Supporting Information

Photoinduced Electron Transfer in Porphyrin-Oligothiophene-Fullerene Linked Triads by Excitation of Porphyrin Moiety

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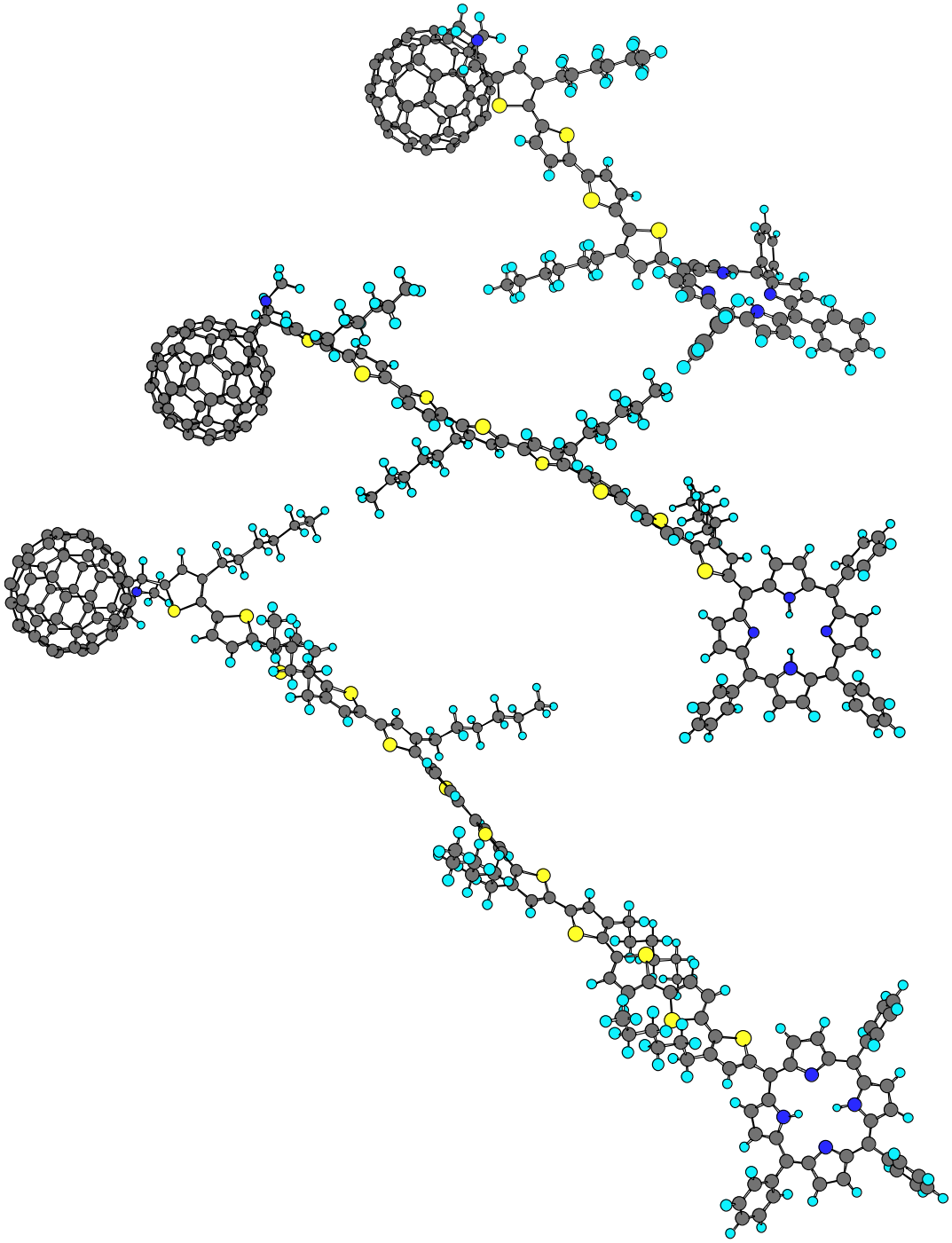

Figure S1. Optimized structures of H_2P-nT-C_{60} in a polar solvent (ε = 9.93). The structures were calculated by MM3 method modified for MacroModel.

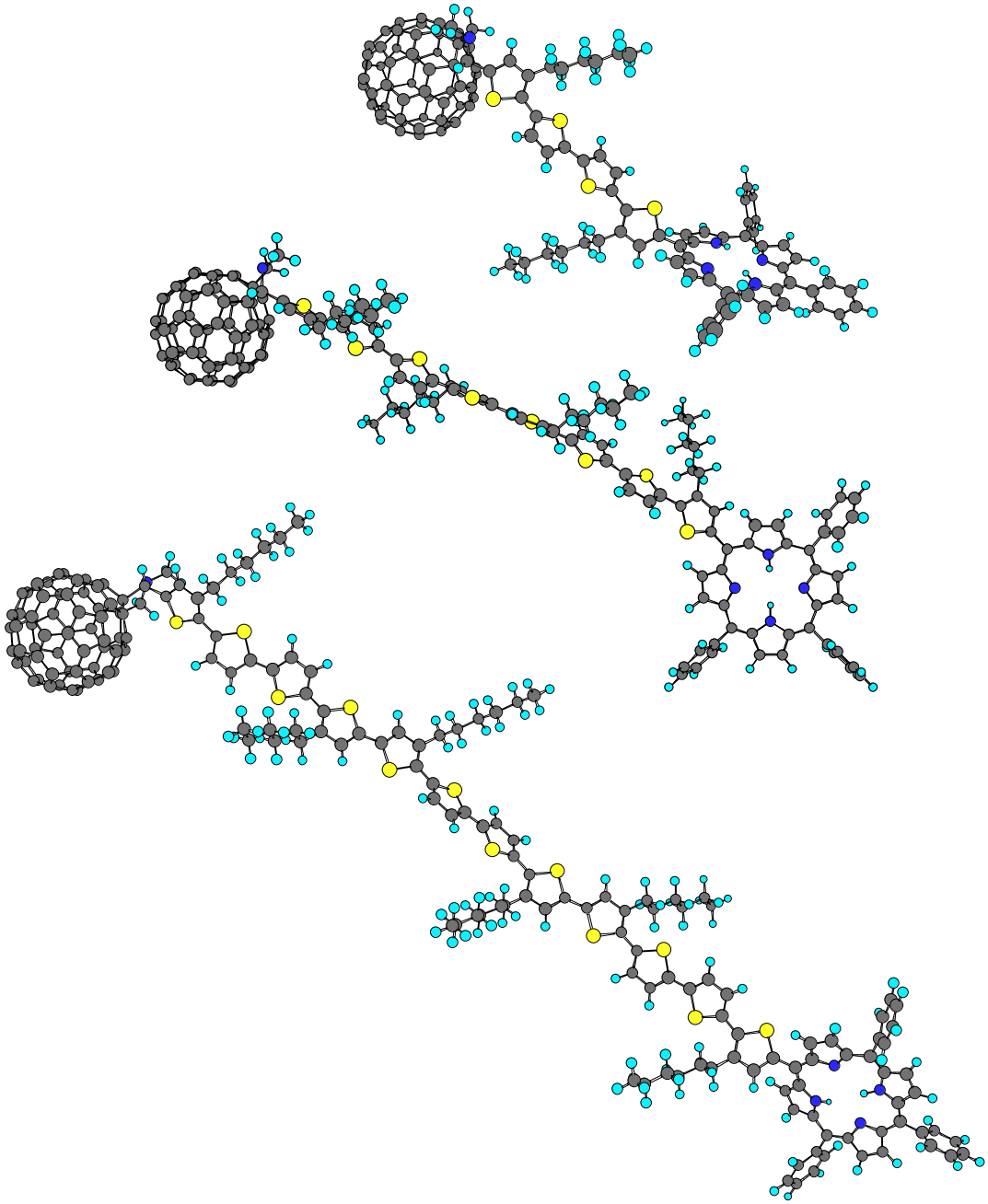

Figure S2. Optimized structures of H_2P-nT-C_{60} in vacuum condition. The structures were calculated by MM3 method modified for MacroModel.

Table S1. Free Energy Changes for Charge Separation (ΔG_{CS}) and Charge Recombination (ΔG_{CR}) for H_2P-nT-C_{60} calculated by equations in the footnote of Table

initial state	final state	solvent	$-\Delta G_{CS(P^*-C)}$ [a]/eV			$-\Delta G_{CR}$ [a]/eV		
			n = 4	n = 8	n = 12	n = 4	n = 8	n = 12
$^1H_2P^*$-nT-C_{60}	$H_2P^{\cdot+}$-nT-$C_{60}^{\cdot-}$	toluene	-0.76	-0.73	-0.65			
		PhCN	0.14	0.25	0.33			
		o-DCB	0.07	0.17	0.24			
$H_2P^{\cdot+}$-nT-$C_{60}^{\cdot-}$	H_2P-nT-C_{60}	toluene				2.65	2.62	2.54
		PhCN				1.75	1.64	1.56
		o-DCB				1.86	1.72	1.65
H_2P-nT$^{\cdot+}$-$C_{60}^{\cdot-}$	H_2P-nT-C_{60}	toluene				2.02	2.62	2.54
		PhCN				1.40	1.32	1.25
		o-DCB				1.52	1.42	1.35

[a] $-\Delta G_{CR(D-A)}$ indicates the free-energy change for the CS state, where D and A are referred to electron donor and acceptor, respectively. $-\Delta G_{CR(D-A)} = E_{ox} - E_{red} + \Delta G_S$; $-\Delta G_S = (e^2/(4\pi\varepsilon_0))[(1/(2R_+) + 1/(2R_-) - 1/R_{D-R})1/\varepsilon_S - (1/(2R_+) + 1/(2R_-))1/\varepsilon_R]$; R_+ = radius of cation; R_- = radius of anion; R_{D-R} = center-to-center distance between donor and acceptor; ε_S = dielectric constant of solvent used for photophysical studies; ε_R = dielectric constant of solvent used for measuring the redox potentials. [b] $-\Delta G_{CS(D-A)} = \Delta E_{0-0} - (-\Delta G_{CR(D-A)})$, ΔE_{0-0} is the singlet energy of H_2P.

Table S2. ΔG_{CS} and ΔG_{CR} between H_2P and nT calculated by equations in the footnote of Table S1

Materials		Toluene		*o*-DCB		PhCN	
initial state	final state	$-\Delta G_{CS}$ [eV]	$-\Delta G_{CR}$ [eV]	$-\Delta G_{CS}$ [eV]	$-\Delta G_{CR}$ [eV]	$-\Delta G_{CS}$ [eV]	$-\Delta G_{CR}$ [eV]
$^1H_2P^*$-4T	$H_2P^{\cdot+}$-4T$^{\cdot-}$	–0.64	2.53	–0.24	2.13	–0.17	2.06
$^1H_2P^*$-4T	$H_2P^{\cdot-}$-4T$^{\cdot+}$	–0.31	2.20	0.02	1.89	0.07	1.82
$^1H_2P^*$-8T	$H_2P^{\cdot+}$-8T$^{\cdot-}$	–0.55	2.44	–0.15	2.04	–0.09	1.98
$^1H_2P^*$-8T	$H_2P^{\cdot-}$-8T$^{\cdot+}$	–0.34	2.23	0.04	1.85	0.11	1.78
$^1H_2P^*$-12T	$H_2P^{\cdot+}$-12T$^{\cdot-}$	–0.49	2.38	–0.10	1.99	–0.03	1.92
$^1H_2P^*$-12T	$H_2P^{\cdot-}$-12T$^{\cdot+}$	–0.29	2.18	0.12	1.77	0.18	1.70
$^1H_2P^*$-4T-C_{60}	$H_2P^{\cdot+}$-4T$^{\cdot-}$-C_{60}	–0.65	2.54	–0.25	2.14	–0.18	2.07
$^1H_2P^*$-4T-C_{60}	$H_2P^{\cdot-}$-4T$^{\cdot+}$-C_{60}	–0.31	2.20	0.02	1.89	0.07	1.82
$^1H_2P^*$-8T-C_{60}	$H_2P^{\cdot+}$-8T$^{\cdot-}$-C_{60}	–0.62	2.51	–0.18	2.07	–0.12	2.01
$^1H_2P^*$-8T-C_{60}	$H_2P^{\cdot-}$-8T$^{\cdot+}$-C_{60}	–0.31	2.20	0.07	1.82	0.14	1.75
$^1H_2P^*$-12T-C_{60}	$H_2P^{\cdot+}$-12T$^{\cdot-}$-C_{60}	–0.50	2.39	–0.11	2.00	–0.04	1.93
$^1H_2P^*$-12T-C_{60}	$H_2P^{\cdot-}$-12T$^{\cdot+}$-C_{60}	–0.30	2.19	0.11	1.78	0.17	1.71

Table S3. Rate Constants and Quantum Yields for Charge Separation, Energy Transfer and Triplet Generating Rate Constants

Materials	$k_d/s^{-1,a}$	$\Phi_d{}^{,c}$	$k_{EN(P^*-C)}/s^{-1,b}$	$\Phi_{EN(P^*-C)}{}^{,c}$	$k_{CS(P^*-T)}/s^{-1,b}$	$\Phi_{CS(P^*-T)}{}^{,c}$	$k_{CS(P^*-C)}/s^{-1,b}$	$\Phi_{CS(P^*-C)}{}^{,c}$
				PhCN				
$^1H_2P^*$-4T-C_{60}	2.6×10^8	0.04	3.6×10^9	0.65	4.7×10^7	0.01	1.7×10^9	0.30
$^1H_2P^*$-8T-C_{60}	2.6×10^8	0.11	1.0×10^8	0.04	4.6×10^8	0.19	1.6×10^9	0.66
$^1H_2P^*$-12T-C_{60}	2.6×10^8	0.17	1.4×10^7	0.01	5.1×10^8	0.35	6.9×10^8	0.47
				o-DCB				
$^1H_2P^*$-4T-C_{60}	2.6×10^8	0.05	3.6×10^9	0.76	5.6×10^7	0.01	8.6×10^8	0.18
$^1H_2P^*$-8T-C_{60}	2.6×10^8	0.44	1.0×10^8	0.17	8.8×10^7	0.15	1.4×10^8	0.24
$^1H_2P^*$-12T-C_{60}	2.6×10^8	0.67	1.4×10^7	0.035	1.0×10^8	0.26	1.4×10^7	0.035

[a] $k_d = k_{ic} + k_{isc} + k_{fl}$, where the value of this sum is the singlet quenching rate for H_2P-nT in toluene. The k_{ic}, k_{isc} and k_{fl} indicate the rate constants for the intersystem crossing, internal conversion and fluorescence, respectively. [b] The rate constants were calculated using $\tau_F^{-1} = k_d + k_{EN} + k_{CS(P^*-T)} + k_{CS(P^*-C)}$. [c] $\Phi_X = k_X / \tau_F^{-1}$.

For the energy transfer (Figure S3).

According to the Förster theory,[S1] the energy-transfer rate constant, k_{EN}(theory), can be estimated using equation S1.

$$k_{EN}(\text{theory}) = 8.79 \times 10^{-25} (k_D \kappa^2 J/n^4 R_{DA(P\text{-}C)})^6) \qquad \text{(S1)}$$

Hereby, k_D is refereed to the radiative rate constant which is calculated from fluorescence quantum yield and the fluorescence lifetime of the dyad. The n is the reflective index of solvent and κ is the orientation factor. The spectral overlap integrations (J = 6.0 × 10^{-21}, 6.0 × 10^{-21} and 2.4 × 10^{-20} M^{-1} cm^3 for H_2P-4T-C_{60}, H_2P-8T-C_{60} and H_2P-12T-C_{60}, respectively) are estimated from the absorption spectrum of acceptor (ε(λ)) and the normalized emission spectrum of donor (F(λ)) as equation S2.

$$J = \int \varepsilon(\lambda) F(\lambda) \lambda^4 d\lambda \qquad \text{(S2)}$$

The k_{EN}(theory) values were estimated to be 1.4 × 10^{-9}, 2.7 × 10^{-7} and 2.2 × 10^{-6} s^{-1} for H_2P-4T-C_{60}, H_2P-8T-C_{60} and H_2P-12T-C_{60}, respectively. These values are in good agreement with the $k_{EN(P^*\text{-}C)}$ values evaluated experimentally, which indicates that the energy transfer obeys the Förster mechanism. The Förster radii were evaluated based on the model compounds as half distance between the H_2P moiety and the C_{60} moiety (12.8 Å, 20.2 Å and 27.9 Å for H_2P-4T-C_{60}, H_2P-8T-C_{60} and H_2P-12T-C_{60}, respectively).

This energy transfer is a reasonable process even in polar solvents, although the quantum yields drastically decrease with R.

Reference

S1 (a) Förster, T. *Natuwissenschaften* **1946,** *33*, 166-175. (b) Förster, T. *Ann. Phys.*

1948, *2*, 55 (c) Calvert, J. G.; Pitts, Jr, J. N.; *Photochemistry*; John Wiley & sons, New York, 1967, pp. 339–365.

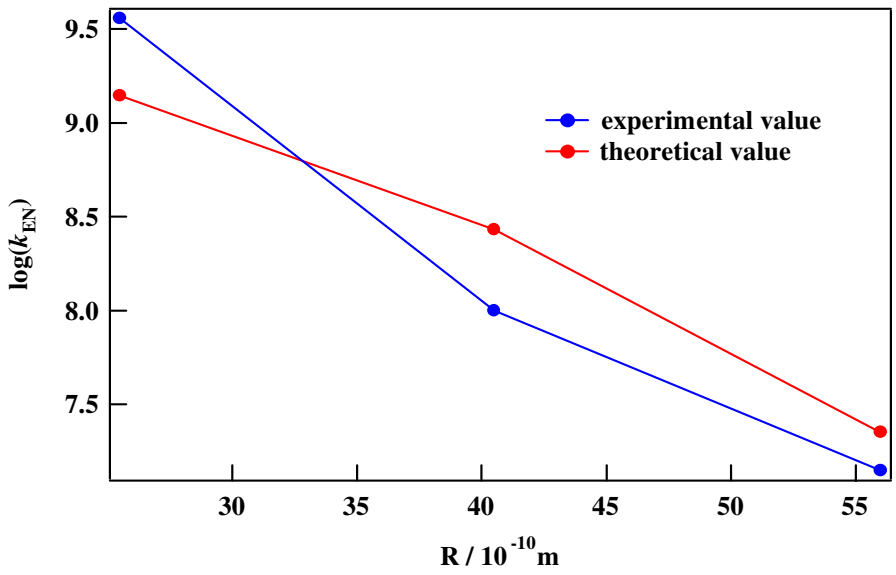

Figure S3. Donor-acceptor distance (*R*) dependence of the rate constants for EN. Plots of ln($k_{EN(P-C)}$) vs. R for H_2P-nT-C_{60}, where *R* is referred to distance of the energy donor (H_2P) to the energy acceptor (C_{60}).

Picosecond Transient Absorption Study of H_2P-nT Dyad.

Figure S4 shows the picosecond-transient absorption spectra of H_2TPP and H_2P-12T in PhCN. As seen in Figure S4, an absorption band appeared around 1000 nm at 100 ps after 388-nm laser irradiation, which is attributed to the $^1H_2TPP^*$ moiety. This characteristic absorption was also confirmed in H_2P-12T.

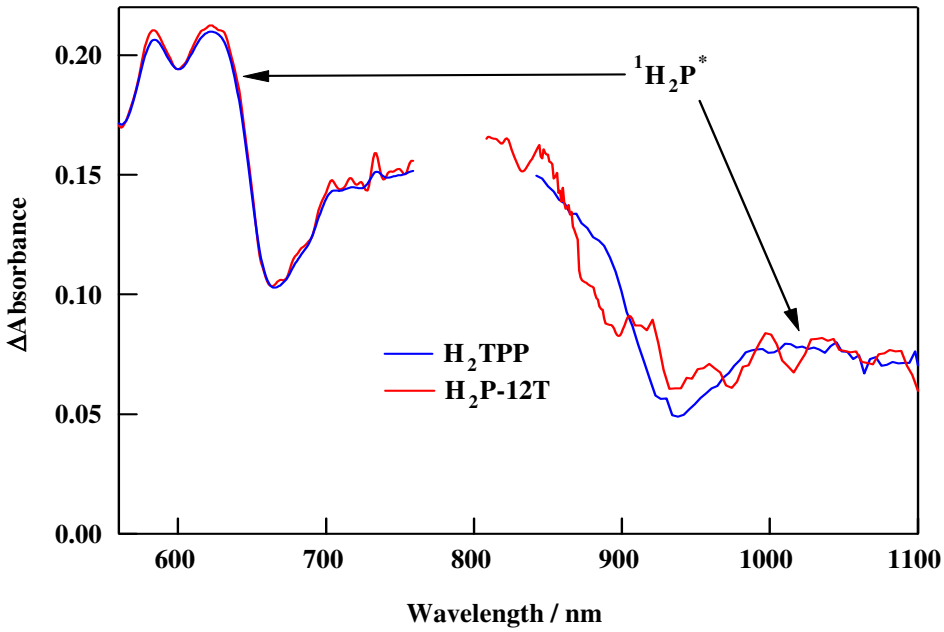

Figure S4. Picosecond transient absorption spectra of H_2TPP (2.0×10^{-4} M) and H_2P-12T (2.0×10^{-4} M) at 100 ps after 388-nm laser irradiation in PhCN.

For $H_2P^{\cdot-}$-$nT^{\cdot+}$-C_{60}.

In all triads, although the main initial CS process produced $H_2P^{\cdot+}$-nT-$C_{60}^{\cdot-}$, small amount of $H_2P^{\cdot-}$-$nT^{\cdot+}$-C_{60} is suggested to form from the fluorescence lifetime analysis, giving $k_{CS(P^*\text{-}T)} = (0.5 - 5) \times 10^8\ s^{-1}$ and $\Phi_{CS(P^*\text{-}T)} = 0.01 - 0.35$. If $H_2P^{\cdot-}$-$nT^{\cdot+}$-C_{60} contributes to Figure 9 in text, decay of the $nT^{\cdot+}$ moiety should show two-component decay. However, the observed decay of the $nT^{\cdot+}$ moiety seems to be a single

exponential; furthermore, the decay-rate constant for the $nT^{\cdot+}$ moiety is almost the same as that of the $C_{60}^{\cdot-}$ moiety. This observation suggests that the CR rate for $H_2P^{\cdot-}$-$nT^{\cdot+}$-C_{60} is much faster than the CR rate of H_2P-$nT^{\cdot+}$-$C_{60}^{\cdot-}$.