Mimicking the electron transfer chain in photosystem II with a molecular triad thermodynamically capable of water oxidation

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In the photosynthetic photosystem II, electrons are transferred from the manganese-containing oxygen evolving complex (OEC) to the oxidized primary electron-donor chlorophyll P680+ by a proton-coupled electron transfer process involving a tyrosine-histidine pair. Proton transfer from the tyrosine phenolic group to a histidine nitrogen positions the redox potential of the tyrosine between those of P680+ and the OEC. We report the synthesis and time-resolved spectroscopic study of a molecular triad that models this electron transfer. The triad consists of a high-potential porphyrin bearing two pentafluorophenyl groups (PF10), a tetracyano-porphyrin electron acceptor (TCNP), and a benzimidazole-phenol secondary electron-donor (Bi-PhOH). Excitation of PF10 in benzonitrile is followed by singlet energy transfer to TCNP (τ = 41 ps), whose excited state decays by photoinduced electron transfer (τ = 830 ps) to yield Bi-PhOH-PF10+-TCNP+. A second electron transfer reaction follows (τ < 12 ps), giving a final state postulated as BiH–-PhO−-PF10–TCNP−, in which the phenolic proton now resides on benzimidazole. This final state decays with a time constant of 3.8 μs. The triad thus functionally mimics the electron transfers involving the tyrosine-histidine pair in PSII. The final charge-separated state is thermodynamically capable of water oxidation, and its long lifetime suggests the possibility of coupling systems such as this system to water oxidation catalysts for use in artificial photosynthetic fuel production.

photochemistry | biomimicry

The machinery of photosynthesis is an elaborate nanosystem composed of organic and inorganic cofactors assembled in large organized protein arrays that cooperatively perform the specific tasks needed to convert sunlight into biofuel. Through eons of evolution, nature has developed specialized enzymes able to oxidize water molecules and use the resulting electrons to reduce carbon dioxide to carbohydrates. The central component in the water oxidation process is the protein complex known as photosystem II (PSII), which uses sunlight to split water into oxygen and protons, and reducing equivalents (1).

Essential to the function of PSII is its ability to combine single-photon excitation with the multielectron process of water oxidation. To perform this thermodynamically challenging reaction, PSII is equipped with the oxygen evolving complex (OEC), an inorganic complex featuring one calcium and four manganese ions (2–4). Functionally, the OEC is a charge accumulator able to store the four oxidizing equivalents needed for water oxidation. The OEC is electronically coupled to the chlorophyll complex P680 through a redox-active tyrosine-histidine pair (TyrZ-D, His190). This pair acts as an electron relay between P680 and the OEC components through proton-coupled electron transfer (PCET) (5–8).

In PSII, the oxidizing equivalents are produced through photoexcitation of the chlorophyll molecules in the P680 complex, which decay by electron transfer to the quinone cofactors QA and QB via a pheophytin primary electron acceptor. The highly oxidizing P680++ is reduced by the TyrZ residue on the nanosecond timescale. In this process, TyrZ loses its phenolic proton, likely to the nearby D1His190 group, to generate the neutral tyrosine radical TyrZ-O° (E° = 0.9–1.0 V vs. SCE). The radical TyrZ-O° then removes one electron from the OEC on the microsecond timescale, increasing its oxidation state (6, 9–11). After four light-induced charge separations, the OEC oxidizes two water molecules, releases molecular oxygen, and returns to its initial oxidation state.

The functional principles of PSII can be used to guide the design of artificial photosynthetic devices. The highly efficient initial light-induced charge separation is a particularly attractive biomimetic target because the resulting electron-hole pair can in principle be used for conversion to electrical power or to generate a redox gradient to drive chemical reactions for fuel production. Therefore, development of synthetic systems able to produce useful forms of energy from abundant sunlight and water requires a better understanding of the thermodynamic and kinetic parameters of the primary processes of PSII.

In this context, we report the preparation and photophysical investigation of a bioinspired molecular triad engineered to functionally mimic the initial charge-separation events of PSII. The three units are designed and covalently assembled to simulate the specific interactions between P680, pheophytin, and the TyrZ-D, His190 pair of PSII. The energetics of the model are designed so that the final charge-separated state is thermodynamically capable of oxidizing water. A detailed spectroscopic investigation highlights the importance of electron transfer reactions associated with proton translocation in stabilizing the photoinduced charge-separated state and provides unique insight into how electron and proton motion can be used to bridge the gap between light and chemistry.

Results

Design and Synthesis. Porphyrins are useful artificial alternatives to synthetically demanding and relatively unstable chlorophylls found in natural systems. In the case of PSII, the photogenerated P680++ must be an extremely strong oxidant to provide the overpotential required for efficient water oxidation. Chlorophyll a in solution is incapable of carrying out such photo-oxidations, and the potential of chlorophyll in PSII is tuned by the protein environment to achieve the necessary redox power (12–14). Molecular triad (Fig. 1) was engineered with the redox potentials of the triad components through proton-coupled electron transfer (PCET) (5–8).


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tials of the porphyrin components designed to fulfill thermodynamic requirements similar to those found in P680 by adjusting the substituents on the macrocycles. In the design of I, the tetracyanoporphyrin (TCNP) unit (Fig. 1, blue) acts as a powerful electron acceptor due to the electron withdrawing effects of the four cyano groups at the β-positions of the tetrapyrrolic core. The two pentafluorophenyl groups provide the primary electron-donor porphyrin (PF$_{10}$) (Fig. 1, red) with the right redox balance to transfer one electron to the TCNP acceptor after irradiation of the complex, resulting in the PF$_{10}^{++}$ cation, which is thermodynamically competent to oxidize the benzimidazole-phenol (Bi-PhOH) secondary electron-donor component (Fig. 1, green). The Bi-PhOH unit features an intramolecular hydrogen bond between the phenolic proton and the lone pair of the nitrogen atom in the benzimidazole moiety. In the course of oxidation of Bi-PhOH by the photo-generated PF$_{10}^{++}$, the phenol is designed to transfer its proton to the benzimidazole group by a PCET mechanism to produce a neutral phenoxyl radical (E$_0$ = +0.6 V vs. SCE in the case of I) suitably poised for water oxidation (E$_0$ = +0.58 V vs. SCE, pH 7), thus mimicking the role of the TyrZ-D$_1$His$_{190}$ in PSII.

To assemble the three active units of I, we developed the synthetic strategy depicted in Scheme 1. The synthesis begins with the preparation of porphyrin 4, which relies on an approach based on the selective condensation of the para-formyl group of compound 3. This selectivity is grounded in the reduced chemical reactivity of the formyl group involved in the intramolecular O-H...O = C hydrogen bond, which efficiently discourages its activation by acid catalysts. The benzimidazole moiety is then formed upon cyclization of the formyl group in 4 with orthophenylene diamine to afford 5, which is in turn hydrolyzed under acid conditions to yield 6. The resulting carboxylic acid in 6 is transformed into an amine group by a Curtius reaction to afford dyad 7. The TCNP 10 is efficiently prepared from tetrabromo derivative 8 (15) using a cyanation procedure developed in our laboratory. Finally, triad I is afforded through an amide-coupling reaction between 7 and 10. The dyad PF$_{10}^{++}$-TCNP model compound 2 (Fig. 1) is prepared from the required precursors following similar procedures (SI Appendix).

**Photophysical Investigation.** Spectroscopic investigations were carried out with triad I, PF$_{10}^{++}$-TCNP dyad 2, and Bi-PhOH-PF$_{10}$ model compound 5, as well as with porphyrin references TCNP 9 and PF$_{10}$ 11 to gain insight into the photophysical properties of the photoactive units.

**Steady-State Spectroscopic Investigations and Electrochemical Studies.** The absorption spectrum of PF$_{10}$ 11 in cyclohexane solution (Fig. 2, black line) exhibits characteristic electronic transitions of free base porphyrins (Soret absorption at 419 nm and Q-bands at
512, 547, 592, and 648 nm). The TCNP 9 (Fig. 2, solid red line) features a split in the Soret region with maxima at 440 and 444 nm, and broader Q-bands that appear at 543, 588, 654, and 711 nm (Fig. 2). These spectroscopic features are characteristic of a nonplanar porphyrin (16–22). Steric repulsion between the β-cyano groups and the meso-phenyl substituents leads to deformation of the tetrapyrrolic ring from its original planar geometry. The red shift is explained by two different phenomena, which operate cooperatively to reduce the highest-occupied molecular orbital–lowest-unoccupied molecular orbital (HOMO–LUMO) gap. The strong electron withdrawing effect induced by the four cyano groups is known to stabilize the LUMO orbital, whereas distortion of the porphyrin macrocycle destabilizes the HOMO orbital (22).

The absorption spectrum of Bi-PhOH-PF$_{10}$ model compound 5 (Fig. 2, solid blue line) shows a slight broadening of the Soret band compared to that of 11, suggesting some electronic interaction between the Bi-PhOH and PF$_{10}$ components in the ground state. On the other hand, the spectrum of PF$_{10}$-TCNP dyad 2 (solid green line) is similar to a linear combination of the absorption spectra of its components, indicating no strong electronic interactions between the photoactive units when covalently linked to each other. Triad 1 is not sufficiently soluble in cyclohexane to obtain a useful absorption spectrum, but the spectrum in benzonitrile (Fig. 2, magenta broken line) resembles that of 2 in the same solvent (green broken line).

Steady-state fluorescence investigations in cyclohexane with excitation in the corresponding Soret region (SI Appendix, Fig. S2) disclose that PF$_{10}$ reference 11 emits at 657 and 723 nm, whereas TCNP 9 fluoresces at 727 and 815 nm. From the absorption and emission data, the energies of the first singlet excited states (E$_{00}$) are estimated as 1.90 eV for 11 and 1.72 eV for 9.

Estimation of the energies of the charge-separated states was afforded from electrochemical studies (SI Appendix, Figs. S6 and S7; Table S1). The first redox potentials (vs. SCE) of a PF$_{10}$ model (SI Appendix, Fig. S8) are at E$_{ox}$ = +1.29 V and E$_{red}$ = −0.96 V, whereas the Bi-PhOH first oxidation model in compound 5 occurs at E$_{ox}$ = +1.04 V. The first reduction of TCNP in triad 1 takes place at E$_{red}$ = −0.27 V. Therefore, the intermediate Bi-PhOH-PF$_{10}$*-TCNP*- and final BiH+–PhO–PF$_{10}$-TCNP*- charge-separated states are roughly 1.56 eV and 1.34 eV above the ground state in triad 1.

**Time-Resolved Spectroscopic Investigations.** Time-resolved emission experiments in cyclohexane with excitation in the corresponding Soret regions yielded lifetimes of 8.89 ns ($\chi^2 = 1.17$) for the first singlet excited state of PF$_{10}$ 11 and 9.00 ns ($\chi^2 = 1.03$) for that of Bi-PhOH-PF$_{10}$ model compound 5. The decay of reference TCNP 9 requires three components to satisfactorily fit the decay data ($\chi^2 = 1.07$): 102 ps, 2.47 ns, and 4.87 ns. A preliminary investigation of the photophysical properties of 9 revealed that the singlet excited state dynamics significantly depend on the solvent polarity and viscosity, which signals a complex excited state manifold and the possibility of different conformations in the excited state. We postulate that the $^1$TCNP state formed immediately after excitation undergoes a rather slow, solvent dependent (102 ps in cyclohexane) structural reorganization that yields a relaxed singlet excited state, which then decays via ordinary relaxation pathways with a fluorescence lifetime of 2.47 ns. The 4.87 ns component may represent the decay of an additional minor conformation, or in principle a minor impurity, although no other evidence for impurities was found.

Global analysis ($\chi^2 = 1.07$) of transient fluorescence experiments on dyad 2 in cyclohexane with excitation at 400 nm yielded five decay components, which are depicted in the form of decay-associated spectra (DAS) in Fig. 3. The 41 ps DAS spectrum shows positive amplitude at approximately 650 nm, where most of the fluorescence comes from the PF$_{10}$ subunit, and negative amplitude at 700–800 nm, where the fluorescence is primarily due to the TCNP moiety (SI Appendix, Fig. S2). This spectrum reflects singlet-singlet energy transfer from PF$_{10}$ to TCNP. Thus, the lifetime of $^1$PF$_{10}$ in dyad 2 is reduced from the 8.89 ns found for PF$_{10}$ model 11 to 41 ps by the addition of the energy transfer decay pathway. From these numbers, we calculate a rate constant of $k_{ET} = 2.4 \times 10^{10}$ s$^{-1}$ and a quantum yield of 98% for the energy transfer process in 2.

The 136 ps, 2.4 ns, and 4.15 ns DAS spectra have very similar lifetimes to those obtained for the TCNP model 9 in cyclohexane. The 136 ps spectrum shows band-shift-like character with positive amplitude at the blue side and negative amplitude at the red side of the TCNP fluorescence emission bands and can be attributed to the relaxation of the singlet excited state in the complex excited state manifold to form a relaxed singlet excited state that lives for 2.4 ns (Fig. 3, red and green lines). The two minor components (4.15 and 7.94 ns) required in the global analysis may reflect conformational heterogeneity, minor impurities, and/or fitting artifacts. The fact that the decay time constants observed for $^1$TCNP in 2 are essentially identical to those observed for model 9 show that no charge-separated states are formed by decay of $^1$PF$_{10}$ or $^1$TCNP in cyclohexane. Therefore, spectroscopic investigations of 2 were carried out in a more polar medium, benzonitrile, to facilitate charge transfer processes through driving force and reorganization energy effects.

Time-resolved emission experiments with 2 in benzonitrile reveal a different scenario. Global analysis of the fluorescence decays ($\chi^2 = 1.16$) reveals time constants of 41 ps, 129 ps, 536 ps, 1.8 ns, and 9.3 ns. The first two decays represent energy transfer from $^1$PF$_{10}$ to TCNP and relaxation of $^1$TCNP, respectively, as was observed in cyclohexane. The 536 ps component indicates a new decay pathway for $^1$TCNP that was not present.

![Fig. 2. Ground state absorption spectra in cyclohexane (solid lines) and benzonitrile (broken lines). In cyclohexane: PF$_{10}$ reference 11 (black solid line), TCNP 9 (red solid line), Bi-PhOH-PF$_{10}$ model compound 5 (blue solid line), and PF$_{10}$-TCNP dyad 2 (green solid line). In benzonitrile: PF$_{10}$-TCNP dyad 2 (green broken line) and triad 1 (magenta broken line).](https://www.pnas.org/cgi/doi/10.1073/pnas.1118348109)

![Fig. 3. Fluorescence DAS in cyclohexane of dyad 2 following approximately 100 fs laser pulse excitation at 400 nm. Global analysis ($\chi^2 = 1.07$) yields five exponential components with lifetimes of 41 ps (black), 136 ps (red), 2.41 ns (green), 4.15 ns (blue), and 7.94 ns (turquoise).](https://www.pnas.org/cgi/doi/10.1073/pnas.1118348109)
in 9 or in 2 in cyclohexane. The most likely mechanism is photoinduced electron transfer to form PF$^{10+}$-TCNP$^{8-}$. This interpretation is consistent with the strong solvent dependence of the time constant and the spectroscopic and electrochemical results discussed above. Photoinduced electron transfer between porphyrins joined by similar linkages has been reported (23, 24). The fact that the shortest decay component in benzotriazole has a time constant that is essentially identical to the corresponding component in cyclohexane is consistent with an absence of significant photoinduced electron transfer from PF$^{10+}$-TCNP in both solvents. The 1.8 and 9.3 ns DAS are attributed to minor impurities or conformations, or fitting artifacts.

Transient spectroscopic techniques were used to gain further insights into the spectral evolution of dyad 2. To identify the transient spectroscopic changes that are indicative of the formation of charge-separated states upon excitation, we first determined the spectroscopic absorption signatures of each possible cation and anion by spectroelectrochemical investigation of reference compounds 4 and 9. The results reveal that the PF$^{10+}$ cation is characterized by a broad absorption in the 650–780 nm region, whereas the TCNP$^{8-}$ anion has maximum absorptions at 660 and 940 nm (SI Appendix). The redox processes are reversible in both cases, reflecting the redox stability of the porphyrins.

Excitation at 740 nm of an air-saturated benzotriazole solution of TCNP model porphyrin 9 yielded evolution associated difference spectra (EADS) with time constants of 116 ps, 1.9 ns, and a component with a lifetime too long to resolve on the timescale of the experiment (SI Appendix, Fig. S3). The 116 ps component is assigned to relaxation of the initially formed $^1$TCNP to a more stable species (spectral evolution shows band shift character), which decays in 1.9 ns. One of the products of this 1.9 ns decay is $^3$TCNP, which decays very slowly in the absence of oxygen (last, nondecaying EADS).

The results of a similar experiment with 2, excited at 740 nm in benzotriazole, where only TCNP absorbs, are presented in Fig. 4A. Five EADS with time constants of 12 ps, 120 ps, 590 ps, 1.8 ns (very minor EADS), and a component that did not decay on the <10 ns timescale were obtained. Based on the EADS shapes, the time-resolved fluorescence results for 2 and 9, and the transient absorption data for 9, we interpret the 120 ps process as relaxation of the initially formed $^1$TCNP, which has a strong induced absorption with a maximum at approximately 520 nm. The 590 ps component, with strong induced absorption at approximately 570 nm, is due to decay of the resulting relaxed excited state by photoinduced electron transfer to yield PF$^{10+}$-TCNP$^{8-}$. The nondecaying component is assigned to porphyrin triplet states having induced absorption maxima at approximately 540 nm; consistent with this interpretation, the lifetime is reduced in the presence of oxygen. This triplet is formed in part by intersystem crossing of $^1$TCNP, and potentially in part by decay of the charge-separated state. Consistent with the fluorescence results discussed above, the 1.8 ns EADS is attributed to minor impurities, conformations, or fitting artifacts. The EADS with the 12 ps lifetime can be attributed to charge recombination of PF$^{10+}$-TCNP$^{8-}$, at least in part to the ground state. The kinetic traces depicted in Fig. 4, Inset clearly show a rise/formation of stimulated emission at 780 nm and characteristic induced absorption due to the PF$^{10+}$ radical cation at 650 nm. The combined transient absorption and fluorescence results therefore reveal that the formation (590 ps) of the PF$^{10+}$-TCNP$^{8-}$ state is slower than its decay (12 ps). This order of rate constants is an example of inverted kinetics, where the rate constant for recombination is larger than that for charge separation, and transient signals can be inverted in amplitude relative to their usual appearance (24, 25).

A quantum yield of 77% is calculated for formation of PF$^{10+}$-TCNP$^{8-}$ in 2. This yield is independent of which porphyrin is excited, as the quantum yield of PF$^{10+}$-TCNP from $^1$PF$^+$-TCNP is essentially unity.

Turning now to triad 1, incorporation of Bi-PhOH into the structure creates a redox gradient that provides sufficient driving force for secondary electron transfer from the Bi-PhOH to the PF$^{10+}$ cation. The resulting oxidation of the Bi-PhOH unit dramatically enhances the acidity of the phenolic proton ($\Delta pK_a \sim 12$) (25, 26), which creates the chemical potential required for proton transfer to the hydrogen-bonded benzimidazole moiety (27–30). Therefore, excitation of triad 1 is expected to lead to eventual formation of a charge-separated state characterized by cationic benzimidazole, a phenoxyl radical, a neutral PF$^{10+}$, and a reduced TCNP porphyrin (BiH$^{1+}$-PhOH$^{-}$-PF$^{10+}$-TCNP$^{8-}$). Transient absorption techniques were employed to investigate this possibility. Based on the observation that excitation of the PF$^{10+}$ unit leads to a fast and nearly quantitative energy transfer to the TCNP moiety, the transient absorption experiments with 1 were carried out with exclusive excitation of the TCNP component at 740 nm.

Global analysis of the femtosecond excitation data for 1 in the form of EADS (Fig. 4B) gives four time constants of 120 ps, 610 ps, 2.1 ns, and a long-lived nondecaying component. As with the model compounds, the 120 ps component is assigned to decay of the initially formed $^1$TCNP to a relaxed first excited singlet state. The 610 ps EADS is ascribed to decay mainly by photoinduced electron transfer to give Bi-PhOH-PF$^{10+}$-TCNP$^{8-}$ ($k_{ET} = 1.2 \times 10^8$ s$^{-1}$). An important observation from these experiments is the absence of the 12 ps component in the triad dynamics (Fig. 4A, Inset, blue line). According to our interpretation of the dyad spectral evolution, this 12 ps component represents charge recombination of the PF$^{10+}$-TCNP$^{8-}$ radical ion pair. Therefore, the Bi-PhOH-PF$^{10+}$-TCNP$^{8-}$ intermediate charge-separated state is rapidly quenched due to a new decay channel, which we interpret as charge shift to yield the BiH$^{1+}$-PhOH$^{-}$-PF$^{10+}$-TCNP$^{8-}$ state.

Complementary nanosecond transient absorption experiments on triad 1 dissolved in air-saturated benzotriazole solutions were carried out to investigate the relatively long-lived transient species. Global analysis of data for 1 in benzotriazole excited at 735 nm is presented in the form of DAS in Fig. 5. The first DAS (0.8 μs, black line) clearly shows TCNP ground state bleaching at 450 nm and $^3$TCNP excited state absorption at 540 nm. This DAS corresponds to the TCNP triplet excited state quenched by molecular oxygen. This lifetime increases when oxygen is removed from the sample. The 3.8 μs DAS (Fig. 5, red line), whose amplitude is also shown magnified ten times for better visualization (open symbols), shows ground state bleaching at 450 and 740 nm as well as induced absorptions in the 560–700 nm and >800 nm regions. A closer inspection of the spectrum <490 nm clearly reveals competition between the TCNP ground state bleaching at 450 nm and an induced absorption with a maximum at approximately 400 nm. Based on the spectroelectrochemistry...
results (SI Appendix, Figs. S9 and S10), the induced absorption at 400–500 nm and >800 nm is assigned to formation of BiH⁺-PhO⁺, whereas those at 660 and 940 nm are due to TCNP**-. Therefore, the 3.8 μs DAS contains the spectroscopic signature of the BiH⁺-PhO⁺-PF₁₀⁻-TCNP**- final charge-separated state, providing compelling evidence that such a state is indeed produced upon excitation of triad 1 in benzonitrile. From comparison of triad and dyad kinetic traces at 940 nm, where the TCNP**- radical anion has a transient signature, the quantum yield of the final charge-separated state is estimated as approximately 52% (SI Appendix, Fig. S5).

These spectroscopic observations together with the electrochemical data allow elaboration of the energy diagram depicted in Fig. 6, which highlights the photophysical decay pathways for 1 in benzonitrile. The first singlet excited state ¹PF₁₀- decays quantitatively through energy transfer to the TCNP unit with a time constant k₄ = 2.4 × 10¹⁰ s⁻¹. The ¹TCNP excited state undergoes an excited state relaxation/structural reorganization (k = 8.3 × 10⁹ s⁻¹) to yield a relaxed first excited singlet state that decays through electron transfer to form the Bi-PhOH-PF₁₀⁺-TCNP**- radical ion pair (k₁ = 1.2 × 10¹⁰ s⁻¹). Favorably competing with charge recombination of Bi-PhOH-PF₁₀⁺-TCNP**- is the extremely fast charge shift reaction that oxidizes the phenol (k₄ = 8 × 10¹⁰ s⁻¹). This proton-coupled electron transfer reaction involves both electron transfer from the phenol to PF₁₀⁻ and transfer of the phenolic proton to the appended benzimidazole group to afford the BiH⁺-PhO⁺-PF₁₀⁻-TCNP**- final charge-separated state. The final state undergoes charge recombination with k₄ = 2.6 × 10⁹ s⁻¹.

Previous studies of benzimidazole-phenol systems with internal hydrogen bonds have suggested that oxidation of the phenol is accompanied by transfer of a proton to the hydrogen-bonded imidazole, thereby lowering the oxidation potential of the phenol unit (31, 32). The ultrafast secondary charge shift (<12 ps) observed for 1 is consistent with such a PCET mechanism. The PCET avoids formation of a Bi-PhOH⁺⁺-PF₁₀⁻-TCNP**- intermediate. Electrochemical studies of a model phenol that lacks the internal hydrogen bond, 2,4,6-tri-tert-butylphenol, show that the oxidation potential of the phenol is approximately 1.36 V vs. SCE (32, 33). Using this number, we estimate the energy of Bi-PhOH⁺⁺-PF₁₀⁻-TCNP**- to be approximately 1.63 eV. This formation of this state from Bi-PhOH-PF₁₀⁺-TCNP**- at 1.56 eV would be endergonic, and would be expected to occur slowly or not at all. As mentioned above, electron transfer in the photosynthetic OEC is thought to occur by a similar pathway.

The final charge-separated state, proposed to be BiH⁺-PhO⁺-PF₁₀⁻-TCNP**- is relatively long-lived (~4 μs). In related triads of the carotenoid-porphyrin-porphyrin (C-P-P) type, where the carotenoid is the secondary electron-donor and no proton transfer is involved in the charge-separation or recombination processes, the final charge-separated states C⁺⁺-P-P⁺⁺- typically live only hundreds of nanoseconds at room temperature (23, 24). The systems are not strictly comparable to 1, as the thermodynamic driving forces and solvents differ in the various systems. However, it is possible that nuclear rearrangements resulting from the PCET process may increase the energy barrier for charge recombination. Such a possibility has been suggested for the natural photosynthetic system (25) and we are in the process of investigating this hypothesis by femtosecond infrared spectroscopy using molecules related to the one described in this work.

Conclusion
The results for triad 1 demonstrate that structural and mechanistic motifs involving proton-coupled electron transfer in the Tyr-D₁-His₁₉₀ couple that are found in natural PSII can also be realized in a synthetic model system. Excitation of either porphyrin moiety of the triad powers a sequence of rapid electron transfer reactions that generate a long-lived charge-separated state in good yield. The results are consistent with the involvement of PCET in the second step of the charge-separation, a charge shift reaction. Furthermore, the design of the triad incorporates both a high-potential electron-donor porphyrin and a low-potential electron accepting porphyrin, leading to a final charge-separated state that is thermodynamically capable of water oxidation. Such constructs may be of value in the development of synthetic fuel production systems that draw their energy from sunlight in this issue of PNAS (34).

Materials and Methods
Synthesis. All chemicals were purchased from Aldrich, Alfa Aesar, and Acros and were used without further purification. Solvents were obtained from EM Science and were used as received unless otherwise noted. Thin layer
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chromatography (TLC) was performed with silica gel coated glass plates from Analtech. Column chromatography was carried out using Silicycle silica gel 60 with 230–400 mesh. All new compounds were characterized by 1H-NMR spectroscopy and MALDI-TOF mass spectrometry. Details of the synthesis and characterization are given in SI Appendix.

Spectroscopy. Steady-state absorption spectra were measured on a Shimadzu UV2100U UV-visible (UV-vis) and/or UV-3101PC UV-vis-near infrared spectrometer. Steady-state fluorescence spectra were measured using a Photon Technology International MP-1 spectrorometer and corrected for detection system response. All time-resolved spectroscopic studies were carried out with laboratory-build instrumentation (SI Appendix).

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Supporting Information

1. Photophysical Section

1.1 - Steady-state spectroscopy

Absorption spectra were measured on a Shimadzu UV2100U UV-vis and/or UV-3101PC UV-vis-NIR spectrometer. Steady-state fluorescence spectra were measured using a Photon Technology International MP-1 spectrometer and corrected for detection system response. Excitation was provided by a 75 W xenon-arc lamp and single grating monochromator. Fluorescence was detected 90° to the excitation beam via a single grating monochromator and an R928 photomultiplier tube having S 20 spectral response and operating in the single photon counting mode.

1.2 - Time-resolved fluorescence

Fluorescence decay measurements were performed by the time-correlated single-photon-counting method. The excitation source was a mode-locked titanium sapphire (Ti:S) laser (Spectra Physics, Millennia-pumped Tsunami) with a 130 fs pulse duration operating at 80 MHz. The laser output was sent through a frequency doubler and pulse selector (Spectra Physics Model 3980) to obtain 370-450 nm pulses at 4 MHz. Fluorescence emission was detected at the magic angle using a double grating monochromator (Jobin Yvon Gemini-180) and a microchannel plate photomultiplier tube (Hamamatsu R3809U-50). The instrument response function was 35-55 ps. The spectrometer was controlled by software based on the LabView programming language and data acquisition was done using a single photon counting card (Becker-Hickl, SPC-830).

1.3 - Transient absorption

For the single kinetics transient absorption measurements a kilohertz pulsed laser source and a pump-probe optical setup were employed. Laser pulses of 100 fs at 800 nm were generated from an amplified, mode-locked titanium sapphire kilohertz laser system (Millennia/Tsunami/Spitfire, Spectra Physics). Part of the laser pulse energy was sent through an optical delay line and focused on to a 2 mm sapphire plate to generate a white light continuum for probe beam. The remainder of the pulse energy was used to pump an optical parametric amplifier (Spectra Physics) to generate excitation pulses, which were modulated using a mechanical chopper. The excitation intensity was adjusted using a continuously variable neutral density filter. The probe beam was sent through a monochromator (SP150, Action Res. Corp.)
and recorded by a diode detector (Model 2032, New Focus Inc.) and box car (SR250, Stanford Research Systems). Instrument response function was ca. 150 fs.

Nanosecond transient absorption measurements were made with excitation from an optical parametric oscillator driven by the third harmonic of a Nd:YAG laser (Ekspla NT342B). The pulse width was ~4-5 ns, and the repetition rate was 10 Hz. The detection portion of the spectrometer (Proteus) was manufactured by Ultrafast Systems. The instrument response function was ca. 4.8 ns.

Data analysis was carried out using locally written software (ASUFIT) developed in a MATLAB environment (Mathworks Inc.). Decay-associated spectra were obtained by fitting the transient absorption or fluorescence change curves over a selected wavelength region simultaneously as described by Eq 1 (parallel kinetic model),

\[ \Delta A(\lambda, t) = \sum_{i=1}^{n} A_i(\lambda) \exp(-t/\tau_i) \]  

where \( \Delta A(\lambda, t) \) is the observed absorption (or fluorescence) change at a given wavelength at time delay \( t \) and \( n \) is the number of kinetic components used in the fitting. A plot of \( A_i(\lambda) \) versus wavelength is called a decay-associated spectrum (DAS), and represents the amplitude spectrum of the \( i^{th} \) kinetic component, which has a lifetime of \( \tau_i \).

Evolution-associated difference spectra (EADS) were obtained by global analysis of the transient absorption data using a kinetic model consisting of sequentially interconverting species, e.g. \( 1 \rightarrow 2 \rightarrow 3 \rightarrow \ldots \). The arrows indicate successive mono-exponential decays with increasing time constants, which can be regarded as the lifetimes of each species. Associated with each species is a lifetime and a difference spectrum. Each EADS corresponds in general to a mixture of states and does not portray the spectrum of a pure state or species. This procedure enables us to visualize clearly the evolution of the transient states of the system.

The global analysis procedures described here have been extensively reviewed. \( (S1) \) Random errors associated with the reported lifetimes obtained from fluorescence and transient absorption measurements were typically \( \leq 5\% \).

1.4 Photophysical Data

![Absorption spectra](image)

**Fig. S1.** Ground state absorption spectra in benzonitrile. Bi–PhOH–PF\(_{10}\)–TCNP triad 1 (black line) and PF\(_{10}\)–TCNP dyad 2 (red line).
**Fig. S2.** Fluorescence emission in cyclohexane. PF$_{10}$ model 4 (black line), dyad 2 (red line).

**Fig. S3.** Transient absorption spectra of TCNP 9 in benzonitrile upon excitation at 740 nm presented in the form of evolution associated difference spectra (EADS). The 116 ps EADS decays into the 1.9 ns EADS and may be attributed to the singlet excited state relaxation of TCNP. This spectral transformation is manifested as a red shift of the induced absorption and stimulated emission. The 1.9 ns EADS shows decay of the relaxed singlet excited state of TCNP into the nondecaying EADS associated with the triplet excited state.
Fig. S4. Transient absorption spectra of triad 1 in benzonitrile upon excitation at 740 nm presented in the form of evolution associated difference spectra (EADS). The 120 ps EADS decays into the 610 ps EADS and is attributed to the singlet excited state relaxation of TCNP. This spectral transformation is manifested as a red shift of the induced absorption and stimulated emission. The 610 ps EADS shows decay of the relaxed singlet excited state of TCNP into the next, 2.1 ns EADS and eventually to the last, nondecaying EADS which is associated with the triplet excited state and BiH$^+\text{–PhO}^\bullet\text{–PF10}^\bullet\text{–TCNP}^\bullet$ state. The lifetime of the singlet excited state of the TCNP (610 ps) is quenched due to formation of the Bi–PhOH–PF10$^\bullet$–TCNP$^\bullet$ state. As charge shift from the Bi-PhOH moiety to the PF10$^\bullet$ is much faster than 610 ps, it cannot be observed in the transient evolution.

Figure S5. Transient absorption kinetics at 940 nm (induced absorption mostly due to TCNP singlet excited state absorption and radical cation absorption) with excitation at 740 nm of triad 1
(magenta and blue lines) and dyad 2 in benzonitrile solutions with identical optical densities at 740 nm. Kinetics analysis shows formation of induced absorption due to TCNP$^{-}$ radical anion with 12 ps, 31% amplitude, in dyad 2. The nondecaying components correspond only to the TCNP triplet excited state in the dyad case, whereas in the triad the long-lived component has contributions from the porphyrin triplet excited state as well as from the BiH$^{-}$–PhO$^{−}$–PF10–TCNP$^{-}$ final charge separated state. Assuming equivalent formation of triplet excited states in the dyad and triad structures and negligible amount of induced absorption due to BiH$^{-}$–PhO$^{−}$ at 940 nm, the amplitude of contribution from the final charge separated state in triad 1 can be estimated as 21%. From time resolved emission experiments on dyad 2, we calculated a quantum yield of 77% for the PF10$^{++}$–TCNP$^{-}$ charge separated state, which corresponds to a 31% amplitude in the kinetic trace. Thus, a rough estimate of the BiH$^{-}$–PhO$^{−}$–PF10–TCNP$^{-}$ quantum yield can be calculated by the Eq 2, which gives x=52%.

$$\frac{31}{21} = \frac{77}{x}$$  \hspace{1cm} (2)

1.5 References


2. Electrochemical and Spectroelectrochemical Studies

All electrochemical and spectroelectrochemical studies were carried out using a CH Instruments 760D potentiostat. For electrochemical experiments, a custom glass cell with Teflon top accommodating a three electrode setup and 1-2 mL of solutions was used. The working electrode was either a platinum or glassy carbon disc electrode as indicated for the particular experiment. The working electrode was combined with a platinum mesh counter electrode and a Ag$^{+}$/Ag quasi reference. The potential of the Ag$^{+}$/Ag quasi reference was determined with ferrocenium/ferrocene (Fc$^{+}$/Fc) as an internal reference, with the potential of the Fc$^{+}$/Fc couple taken as 0.45 V vs. SCE. The compound of interest was dissolved in the indicated solvent, and tetrabutylammonium hexafluorophosphate at a concentration of 100 mM was used as a supporting electrolyte for all experiments. Prior to any experiment, the solution was purged with argon and then run under an argon atmosphere. Spectroelectrochemical experiments were performed with an indium doped tin oxide (ITO) working electrode, with a glass cover slip attached over the conductive face of the ITO with heat-shrink plastic. When immersed in solution, capillary action fills the cavity between the ITO and cover slip and thereby creates a small volume to ensure bulk electrolysis of the solution in the path length of the spectrophotometer in the course of the experiment. The spectroelectrochemical setup was contained in a 1 cm quartz cuvette under a constant Ar flow, and a Shimadzu UV-3101PC spectrophotometer was used for all experiments.
Figure S6. Cyclic Voltammetry of Bi–PhOH–PF$_{10}$ 5. The voltammogram was taken in dichloromethane with a platinum working electrode and at a scan rate of 100 mV s$^{-1}$. A reversible oxidation of the complex occurs at 1.04 V $\text{vs. SCE}$, corresponding to the Bi–PhOH moiety, and a reversible reduction occurs at -1.05 V $\text{vs. SCE}$, corresponding to the PF$_{10}$ moiety.

Figure S7. Cyclic Voltammetry of TCNP 9. This plot is a combination of two scans, one from 0 to -1.0 V, the other from 0 to 1.4 V $\text{vs. SCE}$. The cyclic voltammograms were recorded in dichloromethane with a platinum working electrode. Sequential reductions of the TCNP occurred at -0.30 V $\text{vs. SCE}$ and -0.58 V $\text{vs. SCE}$, and an oxidation was observed at 1.28 V $\text{vs. SCE}$.
Figure S8. Spectroelectrochemistry of PF_{10} model compound. The structure of the model PF_{10} used is shown on the left. The plot to the right shows the absorbance spectrum of the PF_{10} solution at different times (0 min. (red), 2 min. (green), 4 min. (cyan), and 6 min. (blue)) while poising the solution at 1.30 V \textit{vs.} SCE. The spectrum of the oxidized form of PF_{10} (blue) shows bleaching of the Q bands and a new absorption at around 700 nm. The experiments for this Figure were done in dichloroethane containing TBAPF_{6} as the supporting electrolyte.

Figure S9. Spectroelectrochemistry of PF_{10} model compound. This plot shows the difference in absorption between the absorbance of PF_{10} when poised at 1.30 V \textit{vs.} SCE (singly oxidized) and its absorbance at 0 V \textit{vs.} SCE (neutral state). The spectrum of the oxidized form of PF_{10} shows a bleaching of the Soret band (near 420 nm) and a positive absorption at around 700 nm. The experiments for this Figure were done in dichloroethane containing TBAPF_{6} as the supporting electrolyte, and the spectra of the neutral and oxidized forms of the porphyrin were taken after poising the working electrode at constant voltage for 6 min.
Figure S10. Spectroelectrochemistry of TCNP 9. This plot shows the difference in absorption between the absorbance of 9 when poised at -0.64 V vs. SCE (singly reduced) and its absorbance at -0.04 V vs. SCE (neutral state). The spectrum of the reduced form of 9 shows a bleaching of the Soret band (near 450 nm) and induced absorption at 660 nm and 940 nm. The experiments for this Figure were done in benzonitrile and the spectra of the uncharged and reduced forms of the porphyrin were taken after poising the working electrode at constant voltage for 15 min.

Figure S11. Spectroelectrochemistry of BIP 1 (blue) and BIP 2 (red). The blue and red traces of the spectrum to the left show the difference in absorption between the oxidized and neutral forms of the corresponding BIP structure. The oxidized form of BIP 1 was generated by poising the working electrode at 1.05 V vs. SCE and that of BIP 2 was formed by poising at 0.80 V vs. SCE. The spectrum of the oxidized form of BIP 1 shows four positive bands at 370, 400, 445 (shoulder), and 780 nm. For BIP 2, two bands near 390 and 580 nm can be seen. The experiments for this Figure were done in dichloroethane, and the spectra of the neutral and oxidized forms of the molecules were taken after poising the working electrode at constant voltage for 6 min.
Table 1. Redox potentials (V vs. SCE). For reversible processes, the peak separation ($\Delta E_p$) is given in mV.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ox(2), ($\Delta E_p$)</th>
<th>Ox(1), ($\Delta E_p$)</th>
<th>Red(1), ($\Delta E_p$)</th>
<th>Red(2), ($\Delta E_p$)</th>
<th>Red(3), ($\Delta E_p$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIP-PhOH$^a$</td>
<td>-</td>
<td>0.95 (88)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PF$_{10}$$^a$</td>
<td>1.53 (65)</td>
<td>1.29 (65)</td>
<td>-0.96 (84)</td>
<td>-1.37 (82)</td>
<td>-</td>
</tr>
<tr>
<td>9$^b$</td>
<td>1.51 (irr)</td>
<td>1.28 (93)</td>
<td>-0.30 (63)</td>
<td>-0.58 (92)</td>
<td>-</td>
</tr>
<tr>
<td>5$^b$</td>
<td>-</td>
<td>1.04 (81)</td>
<td>-1.05 (67)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2$^c$</td>
<td>-</td>
<td>1.23 (irr)</td>
<td>-0.25 (69)</td>
<td>-0.53 (70)</td>
<td>-0.97 (60)</td>
</tr>
<tr>
<td>1$^d$</td>
<td>-</td>
<td>1.06</td>
<td>-0.27</td>
<td>-0.61</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ These model structures are not included in this work but have been reported in previous studies with a related system (Moore, G. F., et al. J. Am. Chem. Soc. 2008, 130: 10466-10467).
$^b$ Cyclic voltammetry done in dichloromethane solution with a platinum working electrode.
$^c$ Cyclic voltammetry done in acetonitrile solution with a glassy carbon working electrode.
$^d$ Values obtained by differential pulse voltammetry in benzonitrile with a glassy carbon working electrode.

3. Synthetic Section

3.1 – Materials

All chemicals were purchased from Aldrich, Alfa Aesar, and Acros and were used without further purification. Solvents were obtained from EM Science and were used as received unless otherwise noted. Thin layer chromatography (TLC) was performed with silica gel coated glass plates from Analtech. Column chromatography was carried out using Silicycle silica gel 60 with 230-400 mesh.

3.2 – Spectroscopic Measurements

The $^1$H-NMR spectra were recorded on a Varian spectrometer at 400 MHz or 500 MHz. NMR samples were prepared in deuteriosolvents with tetramethylsilane as an internal reference using a Wilmad 528-PP 5 mm NMR tube. Deuterated chloroform was distilled from CaH. Mass spectra were obtained with a matrix-assisted laser desorption/ionization time-of-flight spectrometer (MALDI-TOF), using (1E, 3E)-1,4-diphenylbuta-1,3-diene (DPB), cyano-4-hydroxycinnamic acid (CCA) or terthiophene as a matrix. The reported mass is of the most abundant isotopic ratio observed. To facilitate comparison, calculated values of the expected most abundant isotopic ratio are listed after the experimental result.

3.3. – Synthesis of Building Blocks, Synthetic Intermediates and Their Spectroscopic Characterization
Overview of Synthetic Strategy:

Synthesis of 5-formyl-3-tert-butyl-2-hydroxybenzaldehyde 3:\[\text{S2}\]

A solution of commercially available 2-tert-butylphenol (6.00 g, 40 mmol, 1 equiv.), hexamethylenetetramine (14.00 g, 100 mmol, 2.5 equiv.) and trifluoroacetic acid (40 mL) was heated at reflux for 12 h. The reaction was quenched while hot with a 33% (v/v) aqueous H\textsubscript{2}SO\textsubscript{4} solution (20 mL) and the resulting mixture was allowed to cool to room temperature with stirring. The crude product was extracted with diethyl ether (3 \times 50 mL), and the extract was neutralized with a saturated aqueous solution of sodium bicarbonate (2 \times 100 mL) and finally washed with water (3 \times 100 mL). The organic phase was dried over sodium sulfate, filtered through paper and concentrated under reduced pressure. Final purification was achieved by column chromatography (SiO\textsubscript{2}), using hexanes/EtOAc (9:1, v/v) as eluent to afford the title compound as a light yellow solid in 55% yield (4.53 g). \[\text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, \delta ppm):}\]

\text{12.37 (s, 1H, OH); 9.96 (s, 1H, CHO); 9.89 (s, 1H, CHO); 8.03 (d, J = 2.0 Hz, 1H, Ar\textsubscript{6}); 7.96 (d, J = 2.0 Hz, 1H, Ar\textsubscript{4}); 1.42 (s, 9H, Bu\textsubscript{t}).}
Synthesis of 5-(pentafluorophenyl)dipyrromethane (S2):

A solution of pentafluorobenzaldehyde (2.0 mL, 16.2 mmol) in freshly distilled pyrrole (50 mL, 720 mmol) was degassed with a stream of argon for 10 min before adding trifluoroacetic acid (120 μL, 1.62 mmol). The mixture was stirred for 30 min at room temperature, diluted with CH₂Cl₂ (400 mL), and then washed with 0.1M NaOH (400 mL), and then washed with 0.1M NaOH (400 mL), and then washed with 0.1M NaOH (400 mL), and then washed with 0.1M NaOH (400 mL), and then washed with 0.1M NaOH (400 mL), and then washed with 0.1M NaOH (400 mL), and then washed with 0.1M NaOH (400 mL), and then washed with 0.1M NaOH (400 mL), and then washed with 0.1M NaOH (400 mL), and then washed with 0.1M NaOH (400 mL), and then washed with 0.1M NaOH (400 mL). The organic phase was washed with water (400 mL) and dried over Na₂SO₄. Evaporation of the solvent at reduced pressure gave a brown oil. Unreacted pyrrole was removed under high vacuum at room temp, yielding a tacky solid that was purified by flash chromatography on a column of silica using a mixture of hexanes:ethyl acetate:triethylamine (80:20:1) as the eluent. The product was recrystallized from dichloromethane/hexanes to yield 3.29 g of 5-(pentafluorophenyl)dipyrromethane as a white powder in 65% yield (3.28 g). ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.11 (2H, brs, NH), 6.73 (2H, m, CH₁ and CH₉), 6.16 (2H, m, CH₂ and CH₈), 6.02 (2H, brs, CH₃ and CH₇), 5.89 (1H, brs, CH₂), 5.29 (residual solvent CH₂Cl₂), 1.56 (residual water in the deuterated solvent).
Figure S13. $^1$H NMR spectrum of 5-(pentafluorophenyl)dipyrrromethane, 400 MHz, CDCl$_3$, 25$^\circ$C.

Synthesis of 5,15-bis(2,3,4,5,6-pentafluorophenyl)-10-(4-carbomethoxyphenyl)-20-(3-formyl-4-hydroxy-5-tert-butylpheynyl)porphyrin 4:

Compound 3 (0.265 g, 1.28 mmol), pentafluorophenyl-dipyrrromethane (0.800 g, 2.56 mmol) and carboxymethyl benzoate (0.211 g, 1.56 mmol) were dissolved in 325 mL of chloroform containing 2.45 mL (0.75 %, v/v) of ethanol under a nitrogen atmosphere, followed by addition of boron-trifluoride etherate (BF$_3$OEt$_2$) (0.142 g, 0.125 mL, 1.00 mmol) and the reaction mixture was stirred for one hour at room temperature. The resulting dark red porphyrogenic mixture was oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.732 g, 3.25 mmol) for 12 h at room temperature, yielding a black crude mixture. Filtration through a silica pad to remove tar and polymeric byproducts, followed by concentration under reduced pressure afforded a deep purple reddish solid. Purification through column chromatography (SiO$_2$, hexanes/dichloromethane as eluent) yielded three porphyrin fractions (23% total porphyrin yield). The first porphyrin fraction corresponded to compound 4a (0.178 g, 7% yield) followed by target porphyrin 4 (0.268 g, 11% yield) and compound 4b (0.116 g, 5% yield). A small amount of the target porphyrin 4 was recrystallized from slow evaporation of an acetonitrile solution of 4 in order to afford an analytical sample for spectroscopic characterization.

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$ ppm): 12.20 (1H, s, OH), 10.12 (1H, s, CH$_O$), 8.93 (2H, d, $J$ = 5.0 Hz, H$_8$ and H$_{12}$), 8.67 (2H, d, $J$ = 5.0 Hz, H$_2$ and H$_{18}$), 8.79 (4H, t, H$_3$, H$_7$, H$_{13}$ and H$_{17}$), 8.45 (2H, d, $J$ = 8.3 Hz, H$_{3''}$ and H$_{5''}$), 8.39 (1H, d, $J$ = 2.0 Hz, H$_2'$), 8.28 (2H, brt, H$_{2''}$ and H$_{6''}$), 8.20 (1H, d, $J$ = 2.0 Hz, H$_6'$), 4.12 (3H, s, COOCH$_3$), 1.58 (9H, s, C(CH$_3$)$_3$), - 2.85 (2H, s, NH).
MALDI-TOF: (positive mode, 1,4-diphenylbutadiene as matrix) 952.46 (M)⁺, calculated 952.21 for C₅₁H₃₀F₁₀N₄O₄.

**Figure S14.** ¹H NMR spectrum of porphyrin 4, 500 MHz, CDCl₃, 25°C.

**Figure S15.** MALDI-TOF spectrum (positive mode, 1,4-diphenylbutadiene as matrix) of compound 4 (top and bottom right) and the corresponding isotope simulation (bottom left) expected for C₅₁H₃₀F₁₀N₄O₄.
Synthesis of 5,15-bis(2,3,4,5,6-pentafluorophenyl)-10-(4-carbomethoxyphenyl)-20-[2’-(3-tert-butyl-2’’-hydroxyphenyl)benzimidazole]porphyrin 5:

Commercially available 1,2-phenylenediamine (0.0045 g, 0.042 mmol) in nitrobenzene (3 mL) was added drop-wise to a solution of porphyrin 4 (0.040 g, 0.042 mmol) in nitrobenzene (7 mL) and the purple solution was heated at reflux (210 °C) in a sand-bath for 12 h. After cooling and without any workup, the crude mixture was transferred to a column chromatography (SiO$_2$ in hexanes) and nitrobenzene was eluted with a mixture of hexanes/dichloromethane (90:10, v/v). The target compound was eluted with a mixture of hexanes/dichloromethane (50:50, v/v), which was washed with hexanes (20 mL) to afford 5 as a purple solid in 70% yield (0.031 g). $^1$H NMR (500 MHz, (CD$_3$)$_2$CO, δ ppm): 14.57 (s, 1H, OH); 12.42 (s, 1H, NH); 9.25 (m, 6H, pyrrolic protons); 9.10 (d, 2H, $J = 4.8$ Hz, pyrrolic protons); 8.82 (d, 1H, $J = 2.0$ Hz, H$_2$); 8.48 (m, 4H, H$_2$, H$_3$, H$_5$ and H$_6$); 8.38 (d, 1H, $J = 2.0$ Hz, H$_6$); 7.84 (d, 1H, $J = 7.6$ Hz, H$_7$); 7.50 (d, 1H, $J = 7.6$ Hz, H$_4$); 7.30 (m, 2H, H$_5$ and H$_6$); 4.10 (s, 3H, COOCH$_3$); 1.70 (s, 9H, but); -2.79 (s, 2H, NH). MALDI-TOF (positive mode, 1,4-diphenylbutadiene as matrix) 1041.41 (M + H)$^+$, calculated 1040.25 for C$_{57}$H$_{34}$F$_{10}$N$_6$O$_3$.

Figure S16. $^1$H NMR spectrum of porphyrin 5, 500 MHz, (CD$_3$)$_2$CO, 25°C.
Figure S17. MALDI-TOF spectrum (positive mode, 1,4-diphenylbutadiene as matrix) of porphyrin 5 (top and bottom right) and corresponding isotope simulation (bottom left) expected for C_{57}H_{34}F_{10}N_{6}O_{3}.

Synthesis of 5,15-bis(2,3,4,5,6-pentafluorophenyl)-10-(4-carboxyphenyl)-20-[2’-(3-tert-butyl-2”-hydroxyphenyl)benzimidazole]porphyrin 6:

Porphyrin 5 (0.042 g, 0.04 mmol) was dissolved in trifluoroacetic acid (10 mL) followed by addition of 20 mL of concentrated HCl. The green mixture was stirred at 90°C for 24 h. After cooling, the mixture was taken upon dichloromethane (50 mL), washed with water (50 mL) and then neutralized with a saturated sodium carbonate aqueous solution. The organic phase was dried over sodium sulfate, filtered through paper, and concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO2) using a mixture of dichloromethane/methanol (9:1, v/v) as eluent to afford 0.041 g (98% yield) of the target porphyrin 6 as a purple solid. MALDI-TOF (positive mode, 1,4-diphenylbutadiene as matrix) 1026.41 (M)+, calculated 1026.20 for C_{56}H_{32}F_{10}N_{6}O_{3}.
Synthesis of \(5,15\text{-bis}(2,3,4,5,6\text{-pentafluorophenyl})-10\text{-}(4\text{-aminophenyl})-20\text{-}[2'\text{-}(3\text{-}tert\text{-}butyl-2''\text{-}hydroxyphenyl)benzimidazole]porphyrin\) 7 (Curtius Rearrangement):

Porphyrin 6 (0.040 g, 0.039 mmol), diphenyl-phosphoryl azide (0.021 g, 0.078 mmol), and triethylamine (20 μL) were dissolved in fresh distilled (from K\(_2\)CO\(_3\)) tert-butanol (10 mL) and heated at 85°C for 24 h. Upon cooling, the reaction mixture was diluted with dichloromethane (50 mL) and then washed with water (3 × 50 mL). The organic phase was dried over sodium sulfate, filtered through paper and concentrated under reduced pressure. Final purification was achieved by column chromatography (SiO\(_2\)) using a mixture of hexanes/ethyl acetate (9:1, v/v) as eluent to afford 0.024 g (58 % yield) of the NH-Boc protected porphyrin 7a as a purple solid. MALDI-TOF (positive mode, 1,4-diphenylbutadiene as matrix) 1097.26 (M\(^+\)), calculated 1097.30 for C\(_{60}\)H\(_{41}\)F\(_{10}\)N\(_7\)O\(_3\). Porphyrin 7a (0.024 g, 0.022 mmol) was dissolved in 10 mL of trifluoroacetic acid and heated at 90°C for 12 h. The cooled reaction mixture was diluted with dichloromethane (20 mL), washed with water (2 × 50 mL) and then neutralized with a saturated solution of aqueous sodium bicarbonate, followed by washing with water (1 × 50 mL). The organic phase was dried over sodium sulfate, filtered through paper and concentrated under reduced pressure. Final purification was achieved by column chromatography (SiO\(_2\)) using dichloromethane as eluent to afford g 0.020 (90% yield) of the amino porphyrin 7 as a purple solid. \(^1\)H NMR (500 MHz, (CD\(_3\))\(_2\)CO, δ ppm): 14.58 (br, 1H, OH); 12.46 (br, 1H, NH); 9.20 (m, 8H, pyrrolic protons); 8.79 (d, 1H, J = 2.0 Hz, H\(_2\)); 8.38 (d, 1H, J = 2.0 Hz, H\(_6\)); 8.02 (dbr, 2H, \(J = 8.0\) Hz, H\(_5\) and H\(_6\)); 7.89 (d, 1H, J = 7.6 Hz, H\(_4\)); 7.53 (d, 1H, J = 7.6 Hz, H\(_4\)); 7.36 (m, 2H, H\(_5\) and H\(_6\)); 7.18 (d, 2H, J = 8.0 Hz, H\(_4\)); 5.23 (s, 2H, NH\(_2\)); 1.72 (s, 9H, Bu); -2.70 (d, 2H, NH).

MALDI-TOF (positive mode, 1,4-diphenylbutadiene as matrix) 997.53 (M\(^+\)), calculated 997.30 for C\(_{55}\)H\(_{33}\)F\(_{10}\)N\(_7\)O.
**Figure S18.** MALDI-TOF spectrum (positive mode, 1,4-diphenylbutadiene as matrix) of porphyrin 7a (top and bottom right) and corresponding isotope simulation (bottom left) expected for C_{60}H_{41}F_{10}N_{7}O_{3}.

**Figure S19.** $^1$H NMR spectrum of porphyrin 7, 500 MHz, (CD$_3$)$_2$CO, 25°C.
**Figure S20.** MALDI-TOF spectrum (positive mode, 1,4-diphenylbutadiene as matrix) of porphyrin 7 (top and bottom right) and corresponding isotope simulation (bottom left) expected for C\textsubscript{55}H\textsubscript{33}F\textsubscript{10}N\textsubscript{7}O.

**Synthesis of 5,10,15-tris(3,5-di-tert-butylphenyl)-20-(4-carboxmethoxyphenyl)-7,8,17,18-tetrabromoporphyrin 8:**

Recrystallized NBS (0.133 g, 0.748 mmol) were dissolved in 50 mL of chloroform and the resulting purple solution was heated at reflux for 3 h. Another portion of NBS (0.041 g, 0.230 mmol) was added and the reaction mixture was stirred at reflux for additional 3 h, followed by a final addition of another portion of NBS (0.041 g, 0.230 mmol) and additional 3 h stirring at reflux. After cooling, water was added and the organic layer washed with water (3 × 100 mL), dried over MgSO\textsubscript{4}, filtered through paper and concentrated. Final purification was achieved by column chromatography (SiO\textsubscript{2}) using a gradient of hexanes/dichloromethane (from 90:10 to 40:60, v/v) to afford the target compound as a dark brownish purple solid in 32% yield (0.05 g, 0.037 mmol). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, δ ppm): 8.82 (brs, 3H, pyrrolic protons); 8.64 (d, 1H, \(J = 5.0\) Hz, pyrrolic proton); 8.45 (d, 2H, \(J = 8.3\) Hz, H3”); 8.28 (d, 2H, \(J = 8.3\) Hz, H2”); 7.99

**Note:** Commercial N-bromosuccinimide (NBS) was freshly recrystallized from hot water, filtered through paper and dried under vacuum prior to use (white solid). In a round bottom flask, starting porphyrin 8a (S3a) (0.116 g, 0.115 mmol) and fresh
(m, 6H, H2'); 7.83 (s, 3H, H4'); 4.10 (s, 3H, COOCH3); 1.51 (s, 54H, Bu); -2.88 (s, 1H, NH); -2.91 (s, 1H, NH). MALDI-TOF (positive mode, 1,4-diphenylbutadiene as matrix) 1324.02 (M)+, calculated 1324.3 for C70H78N4O2Br4.

Figure S21. 1H NMR spectrum of porphyrin 8, 500 MHz, CDCl3, 25°C.
Figure S22. MALDI-TOF spectrum (positive mode, 1,4-diphenylbutadiene as matrix) of porphyrin 8 (top and bottom right) and corresponding isotope simulation (bottom left) expected for C_{70}H_{76}N_{4}O_{2}Br_{4}.

Synthesis of 5,10,15-tris(3,5-di-tert-butylphenyl)-20-(4-carboxmethoxyphenyl)-7,8,17,18-tetracyanoporphyrin 9:

First step: Synthesis of porphyrin 8b. Porphyrin 8 (0.05 g, 0.037 mmol) and Zn(OAc)_{2} (0.083 g, 0.377 mmol) were dissolved in 100 mL of a mixture of chloroform/methanol (90:10, v/v) and the resulting purple solution was heated at reflux for 1 h. After cooling, water was added and the organic layer washed with water (3 × 100 mL), dried over MgSO_{4}, filtered through paper and concentrated. Final purification was achieved by flash chromatography (SiO_{2}) using dichloromethane as eluent to afford the target compound 8b as a dark purple solid in quantitative yield (0.050 g, 0.037 mmol). \(^{1}\)H NMR (400 MHz, CDCl_{3}, \(\delta\) ppm): 8.87 (m, 2H, pyrrolic protons); 8.33 (d, 1H, \(J = 5\) Hz, pyrrolic proton); 8.67 (d, 1H, \(J = 5\) Hz, pyrrolic proton); 8.36 (d, 2H, \(J = 8.1\) Hz, H3”); 8.15 (d, 2H, \(J = 8.1\) Hz, H2”); 7.85 (s, 6H, H2’); 7.79 (s, 3H, H4’); 4.06 (s,
3H, COOCH₃); 1.51 (s, 54H, Bu). MALDI-TOF (positive mode, 1,4-diphenylbutadiene as matrix) 1388.56 (M)⁺, calculated 1388.2 for C₇₀H₇₄N₄O₂Br₄Zn.

Figure S23. ¹H NMR spectrum of porphyrin intermediate 8b, 400 MHz, CDCl₃, 25°C.

Figure S24. MALDI-TOF spectrum (positive mode, 1,4-diphenylbutadiene as matrix) of porphyrin 8b (top and bottom right) and corresponding isotope simulation (bottom left) expected for C₇₀H₇₄N₄O₂Br₄Zn.
Second step: Synthesis of porphyrin 8c. Porphyrin 8b (0.034 g, 0.0245 mmol), Zn(CN)2 (0.007 g, 0.058 mmol), [1,10-bis-(diphenylphosphino)ferrocene] (dpdf) (0.022 g, 0.039 mmol), zinc dust (0.002 g, 0.03 mmol), zinc(II) acetate (0.002 g, 0.011 mmol) were all dissolved in 5 mL of anhydrous oxygen-free dimethylacetamide and stirred at room temperature for 2 min. Tris(dibenzyldieneacetone)dipalladium(0) (Pd2(dba)3) (0.018 g, 0.019 mmol) was added and the reaction mixture was stirred at 100°C for 12 h under an inert atmosphere. After cooling, dichloromethane (50 mL) was added and the green organic phase was washed with water (2 × 50 mL), dried over sodium sulfate, filtered through paper and concentrated under reduced pressure. Final purification was achieved by column chromatography (SiO₂) using toluene/ethyl acetate (90:10) to afford porphyrin 8c as a bluish green solid in 49% yield (0.014 g). 1H NMR (400 MHz, CDCl₃, δ ppm): 8.87 (m, 3H, pyrrolic protons); 8.70 (d, 1H, pyrrolic protons); 8.39 (d, 2H, J = 8.0 Hz, H3’’); 8.15 (d, 2H, J = 8.0 Hz, H2’’); 7.94 (s, 3H, H4’); 7.67 (s, 6H, H2’); 4.06 (s, 3H, COOCH₃); 1.49 (s, 54H, Bu).

Figure S25. 1H NMR spectrum of porphyrin intermediate 8c, 400 MHz, CDCl₃, 25°C.

Third step: Synthesis of porphyrin 9. Porphyrin 8c (0.014 g, 0.012 mmol) was dissolved in 10 mL of dry dichloromethane and 10 mL of trifluoroacetic acid was added under an inert atmosphere. The brown reaction mixture was stirred for 30 min at room temperature. The crude product was neutralized with triethylamine, washed with water (2 × 10 mL), dried over sodium sulfate, filtered through paper and concentrated under reduced pressure. Final purification was achieved by flash chromatography (SiO₂) using dichloromethane as eluent to afford target porphyrin 9 as a bluish-green solid in 99% yield (0.013 g). 1H NMR (400 MHz, CDCl₃, δ ppm): 9.01 (m, 3H, pyrrolic protons); 8.86 (dd, 1H, pyrrolic proton); 8.49 (d, 2H, J = 8.2 Hz, H3”); 8.26 (d, 2H, J = 8.2 Hz, H2”); 8.05-7.85 (m, 9H, H2’ and H4’); 4.10 (s, 3H, COOCH₃); 1.53 (s, 54H, Bu); -2.43 (s, 1H, NH); -2.45 (s, 1H, NH).
Figure S26. $^1$H NMR spectrum of porphyrin intermediate 9, 400 MHz, CDCl$_3$, 25°C.

Synthesis of 5,10,15-tris(3,5-di-tert-butylphenyl)-20-(4-carboxyphenyl)-7,8,17,18-tetracyanoporphyrin 10:

Porphyrin 8c (0.014 g, 0.012 mmol) was dissolved in 5 mL of tetrahydrofuran followed by addition of a 10% KOH aqueous solution (w/w) and the reaction mixture was stirred for 2 h at room temperature. After the reaction time, dichloromethane (30 mL) was added; the organic phase was copiously washed with water (3 × 100 mL), dried over sodium sulfate, filtered through paper and concentrated under reduced pressure to about 10 mL. The green crude mixture containing 10a was then treated with 10 mL of trifluoroacetic acid for 1 h at room temperature to remove the zinc ion from the porphyrin. The crude mixture was diluted with 20 mL of dichloromethane, neutralized with triethylamine, washed with water (3 × 50 mL), dried over sodium sulfate and concentrated under reduced pressure. Final purification was achieved by flash chromatography (SiO$_2$) using dichloromethane/methanol (9:1, v/v) as eluent to afford target porphyrin 10 as a bluish-green solid in 90% yield (0.011 g). MALDI-TOF (negative mode, 1,4-diphenylbutadiene as matrix) 1094.41 (M)$^-$, calculated 1094.6 for C$_{73}$H$_{74}$N$_8$O$_2$. 
Figure S27. MALDI-TOF spectrum (negative mode, 1,4-diphenylbutadiene as matrix) of porphyrin 10 (top and bottom right) and corresponding isotope simulation (bottom left) expected for C_{73}H_{74}N_{8}O_{2}.

Synthesis of 5,15-bis(2,3,4,5,6-pentafluorophenyl)-10-(4-nitrophenyl)-20-(3-formyl-4-hydroxy-5-tert-butylnaphthyl)zinc(II)porphyrin 2a

Commerically-available 3,5-di-tert-butylbenzaldehyde (0.401 g, 1.84 mmol), 4-nitrobenzaldehyde (0.278 g, 1.84 mmol) and pentafluorophenyl-dipyrromethane (1.15 g, 3.68 mmol) were dissolved in 370 mL of chloroform containing 2.45 mL (0.75 %, v/v) of ethanol under a nitrogen atmosphere, followed by addition of boron-trifluoride etherate (BF_{3}OET_{2}) (0.065 g, 0.065 mL, 0.46 mmol) and the reaction mixture was stirred for one hour at room temperature. The resulting dark red porphyrigenic mixture was oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzquinone (DDQ) (1.25 g, 5.50 mmol) for 12 h at room temperature, yielding a black crude mixture. Filtration through a silica pad to remove tar and polymeric byproducts, followed by concentration under reduced pressure afforded a reddish purple solid, which was dissolved in dichloromethane (100 mL) followed by addition of Zn(OAc)_{2} (1.10 g, 5 mmol) dissolved in 20 mL of methanol. The purple solution was heated at reflux for 1 h. After cooling, water was added, the organic layer separated and washed with water (3 × 100 mL), dried over MgSO_{4}, filtered through paper and concentrated. Final purification was achieved by flash chromatography (SiO_{2}) using dichloromethane as eluent to afford the target compound 2a as a
dark purple solid in 10% yield (0.372 g). $^1$H NMR (400 MHz, CDCl$_3$, δ ppm): 9.15 (d, 2H, pyrrolic protons); 8.95 (m, 6H, pyrrolic protons); 8.64 (d, 2H, J = 8.2 Hz, H3’); 8.42 (d, 2H, J = 8.2 Hz, H2’); 8.07 (s, 2H, H2’); 7.87 (s, 1H, H4’); 1.57 (s, 18H, Bu). MALDI-TOF (positive mode, 1,4-diphenylbutadiene as matrix) 1013.30 (M$^+$), calculated 1013.20 for C$_{52}$H$_{33}$F$_{10}$N$_5$O$_2$Zn.

**Figure S28.** $^1$H NMR spectrum of porphyrin intermediate 2a, 400 MHz, CDCl$_3$, 25°C.

**Figure S29.** MALDI-TOF spectrum (positive mode, 1,4-diphenylbutadiene as matrix) of porphyrin 2a (top and bottom right) and corresponding isotope simulation (bottom left) expected for C$_{52}$H$_{33}$F$_{10}$N$_5$O$_2$Zn.
Synthesis of 5,15-bis(2,3,4,5,6-pentafluorophenyl)-10-(4-aminophenyl)-20-(3-formyl-4-hydroxy-5-tert-butylpheynyl)porphyrin 2b

Porphyrin 2a (0.103 g, 0.1 mmol), 10% palladium on carbon (0.10 g) and NaBH₄ (0.019 g, 0.5 mmol) were suspended in 40 mL of a mixture of dichloromethane and methanol (1:1). The suspension was stirred at room temperature for 5 h under nitrogen atmosphere before filtering the reaction mixture through a pad of Celite. The solvent was evaporated under reduced pressure and the crude was re-dissolved in dichloromethane 20 mL, washed with water (3 × 50 mL), dried over MgSO₄ and filtered through paper. The organic phase was then treated with 20 mL of trifluoroacetic acid for 1 h at room temperature. The solution was neutralized with triethylamine, washed with water (3 × 50 mL), dried over MgSO₄, filtered through paper and concentrated. Final purification was achieved by column chromatography (SiO₂) using a gradient of hexanes/dichloromethane (from 90:10 to 50:50, v/v) as eluent to afford the target compound as a purple solid in 65% yield (0.06 g, 0.065 mmol). ¹H NMR (400 MHz, CDCl₃, δ ppm): 9.07 (d, 2H, J = 7 Hz, pyrrolic protons); 8.96 (d, 2H, J = 7 Hz, pyrrolic protons); 8.79 (d, 4H, J = 7 Hz, pyrrolic protons); 8.06 (s, 2H, H2’); 7.99 (d, 2H, J = 8.5 Hz, H2’’); 7.84 (s, 1H, H4’); 7.07 (d, 2H, J = 8.5 Hz, H3’’); 4.03 (s, 2H, NH₂); 1.54 (s, 18H, Bu); -2.78 (s, 2H, NH). MALDI-TOF (positive mode, 1,4-diphenylbutadiene as matrix) 921.38 (M)+, calculated 921.3 for C₅₂H₃₇F₁₀N₅.

Figure S30. ¹H NMR spectrum of porphyrin intermediate 2, 400 MHz, CDCl₃, 25°C.
3.4 – Synthesis and Spectroscopic Characterization of Dyad 2.

Porphyins 2b (0.0055 g, 6.00 µmol) and 10 (0.006 g, 5.48 µmol) were dissolved in 3 mL of dichloromethane under inert atmosphere. Dimethylaminopyridine (DMAP) (0.002 g, 0.01 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (0.002 g, 8.22 µmol) were added and the reaction mixture was stirred at room temperature for 12 h. The crude mixture was diluted with 20 mL of dichloromethane, washed with water (3 × 20 mL), dried over MgSO₄, filtered through paper and concentrated. Final purification was achieved by column chromatography (SiO₂) using a gradient of hexanes/dichloromethane as eluent to afford the target compound as a greenish-purple solid in 56% yield (0.007 g, 3.33 µmol). ¹H NMR (400 MHz, CDCl₃, δ ppm): 9.06 (m, 4H, pyrrolic protons); 9.00 (m, 4H, pyrrolic protons); 8.85 (d, 2H, J = 5.0 Hz, pyrrolic protons); 8.81 (d, 2H, J = 5.0 Hz, pyrrolic protons); 8.70 (s, 1H, NHCO); 8.44 (d, 2H, J = 8.3 Hz, H2’’); 8.39 (d, 2H, J = 8.3 Hz, H3’’); 8.33 (d, 2H, J = 8.4 Hz, H2’’); 8.25 (d, 2H, J = 8.4 Hz, H3’’); 8.08
(s, 3H, Hp'); 8.03-7.90 (m, 7H, Hp and Ho'); 7.84 (s, 2H, Ho); 1.54 (m, 72H, Bu); -2.38 (s, 2H, NH); -2.79 (s, 2H, NH). MALDI-TOF (positive mode, 1,4-diphenylbutadiene as matrix) 1999.53 (M)⁺, calculated 1997.9 for C₁₂₅H₁₀₉F₁₀N₁₃O.

**Figure S32.** ¹H NMR spectrum of dyad 2, 400 MHz, CDCl₃, 25°C.

**Figure S33.** MALDI-TOF spectrum (positive mode, 1,4-diphenylbutadiene as matrix) of dyad 2 (top and bottom right) and corresponding isotope simulation (bottom left) expected for C₁₂₅H₁₀₉F₁₀N₁₃O.
3.5 – Synthesis and Spectroscopic Characterization of Triad 1.

Porphyrs 7 (0.006 g, 6.00 μmol) and 10 (0.006 g, 5.48 μmol) were dissolved in 3 mL of dichloromethane under inert atmosphere. Dimethylaminopyridine (DMAP) (0.002 g, 0.01 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (0.002 g, 8.22 μmol) were added and the reaction mixture was stirred at room temperature for 12 h. The crude mixture was diluted with 20 mL of dichloromethane, washed with water (3 × 20 mL), dried over MgSO₄, filtered through paper and concentrated. Final purification was achieved by column chromatography (SiO₂) using a gradient of hexanes/dichloromethane as eluent to afford the target compound as a greenish-purple solid in 59% yield (0.0067 g, 3.32 μmol). MALDI-TOF (positive mode, 1,4-diphenylbutadiene as matrix) 2074.69 (M + H)⁺, calculated 2073.8 for C₁₂₈H₁₀₅F₁₀N₁₅O₂.

![MALDI-TOF spectrum](image)

**Figure S34.** MALDI-TOF spectrum (positive mode, 1,4-diphenylbutadiene as matrix) of triad 1 (top and bottom right) and corresponding isotope simulation (bottom left) expected for C₁₂₈H₁₀₅F₁₀N₁₅O₂.
3.6 – References
