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Fullerene-terminated Dendritic Multiporphyrin Arrays: "Dendrimer Effects" on Photoinduced Charge Separation

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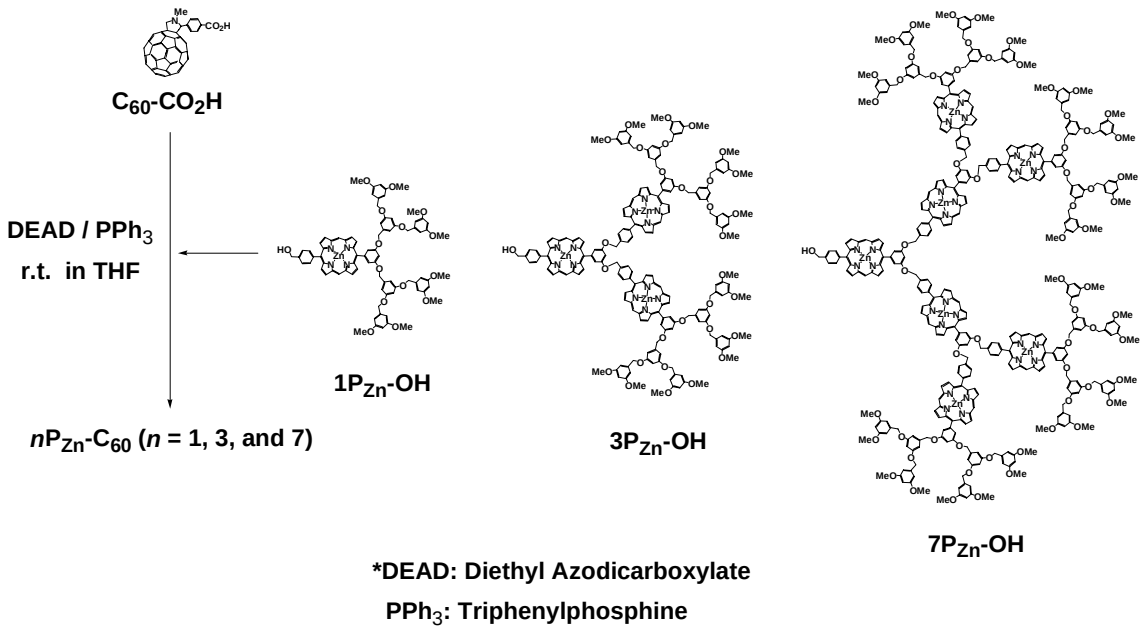
Chart S1. Scheme for the synthesis of C_{60}-terminated dendritic multiporphyrin arrays. Hydroxyl-terminated zinc porphyrin dendrons $1P_{Zn}$-OH, $3P_{Zn}$-OH, and $7P_{Zn}$-OH were prepared in a manner similar to that described in our previous reports,[1] and allowed to react with C_{60}-CO_2H[2] to give $1P_{Zn}$-C_{60}, $3P_{Zn}$-C_{60}, and $7P_{Zn}$-C_{60}, respectively.



[1] a) M. –S. Choi, T. Aida, I. Yamazaki, T. Yamazaki, *Angew. Chem.* **2001**, *113*, 3294; *Angew. Chem., Int. Ed.* **2001**, *40*, 3194; (b) M. –S. Choi, T. Aida, I. Yamazaki, T. Yamazaki, *Chem. Eur. J.* **2002**, *8*, 2667.

[2] T. Da Ros, M. Prato, F. Novello, M. Maggini, E. Banfi, *J. Org. Chem.* **1996**, *61*, 9070.

Synthesis and Characterization of $n\mathbf{P_{Zn}}$-$\mathbf{C_{60}}$ (n = 1, 3, and 7).

$\mathbf{1P_{Zn}}$-$\mathbf{C_{60}}$: To a dry THF (2 mL) solution of a mixture of $1P_{Zn}$-OH (16 mg, 11 μmol), C_{60}-CO_2H (10 mg, 11 μmol), and triphenylphosphine (11 μmol) was slowly added azodicarboxylic acid diethyl ester (11 μmol) with vigorous stirring at room temperature under N_2. After stirred for 3 h, the reaction mixture was subjected to flash column chromatography on silica gel with CH_2Cl_2 as eluent, where the second fraction was collected and evaporated to dryness. The residue was subjected to preparative SEC for further purification, and then freeze-dried from benzene after precipitation from hexane, affording $1P_{Zn}$-C_{60} as red powder in 55% yield (14 mg). IR (KBr): 2927, 1800, 1732, 1717, 1597, 1540, 1507, 1457, 1429, 1374, 1260, 1205, 1156, 1104, 1056, 831, 668 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 2.72 (s, 3H; C_{60}-NCH_3), 3.66 (s, 24H; $Ar(OCH_3)_2$), 3.84 (d, J = 9.4 Hz, 1H; C_{60}-CH_2N), 4.61 (d, J = 8.9 Hz, 1H; C_{60}-CH_2N), 4.62 (s, 1H; C_{60}-CHN), 4.89 (s, 8H; outer *dendron*-CH_2O), 5.14 (s, 4H; inner *dendron*-CH_2O), 5.61 (s, 2H; CH_2 between P_{Zn} and C_{60}), 6.28 (t, J = 2.1 Hz, 8H; *p*-H in outer *dendron*-C_6H_3), 6.46 (d, J = 2.1 Hz, 16H; *o*-H in outer *dendron*-C_6H_3), 6.58 (d, J = 2.1 Hz, 4H; *p*-H in inner *dendron*-C_6H_3), 6.73 (d, J = 2.1 Hz, 8H; *o*-H in inner *dendron*-C_6H_3), 7.07 (s, 1H; *p*-H in P_{Zn}-C_6H_3), 7.50 (d, J = 2.1 Hz, 2H; *o*-H in P_{Zn}-C_6H_3), 7.83 (d, J = 8.1 Hz, 4H, *m*-H in P_{Zn}-C_6H_4 and C_{60}-C_6H_4), 8.20 (t, J = 8.1 Hz, 4H; *o*-H in P_{Zn}-C_6H_4 and C_{60}-C_6H_4), 9.11 (m, 4H; pyrrole-β-H in P_{Zn}), 9.35 (m, 4H; pyrrole-β-H in P_{Zn}), 10.21 (s, 2H; *meso*-H in P_{Zn}); UV-vis λ_{max} (log ε) (THF): 413.5 (5.72), 543.9 (4.10), 580.9 (2.93), 310.5 (4.61).

$\mathbf{3P_{Zn}}$-$\mathbf{C_{60}}$: To a dry THF (1 mL) solution of a mixture of $3P_{Zn}$-OH (19 mg, 5.5 μmol), C_{60}-CO_2H (5 mg, 5.5 μmol), and triphenylphosphine (5.5 μmol) was slowly added azodicarboxylic acid diethyl ester (5.5 μmol) with vigorous stirring at room temperature under N_2. After stirred for 12 h, the reaction mixture was treated in a manner similar to that

for the preparation of $1P_{Zn}$-C_{60}, affording $3P_{Zn}$-C_{60} as red powder in 63% yield (15 mg). IR (KBr): 2925, 1598, 1455, 1428, 1371, 1321, 1203, 1154, 1058, 995, 835, 696 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 2.25 (br s, 3H; C_{60}-NCH_3), 3.46 (s, 51H; $Ar(OCH_3)_2$, C_{60}-CH_2N, and C_{60}-CHN), 4.66 (s, 16H; outer *dendron*-CH_2O), 4.88 (s, 4H; P_{Zn}-CH_2O-P_{Zn}), 4.99 (s, 8H; inner *dendron*-CH_2O), 5.10 (s, 2H; CH_2 between P_{Zn} and C_{60}), 6.06 (s, 8H; *p*-H in outer *dendron*-C_6H_3), 6.24 (s, 16H; *o*-H in outer *dendron*-C_6H_3), 6.39 (s, 4H; *p*-H in inner *dendron*-C_6H_3), 6.56 (s, 8H; *o*-H in inner *dendron*-C_6H_3), 6.96 (s, 3H; *p*-H in P_{Zn}-C_6H_3), 6.56–8.21 (m, 18H; *o*-H in P_{Zn}-C_6H_3 and *o*, *m*-H in P_{Zn}-C_6H_4), 8.52–9.34 (m, 24H; pyrrole-β-H in P_{Zn}), 9.80 (s, 6H; *meso*-H in P_{Zn}); UV-vis λ_{max} (log ε) (THF): 416.4 (5.98), 544.5 (4.52), 581.5 (3.15), 310.5 (4.52).

$7P_{Zn}$-C_{60}: To a dry THF (0.5 mL) solution of a mixture of $7P_{Zn}$-OH (24 mg, 3.3 μmol), C_{60}-CO_2H (3 mg, 3.3 μmol), and triphenylphosphine (3.3 μmol) was slowly added azodicarboxylic acid diethyl ester (3.3 μmol) with vigorous stirring at room temperature under N_2. After stirred for 12 h, the reaction mixture was treated in a manner similar to that for the preparation of $1P_{Zn}$-C_{60}, affording $7P_{Zn}$-C_{60} as red powder in 37% yield (10 mg). IR (KBr): 2924, 1596, 1457, 1428, 1371, 1321, 1295, 1203, 1154, 1058, 993, 833, 784 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 3.46 (s, 102H; $Ar(OCH_3)_2$, C_{60}-NCH_3, C_{60}-CH_2N, and C_{60}-CHN), 4.24–5.24 (m, 62H; CH_2 in *dendron*-CH_2O, P_{Zn}-CH_2O-P_{Zn}, and CH_2 between P_{Zn} and C_{60}), 5.63–6.67 (m, 72H; *dendron*-ArH), 6.93 (br s, 3H; *p*-H in P_{Zn}-C_6H_3), 7.33–8.30 (m, 30H; *o*, *m*-H in P_{Zn}-C_6H_4 and *o*-H in P_{Zn}-C_6H_3), 8.96 (br s, 56H; pyrrole-β-H in P_{Zn}), 9.65 (br s, 14H; *meso*-H in P_{Zn}); UV-vis λ_{max} (log ε) (THF): 416.9 (6.23), 544.5 (4.97), 579.6 (3.96), 310.9 (5.21).

Figure S1. MALDI-TOF-MS spectra of (A) $1P_{Zn}$-C_{60} ($[M]^+$; calcd. 2311, obsd. 2313), (B) $3P_{Zn}$-C_{60} ($[M]^+$; calcd. 4296, obsd. 4298), and (C) $7P_{Zn}$-C_{60} ($[M]^+$; calcd. 8265, obsd. 8266 (matrix; dithranol).

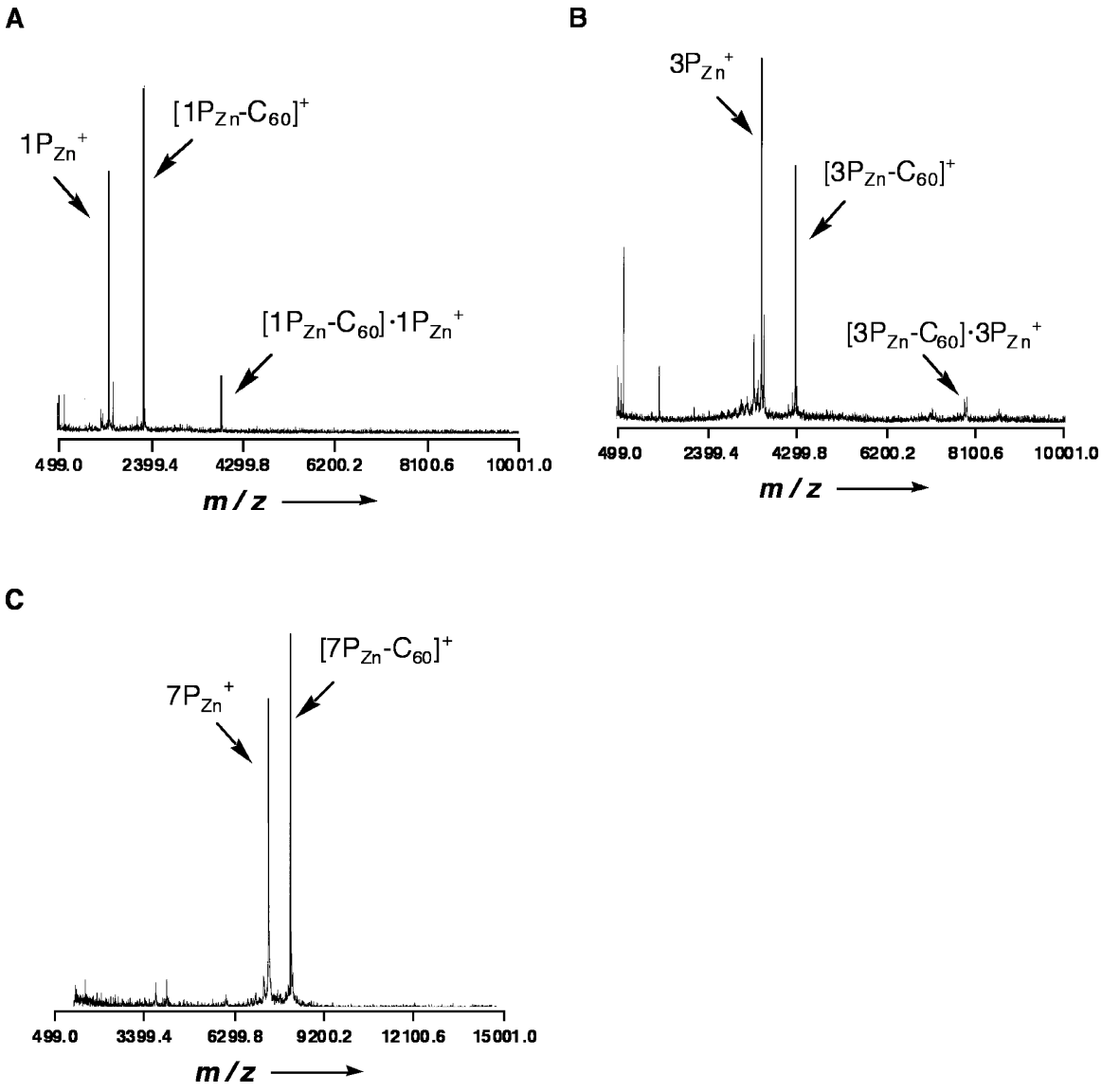


Figure S2. Steady-state absorption spectra in PhCN of nP$_{Zn}$-C$_{60}$ [n = 1 (A), 3 (B), and 7 (C)], together with nP$_{Zn}$-OH (n = 1, 3, and 7) and C$_{60}$-CO$_2$H as references. Concentrations of substances are 2.18 x 10^{-6}, 1.10 x 10^{-6}, and 0.72 x 10^{-6} M for (A), (B), and (C), respectively. The spectra in insets show an absorption band of C$_{60}$ at 700 nm.

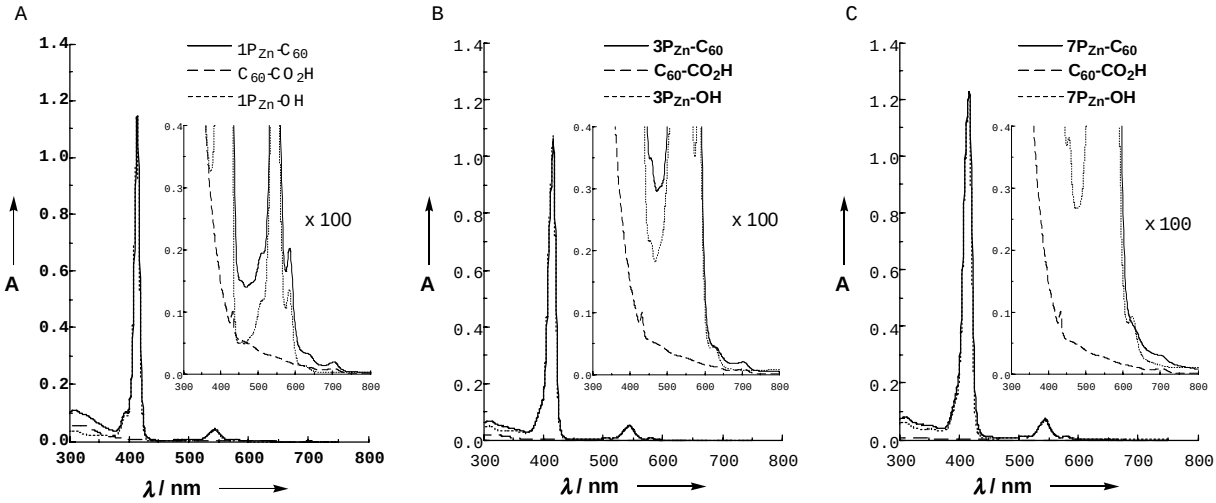


Figure S3. Steady-state fluorescence spectra, upon photoexcitation at 544 nm (abs = 0.07), of nP$_{Zn}$-C$_{60}$ and nP$_{Zn}$-OH [n = 1 (A), 3 (B), and 7 (C)] in PhCN at 22 °C. Degrees of fluorescence quenching were evaluated by quantitative comparison of the spectra of nP$_{Zn}$-C$_{60}$ and nP$_{Zn}$-OH.

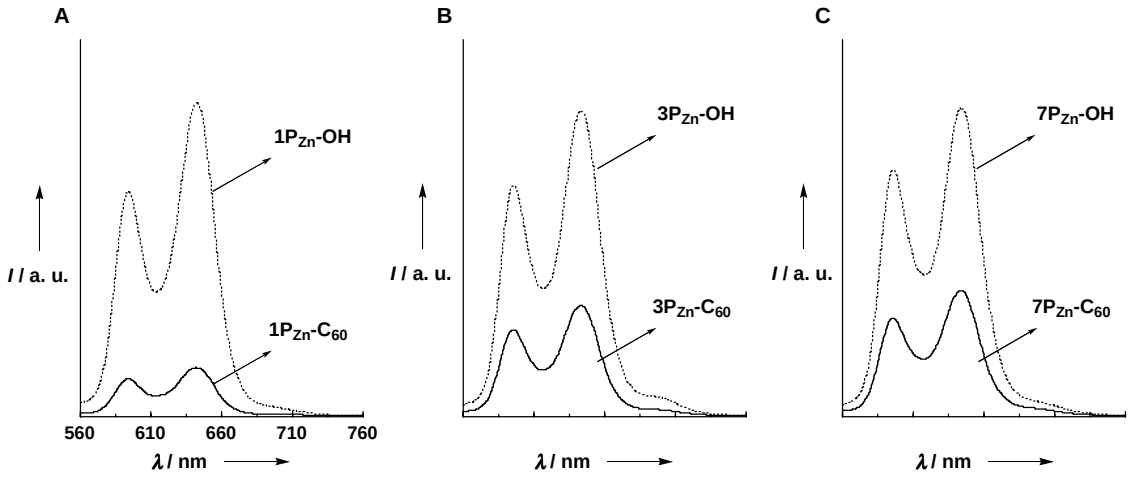


Figure S4. Picosecond transient absorption spectra in PhCN, upon photoexcitation of $7P_{Zn}$-C_{60} at 388 nm with a 150 fs laser pulse, obtained at delay times of 50 and 400 ps.

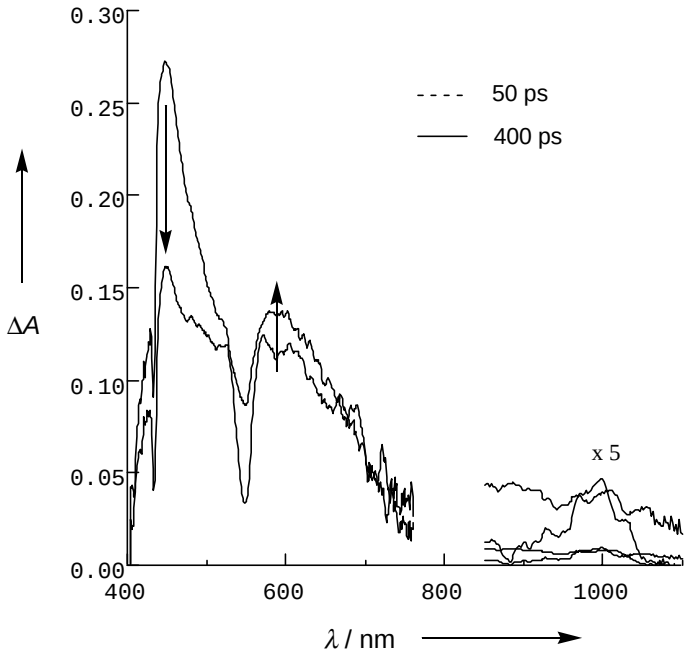


Figure S5. Nanosecond transient absorption spectra in PhCN, upon photoexcitation of $7P_{Zn}$-C_{60} at 532 nm with a 6 ns laser pulse, obtained at delay times of 0.1 and 1 μs.

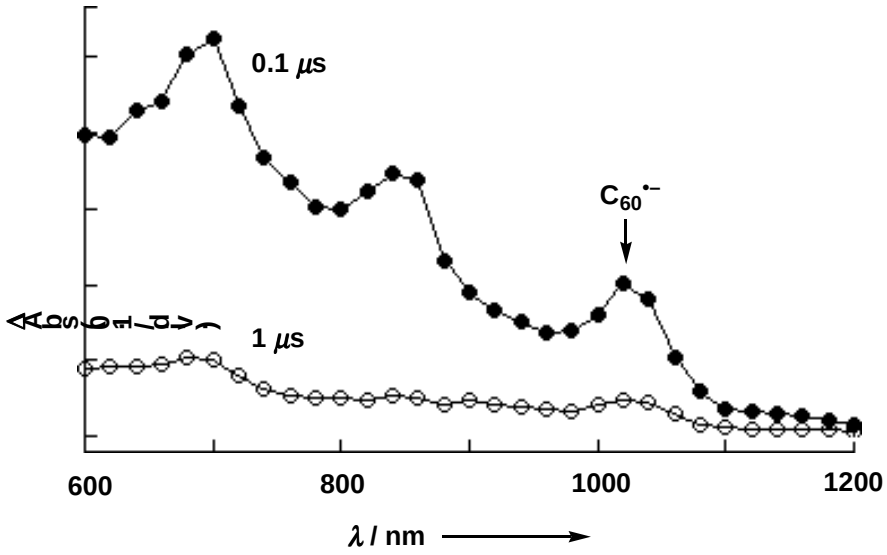


Figure S6. (A) A kinetic model and equations for the simulation of charge recombination process in nP$_{Zn}$-C$_{60}$ (n = 1, 3, and 7), with a hypothesis that the system involves a hole-hopping process. (B) Results of single or dual–exponential curve fitting and the resulting decay rates of cation radical (k_{sim}). With respect to the parameters for the simulation, the rate constant of charge recombination (k_{CR} = 2.9 x 10^6 s^{-1}), observed for 1P$_{Zn}$-C$_{60}$, was used, while a hypothetical value, larger [1.0 x 10^8 s^{-1}; (10 ns)$^{-1}$] or smaller [1.0 x 10^6 s^{-1}; (1000 ns)$^{-1}$] than k_{CR}, was used as the rate constant of hole hopping (k_h).

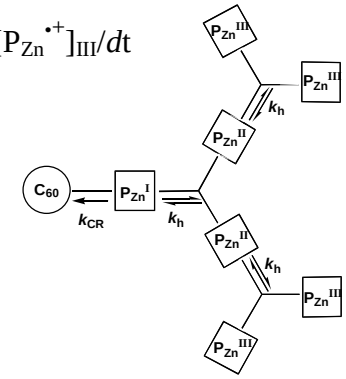
(A)

$$-d[P_{Zn}^{\bullet+}\text{-}C_{60}^{\bullet-}]_{total}/dt = -d[P_{Zn}^{\bullet+}]_I/dt - 2d[P_{Zn}^{\bullet+}]_{II}/dt - 4d[P_{Zn}^{\bullet+}]_{III}/dt$$

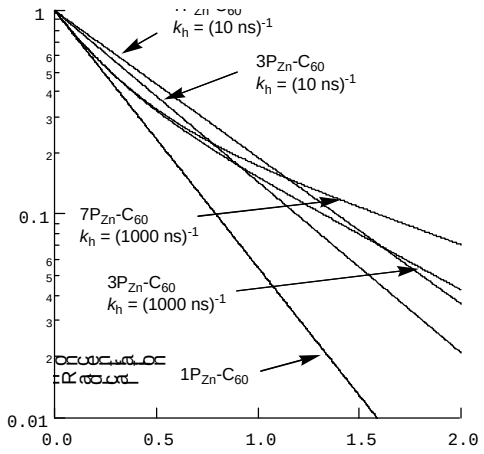
$$-d[P_{Zn}^{\bullet+}\text{-}C_{60}^{\bullet-}]_I/dt = k_{CR}[P_{Zn}^{\bullet+}]_I + k_h[P_{Zn}^{\bullet+}]_I - 2k_h[P_{Zn}^{\bullet+}]_{II}$$

$$-2d[P_{Zn}^{\bullet+}]_{II}/dt = -k_h[P_{Zn}^{\bullet+}]_I + 2k_h[P_{Zn}^{\bullet+}]_{II} - 4k_h[P_{Zn}^{\bullet+}]_{III}$$

$$-4d[P_{Zn}^{\bullet+}]_{III}/dt = -2k_h[P_{Zn}^{\bullet+}]_{I\,I} + 4k_h[P_{Zn}^{\bullet+}]_{III}.$$



(B)



	k_h / s^{-1}	k_{sim} / s^{-1}
1P$_{Zn}$-C$_{60}$	1.0 x 10^8	**2.9 x 10^6**
	1.0 x 10^6	2.9 x 10^6
3P$_{Zn}$-C$_{60}$	1.0 x 10^8	**1.93 x 10^6**
	1.0 x 10^6	4.65 x 10^6 (48.8%)
		1.25 x 10^6 (51.2%)
7P$_{Zn}$-C$_{60}$	1.0 x 10^8	**1.66 x 10^6**
	1.0 x 10^6	4.17 x 10^6 (60.5%)
		9.02 x 10^5 (39.5%)

When the value k_h (hole hopping rate constant) is larger than that of k_{CR} (charge recombination rate constant) for vicinal $P_{Zn}^{\bullet+}$-$C_{60}^{\bullet-}$, substantially single exponential decay kinetics would be expected. Here, the slope of the first order plots decreases with increasing the generation number of the dendritic wedge. The decay curves simulated with a rapid hole-hopping process agreed nicely with those observed experimentally, although they showed certain deviations in a latter stage due to the spectral contamination with slow-decaying triplet excited states. On the other hand, if the value k_{CR} for vicinal $P_{Zn}^{\bullet+}$-$C_{60}^{\bullet-}$ is larger than that of k_h, multi-exponential decay kinetics would be anticipated. Here, the initial decay characteristics would not change with the generation number of the dendritic wedge. Obviously, the decay curves simulated with a slow hole-hopping process did not agree with those experimentally observed.

Figure S7. Arrhenius plots for charge recombination process of $nP_{Zn}^{\bullet+}$-$C_{60}^{\bullet-}$ (1, 3, and 7) in PhCN under argon.

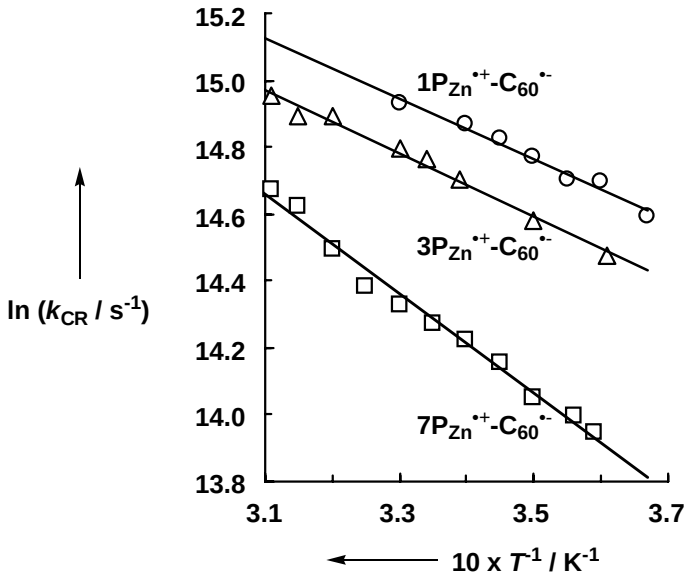


Table S1. Fluorescence lifetimes (τ_{FL}), fluorescence decay rate constants (k_{CS})[a], and charge separation quantum yields (Φ_{CS})[b] of $1P_{Zn}$-C_{60}, $3P_{Zn}$-C_{60}, and $7P_{Zn}$-C_{60} in PhCN. The accuracies of τ_{FL} values were estimated to be ±3.3 ps for $1P_{Zn}$-C_{60}, ±2.3 ps for $3P_{Zn}$-C_{60}, and ±4.6 ps for $1P_{Zn}$-C_{60}.

Compound	τ_{FL} / ns (%)	χ	τ_{FL}^{av} / ns [c]	k_{CS} / s^{-1}	Φ_{CS}
$1P_{Zn}$-C_{60}	0.38 (93%), 2.3 (7%)	0.99	0.51	1.55×10^9	0.80
$3P_{Zn}$-C_{60}	0.40 (25%), 1.5 (75%)	0.90	1.23	0.40×10^9	0.49
$7P_{Zn}$-C_{60}	0.41 (22%), 1.4 (78%)	1.08	1.18	0.43×10^9	0.51

[a] $k_{CS} = (1/\tau_{FL}^{av})_{sample} - (1/\tau_{FL})_{ref}$, where $(\tau_{FL})_{ref}$ = 2.4 ns for $n$$P_{Zn}$-OH ($n$ = 1, 3, and 7) in PhCN.

[b] $\Phi_{CS} = [(1/\tau_{FL}^{av})_{sample} - (1/\tau_{FL})_{ref}] / (1/\tau_{FL}^{av})_{sample}$

[c] τ_{FL}^{av} values represent average fluorescence lifetimes of the P_{Zn} units.