter isomer. This assumption is additionally supported by the near-identical Φ_f for both trans-2C and cis-2C in toluene (Table 1).

Contrary to dyads discussed above, **phen-2C** exhibits narrow, monomer-like emission, with a small Stokes shift, though with split maxima. Such splitting has been reported previously for cofacial chlorin dyads, and it was attributed to the presence of two conformers in the excited state.⁵⁰ This is likely the case here. Relative to monomer **C-PE**, Φ_f for **phen-2C** is much reduced (1.6-fold) but not as extensively as in the case of **cis-2C** (4.1-fold, Table 1).

DFT Calculations. The absorption and emission features of **cis-2C**, **cis-2ZnC**, and **cis-2BC** indicate strong interactions between chromophores, which leads to optical properties substantially different from those observed for both linear strongly conjugated and simple cofacial hydroporphyrin dyads. The overall interactions between hydroporphyrins in these dyads, in principle, are the product of (1) dipole–dipole interactions between chromophores (i.e., long-range excitonic coupling),¹ (2) through-space interaction between overlapped orbitals of closely positioned macrocycles (i.e., short-range excitonic coupling or exchange interactions),¹⁷ and (3)

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cis-2BC disconnected^b

-1.20, -1.15(0.05)

Tab	le 1.	Absorption	and Emission	Properties o	f Dyad	s and	Monomers	Discussed	in	This Pa	per"
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compound	$\lambda_{ m B}$	λ_{Q_x}	$\lambda_{Q_{r}}$	$\lambda_{\rm em}~({\rm FWHM}^b)$	Stokes shift (cm ⁻¹)	$\Phi_{ m f}^{\ c}$
trans-2C	398	551	701	$727 (1008 \text{ cm}^{-1})$	510	0.092
cis-2C	401	507	660, 704	$727 (1008 \text{ cm}^{-1})$	449	0.082 (<0.01)
phen-2C	404	508	653	657, 678		0.21 (0.20)
cis-2ZnC	408		628, 690	$732 (1475 \text{ cm}^{-1})$	832	not determined
cis-2BC	364	535	752, 811	$832 (957 \text{ cm}^{-1})$	311	0.032 (<0.01)
C-PE^d	402, 417	506	656	$659 (285 \text{ cm}^{-1})$	69	0.33 (0.34)
BC-2PE ^e	379	523	752	$753 (323 \text{ cm}^{-1})$	18	0.19

^{*a*}All data were acquired in air-equilibrated toluene at room temperature unless noted otherwise. ^{*b*}Full width at half-maximum. ^{*c*}Tetraphenylporphyrin ($\Phi_f = 0.070^{89}$) was used as a standard for Φ_f determination. Values in parentheses are Φ_f in air-equilibrated dimethylformamide. ^{*d*}Data taken from ref 57. ^{*e*}Data taken from ref 58, determined in Ar-purged toluene.

and 2. Dr r Calculated 1105 Energies for Dyans and 1100cl Compounds								
entry	compound	HOMO – 1 (eV) (ΔE)	HOMO (eV) (ΔE)	LUMO (eV) (ΔE)	LUMO + 1 (eV) (ΔE)			
1	trans-2C	-5.10, -5.08 (0.02)	-5.00, -4.76 (0.24)	-2.79, -2.28 (0.51)	-1.95, -1.75 (0.20)			
2	trans-2C disconnected ^b	-5.12, -5.12 (0.00)	-4.95, -4.94 (0.01)	-2.36, -2.36 (0.00)	-1.77, -1.77 (0.00)			
3	trans-2C twisted ^c	-5.08, -5.09 (0.01)	-4.77, -4.99 (0.22)	-2.76, -2.27 (0.49)	-1.96, -1.75 (0.19)			
4	cis-2C	-5.30, -5.19 (0.11)	-5.13, -4.89 (0.24)	-2.78, -2.38 (0.40)	-1.98, -1.92 (0.06)			
5	cis-2C disconnected ^b	-5.14, -5.07 (0.07)	-4.96, -4.87 (0.09)	-2.38, -2.32 (0.06)	-1.78, -1.74 (0.04)			
6	phen-2C	-5.13, -5.05 (0.08)	-4.96, -4.78 (0.18)	-2.44, -2.27 (0.17)	-1.76, -1.73 (0.03)			
7	phen-2C disconnected ^b	-5.14, -5.07 (0.07)	-4.96, -4.88 (0.08)	-2.38, -2.31 (0.07)	-1.78, -1.74 (0.04)			
8	cis-2ZnC	-5.40, -5.27 (0.13)	-5.07, -4.84 (0.23)	-2.71, -2.35 (0.36)	-1.90, -1.80 (0.10)			
9	cis-2ZnC disconnected ^b	-5.24, -5.12 (0.12)	-4.85, -4.80 (0.05)	-2.30, -2.27 (0.03)	-1.64, -1.63 (0.01)			
10	cis-2BC	-5.21, -5.11 (0.10)	-4.80, -4.58 (0.22)	-2.85, -2.53 (0.32)	-1.97, -1.30 (0.67)			

Table 2. DFT-Calculated MOs Energies for Dyads and Model Compounds^a

-5.08, -5.00(0.08)

^aAll calculations were performed employing the DFT B3LYP 6-31G* method. ^bMOs were calculated for prior energy-minimized structures of corresponding dyads, for which the fumarate (or 1,2-phenylene) part of the linker was removed and replaced by hydrogens, which effectively corresponds to two 13-acetylene-substituted hydroporphyrins, with mutual distance and orientation identical as in corresponding dyads. ^cMOs calculated for the structure where the dihedral angle between the macrocycle plane and the plane formed by enediyne linker is 26°.

-4.61, -4.53(0.08)

through-bond electronic coupling, provided by a conjugated linker.²⁵ The rigorous delineation of effects of each of these three interactions on the observed absorption and emission properties of enediyne dyads, and the evaluation of their possible synergistic effects are far beyond the scope of the current paper and will be discussed in the subsequent publication. Here, we use DFT calculations for the preliminary evaluation of through-bond electronic conjugation and through-space orbitals' overlap contribution to the overall coupling. We focus here on the effect of the electronic interactions between hydroporphyrins on HOMO - 1, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and LUMO + 1, since configurational interactions between these MOs give rise to the spectroscopic properties in tetrapyrrolic macrocycles⁹⁰ (Table 2). First, we calculated the MO energies for each dyad reported here, for their energy-minimized geometries. For each dyad, MOs, which are characteristic for monomers, are split into a pair of new orbitals with the same symmetry and delocalized on both macrocycles. Such splitting is a signature of a strong electronic interaction between macrocycles and is observed for noncovalent bacteriochlorins, investigated as models for photosynthetic reaction centers,^{91,92} and for each strongly conjugated and directly linked hydroporphyrin dyad reported previously.^{56,59,93} The splitting energies (ΔE) for trans-2C, cis-2C, cis-2ZnC, and cis-2BC, are comparable to ethynyl- and butadienyl-linked dyads,^{56,59} suggesting comparable strength of electronic interaction. Next, we calculated the electronic structure for nonconnected acetylene-substituted hydroporphyrin pairs, with interpigment distances and mutual

orientations identical as in corresponding dyads (i.e., beginning from the energy-minimized structure of each enediyne dyad, the fumarate is removed, and for **phen-2C**, the *o*-phenylene is removed (Table 2, entries 2, 5, 7, 9, and 11)). These calculations enable the evaluation of the degree of ground-state through-space electronic interaction in *cis* isomers of dyads. As is shown in Table 2, the nonconnected analogs of *cis* dyads also exhibit splitting of relevant orbitals, albeit with ΔE significantly smaller (>2-fold decrease), than in covalent dyads. As expected, the nonconnected analog of **trans-2C** (entry 2) shows virtually no splitting and instead two sets of degenerate orbitals, localized on a single chlorin, each.

-2.53, -2.45 (0.08)

The through-bond π -conjugation between macrocycles in *cis* isomers is possibly due to the relatively small angle in which the macrocycle is twisted versus the double bond in enediyne linker (around 25°). Such a twist causes only a small perturbation in electronic π -conjugation, when compared to that in the fully planar geometry, as is shown by calculations performed on **trans-2C**, where chlorin macrocycles and the plane defined by enediyne linker are twisted by 25° (entry 3, the corresponding angles in the energy-minimized structure are 7°).

These results show that in cis dyads substantial throughspace and through-bond electronic interactions contribute to the dipole–dipole, long-range excitonic coupling between hydroporphyrins, and their combined effect gives rise to the observed absorption properties. Through-space interactions between chlorins seem to be nearly the same for *cis*-2C and **phen-2C** (compare entries 5 and 7, Table 2), which is expected given very similar distances and mutual orientations

of macrocycles in both dyads. Therefore, a substantially stronger electronic interaction between chromophores in **cis**-**2C** (as inferred from the larger splitting of both Q_y -type band in absorption spectrum and splitting of relevant MOs) is due to stronger through-bond interactions provided by enediyne linker, compared to those by 1,2-diethynylphenylene linker. The DFT calculations, performed on model dyad connected by 1,4-diacetylenephenylene-linker, indeed showed lower values of ΔE than for **trans-2C** (see Table S2, Supporting Information). These results are in accord with the previously reported data for enediyne derivatives. For example, *cis*-1,6diphenylhexa-3-en-1,5-diyne features absorption maximum at slightly longer wavelength compared to 1,2-bis-(phenylethynyl)benzene (352 nm⁶² vs 343 nm,⁹⁴ respectively).

CONCLUSIONS

Trans-cis photoisomerization of the enediyne linker leads to thermally stable slipped cofacial hydroporphyrin dyads, where the distance and mutual orientation of hydroporphyrins resemble those observed for the special pairs of reaction centers in photosynthesis. The close positioning of hydroporphyrins and the presence of a conjugated enediyne linker lead to strong through-bond and through-space electronic interactions between macrocycles, which enhanced the dipole-dipole, long-range excitonic coupling. A strong interchromophoric interaction is manifested by a large splitting of the Q_v-type band and splitting of the MOs. Evidence for the formation of an excimer, i.e., broad emission band, with an unusually large Stokes shift, has been found. The emission features resemble those observed for the special pair. In-depth discussion of the spectroscopic properties and correlation between electronic and spectroscopic properties will be presented in the next paper. We anticipate that since both the geometry and spectral properties of resulting dyads resemble those observed in special pairs of photosynthetic reaction centers, they will be useful components of energy and electron-transfer arrays, for modeling photosynthetic reaction centers and development of artificial solar energy conversion systems. Moreover, the connection of chromophores by a conjugated enediyne linker and subsequent trans-cis photoisomerization appears to be a viable strategy for the development of photonic materials with multiple modes of electronic interactions and thus novel optical properties.

EXPERIMENTAL SECTION

General. ¹H NMR (400 or 500 MHz) and ¹³C NMR (100 or 125 MHz) spectra were collected at room temperature in CDCl₃ unless noted otherwise. Chemical shifts (δ) were calibrated using solvent peaks (¹H signals: residual proton signals: 7.26 ppm for CHCl₃, ¹³C signals: 77.16 for CDCl₃). Commercially available anhydrous solvents were used for palladium coupling reactions. All other solvents and commercially available reagents were used as received. Fourier transform ion cycloctron resonance (FT-ICR) analyzer was used for high resolution mass spectrometry (HRMS) analyzes.

General Procedure for Palladium Cross-Coupling Reactions. All reagents and solvents with the exception of palladium catalyst were placed in a Schlenk flask, and the contents were degassed by two cycles of freeze–pump–thaw, at which time the catalyst is added, and a third cycle of freeze–pump–thaw is performed. The reaction mixture was stirred under N_2 and heated in an oil bath at an indicated temperature.

Characterization. All NMR spectra were acquired on 400 MHz NMR or 500 MHz NMR. All HRMS data were acquired on 12T FT-ICR MS. DFT calculations were performed, and the results were visualized using Spartan 10 for Windows (Wavefunction Inc., Irvine, CA). B3LYP 6-31G* method in vacuum was used for each calculation. Fullstructure optimization was performed on each dyad, and several different conformations were examined to find the global energy minimum. For "disconnected" dyads, the computations were performed on a previously fully optimized corresponding dyad structure, after removing the fumarate fragment in the linker and replacing by hydrogen atoms on the remaining acetylene fragments, without any further structure optimization.

Known compounds: $Ch-E^{57}$ and $BC-E^{55}$ were prepared following reported procedures. Synthesis of dimethyl dibromofumarate 1 was reported numerous times,^{74,75} and here, 1 was synthesized following a slightly modified procedure.⁹⁵

Dimethyl 2,3-Dibromofumarate (1). Following a reported procedure,⁹⁵ a solution of dimethyl acetylene dicarboxylate (2.86 g, 20.0 mmol) in anhydrous CH_2Cl_2 (20 mL) was treated by pyridinium tribromide (2.47 g, 28.1 mmol). The resulting mixture was stirred under argon at room temperature for 6 days. The reaction mixture was treated by an excess of 10% aqueous $Na_2S_2O_3$, and the resulting mixture was extracted by diethyl ether. The organic phase was washed (water and brine), dried (MgSO₄), and concentrated. The resulting oil was purified by column chromatography (silica, CH_2Cl_2 /hexanes (1:1) \rightarrow neat CH_2Cl_2) to afford a pure isomer as a white solid: 2.31 g, 38%. Characterization data (¹H and ¹³C NMR) are consistent with those reported previously for dimethyl 2,3-dibromofumarate.⁷⁵

Sonoaashira Reaction between Ch-E and 1 Performed without Protection from Light. Following the general procedure, a mixture of Ch-E (26.0 mg, 0.054 mmol), 1 (8.2 mg, 27.0 µmol), Pd₂(dba)₃ (7.4 mg, 8.1 μ mol), and P(o-tol)₃ (4.1 mg, 0.014 mmol) in anhydrous toluene/Et₃N (5:1, 12.0 mL) was stirred at 60 °C overnight. After 16 h, the reaction mixture was concentrated. Column chromatography [silica, hexanes/CH₂Cl₂ (3:7)] afforded **b-2C** (first fraction, redbrown, yield not determined), followed by cis-2C as a dark green solid (8.2 mg, 28%). A small amount of trans-2C was also isolated. Data for cis-2C: ¹H NMR (400 MHz, CDCl₃): δ -2.14 (bs, 2H), -1.43 (bs, 2H), -0.48 (s, 12H), 1.91 (s, 12H), 2.11 (s, 4H), 2.60 (s, 6H), 4.13 (s, 6H), 7.25 (s, 4H), 7.67 (s, 2H), 8.43 (d, J = 4.7 Hz, 2H), 8.45 (d, J = 4.4 Hz, 2H), 8.80 (d, J = 4.4 Hz, 2H), 8.93 (s, 2H), 8.95 (d, J = 4.7 Hz, 2H), 9.23 (s, 2H), 9.54 (s, 2H); ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃): δ 21.4, 21.6, 28.8, 29.6, 29.9, 44.8, 49.3, 53.7, 93.0, 93.9, 96.1, 100.2, 106.3, 114.9, 121.6, 124.3, 127.0, 128.0, 128.8, 129.1, 132.1, 132.8, 133.0, 135.7, 137.5, 138.0, 139.1, 139.7, 141.6, 152.6, 152.8, 163.3, 164.9, 176.2; HRMS (electrospray ionization time-of-flight, ESI-TOF) m/z [M + H]⁺ calcd for C₇₂H₆₅N₈O₄, 1105.5123; found 1105.5175.

Data for **b-2C**: ¹H NMR (CDCl₃): δ –1.79 (bs, 2H), –1.41 (bs, 2H), 1.90 (s, 12H), 2.09 (s, 12H), 2.64 (s, 6H), 4.71 (s, 4H), 7.29 (s, 4H), 8.48 (d, *J* = 4.1 Hz, 2H), 8.86–8.84 (m, 6H), 8.92 (d, *J* = 4.6 Hz, 2H), 9.19 (d, *J* = 4.6 Hz, 2H), 9.37 (s, 2H), 9.71 (s, 2H); ¹³C{¹H} NMR (CDCl₃): δ 21.4, 29.8, 31.2, 46.8, 51.8, 94.7, 95.2, 106.8, 108.9, 115.1, 121.5, 124.5, 127.9, 129.1, 129.8, 132.1, 132.8, 133.0, 135.7, 137.4, 138.0, 139.2, 140.8, 142.1, 152.7, 152.8, 163.5, 176.8; HRMS (ESI-TOF): m/z [M + H]⁺ calcd for C₆₆H₅₈N₈, 963.4857; Found 963.4890.

Sonogashira Reaction between Ch-E and Dimethyl 2,3-Dibromofumarate (1) Performed with Protection from Light. The reaction mixture was protected from light using an aluminum foil at each stage of the reaction and purification. All operations were performed in the dark, using a red light-emitting diode headlamp as an only source of light. Following the general procedure, a mixture of **Ch-E** (37.9 mg, 0.079 mmol), 1 (11.9 mg, 0.039 mmol), Pd₂(dba)₃ (10.1 mg, 0.011 mmol), and P(o-tol)₃ (10.8 mg, 0.035 mmol) in anhydrous toluene/Et₃N (5:1, 18.0 mL) was stirred at 60 °C. After 21 h, the reaction mixture was concentrated. Column chromatography [silica, hexanes/dichloromethane (2:1)] yielded **trans-2C** (9.3 mg, 21%) as a brown solid. **cis-2C** was also observed on thin-layer chromatography (TLC) as a minor product but was not isolated cleanly in this procedure. ¹H NMR (400 MHz, CDCl₃): δ –1.69 (bs, 2H), –1.26 (bs, 2H), 1.89 (s, 12H), 2.10 (s, 12H), 2.65 (s, 6H), 4.37 (s, 6H), 4.74 (s, 4H), 7.29 (s, 4H), 8.46 (d, J = 4.3 Hz, 2H), 8.81 (s, 2H), 8.83 (s, 2H), 8.83 (d, J = 4.3 Hz, 2H), 8.92 (d, J = 4.6 Hz, 2H), 9.17 (d, J = 4.6 Hz, 2H), 9.57 (s, 2H), 9.68 (s, 2H); HRMS (ESI-TOF) m/z [M + H]⁺ calcd for C₇₂H₆₅N₈O₄,1105.5123; found 1105.5136.

phen-2C. Following the general procedure, a mixture of Ch-E (30.0 mg, 0.062 mmol), 1,2-dibromobenzene (7.3 mg, 0.031 mmol), $Pd_{2}(dba)_{3}$ (8.6 mg, 9.3 μ mol), and $P(o-tol)_{3}$ (8.5 mg, 0.028 mmol) in anhydrous toluene/Et₃N (5:1, 6.0 mL) was stirred at 60 °C. After 16 h, the reaction mixture was concentrated. Column chromatography [silica, hexanes/dichloromethane (2:1)] yielded a green solid (12.3 mg, 38%). Note that a red fluorescent impurity nearly coeluted with the desired product, and early fractions of the product were discarded. ¹H NMR (400 MHz, $CDCl_3$): δ -2.28 (bs, 2H), -1.68 (bs, 2H), -0.36 (s, 12H), 1.88 (s, 12H), 2.25 (s, 4H), 2.58 (s, 6H), 7.22 (s, 4H), 7.56 (dd, J₁ = 3.3 Hz, J₂ = 5.8 Hz, 2H), 7.78 (s, 2H), 7.99 (dd, J₁ = 3.3 Hz, J_2 = 5.8 Hz, 2H), 8.46 (d, J = 4.3 Hz, 2H), 8.48 (d, J = 4.6 Hz, 2H), 8.83 (d, J = 4.3 Hz, 2H), 8.94 (s, 2H), 8.99 (d, J = 4.6 Hz, 2H), 9.41 (s, 2H), 9.61 (s, 2H); ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃): δ 21.7, 21.8, 29.1, 44.9, 49.8, 77.6, 89.7, 94.1, 96.0, 96.2, 106.7, 117.2, 120.8, 123.9, 126.4, 128.1, 128.5, 128.8, 128.9 131.8, 132.8, 133.1, 133.2, 135.2, 137.9, 138.0, 139.3, 139.9, 141.2, 152.2, 152.8, 163.5, 175.7; HRMS (ESI-TOF) m/z [M + H]⁺ calcd for C₇₂H₆₃N₈, 1039.5170; found 1039.5146.

cis-2ZnC. A solution of **cis-2C** (containing approx 10% of **trans-2C**, 8.0 mg, 7.2 μ mol) in chloroform/methanol (6 mL, 5:1) was treated with zinc acetate dihydrate (79.0 mg, 0.36 mmol) and stirred at room temperature. TLC analysis after 3 h showed the presence of an unreacted starting material. At that time, another portion of zinc acetate dihydrate (79.0 mg, 0.36 mmol) was added, and stirring was continued for another 4 h. Saturated aqueous NaHCO₃ solution was added, and the resulted mixture was extracted with CH₂Cl₂. The organic layer was washed (water and brine), dried (Na₂SO₄), and concentrated. Column chromatography (silica, CH₂Cl₂) yielded a dark green solid (6.0 mg, 67%). ¹H NMR (400 MHz, CDCl₃): δ –0.08 (*s*, 12H), 1.91 (*s*, 12H), 2.44 (*s*, 4H), 2.56 (*s*, 6H), 4.10 (*s*, 6H), 7.19 (*s*, 2H), 7.60 (*s*, 2H), 8.32 (*d*, *J* = 4.3 Hz, 2H), 8.39 (*d*, *J* = 4.3 Hz, 2H), 8.75 (*d*, *J* = 4.3 Hz, 2H), 8.85 (*d*, *J* = 4.4 Hz, 2H), 8.88 (*s*, 2H), 9.06 (*s*, 2H), 9.39 (*s*, 2H); HRMS (ESI-TOF) *m*/*z* [M + H]⁺ calcd for C₇₂H₆₁N₈O₄Zn₂, 1229.3393; found 1229.3453.

cis-2BC. A mixture of **BC-E** (10.5 mg, 20 μ mol), **1** (3.0 mg, 10 μ mol), P(*o*-tol)₃ (3.7 mg, 12 μ mol), and Pd₂(dba)₃ (2.8 mg, 3.1 μ mol) in toluene (10 mL) and Et₃N (2 mL) was stirred at 60°C for 5 h. The resulting mixture was concentrated, and the residue was purified with column chromatography [silica, hexanes/ethyl acetate (2:1)] to afford a red-purple solid (4.1 mg, 35%). Approx. 20% of **b**-**2BC**⁵⁵ was also isolated. ¹H NMR (CDCl₃, 400 MHz) δ –1.96 (s, 2H), –1.50 (s, 2H), 0.54 (s, 12H), 1.87 (s, 12H), 2.80 (s, 4H), 4.18 (s, 6H), 4.40 (s, 4H), 4.47 (s, 6H), 7.40–7.51 (m, 6H), 7.82 (d, *J* = 7.3 Hz, 4H), 7.88 (s, 2H); 8.47 (s, 2H), 8.56 (d, *J* = 2.1 Hz, 2H), 8.87 (d, *J* = 1.9 Hz, 2H), 8.96 (s, 2H); ¹³C{¹H} NMR (CDCl₃, 100 Hz) δ 29.7, 31.0, 44.8, 45.3, 48.1, 49.9, 53.7, 64.8, 87.0, 93.4, 94.4, 96.5, 97.3, 98.3, 100.6, 113.9, 114.1, 124.3, 125.9, 126.9, 127.9, 128.5, 128.7, 131.9, 132.1, 134.9, 135.56, 135.60, 138.2, 157.0, 161.0, 165.1, 169.6, 171.3; HRMS (ESI-TOF) *m*/*z* [M + H]⁺ calcd for C₇₆H₆₉N₈O₆, 1189.5335; found 1189.5274.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b00731.

Additional synthetic scheme, assignment of signals in ¹H NMR spectra, results of additional DFT calculations, results of the studies on thermal isomerization of **cis-2C** and **trans-2C**, atom coordinates and absolute energies for dyads, and copies of ¹H and ¹³C NMR spectra for new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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