Supporting Information

For

Formation of a Hybrid Compound Composed of a Saddle-Distorted Tin(IV)-Porphyrin and a Keggin-Type Heteropolyoxometalate to Undergo Intramolecular Photoinduced Electron Transfer

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X-ray Crystallography. X-ray crystallography on 1 and 2: Refinements on F^2 were performed for all reflections. The weighted R factor (R_w) and goodness of fit (S) are based on F^2, and the conventional R factor (R) on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ was used only for calculating R factors (gt) etc. and was not relevant to the choice of reflections for refinement. R factors based on F^2 are statistically about twice as large as those based on F, and R factors based on all data are even larger. Since the methanol molecule in **2** was disordered, its carbon atom was refined isotropically with occupancies of 0.5. Crystallographic data are summarized in Table S1.

Table S1. X-ray Crystallographic Data for **1** and **2**

	1	2
Formula	$C_{97}H_{69}Cl_5N_4O_4Sn$	$C_{100}H_{80}N_4O_8Sn$
F. W.	1650.59	1584.44
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P–1$
T, K	183	180
a, Å	25.106(7)	11.4345(5)
b, Å	16.854(4)	12.6971(7)
c, Å	37.347(9)	14.1793(8)
α, deg	–	103.943(2)
β, deg	92.653(3)	101.911(2)
γ, deg	–	93.635(2)
V, Å^3	15786(7)	1941.0(2)
Z	8	1
No. of reflections	104400	15908
No. of observations	28696	8777
No. of parameters	2016	511
$R1^a$ $(I > 2.0\sigma(I))$	0.087	0.039
R_w^b (all data)	0.182	0.097
GOF	1.096	1.080

$^aR1 = \sum \|F_o\| – \|F_c\| / \sum |F_o|$.

$^bR_w = [\sum (w(F_o^2 – F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}$.

Figure S1. The displacement of each atom from the least-squares mean plane of 24 atoms of the TMPP(Ph)$_8{}^{2-}$ moiety in (a) **1** and (b) **2** (in unit of 0.01 Å).
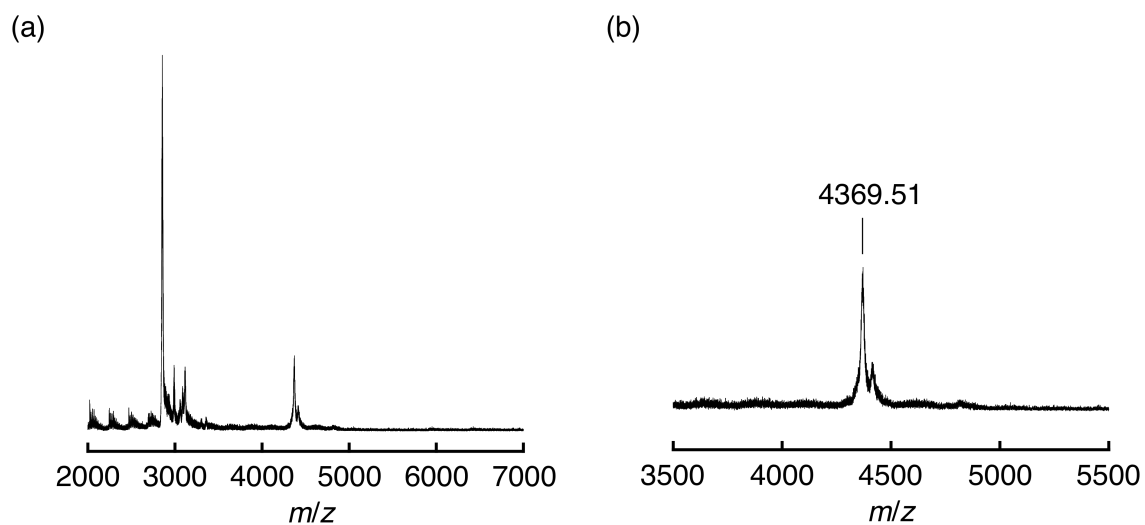
Figure S2. Full range of MALDI-TOF-MS spectrum of conglomerate made of **2** and **3** (m/z = 4369.51) in CH_2Cl_2 (linear negative mode, matrix = α-cyano-4-hydroxycinnamic acid (CHCA)).
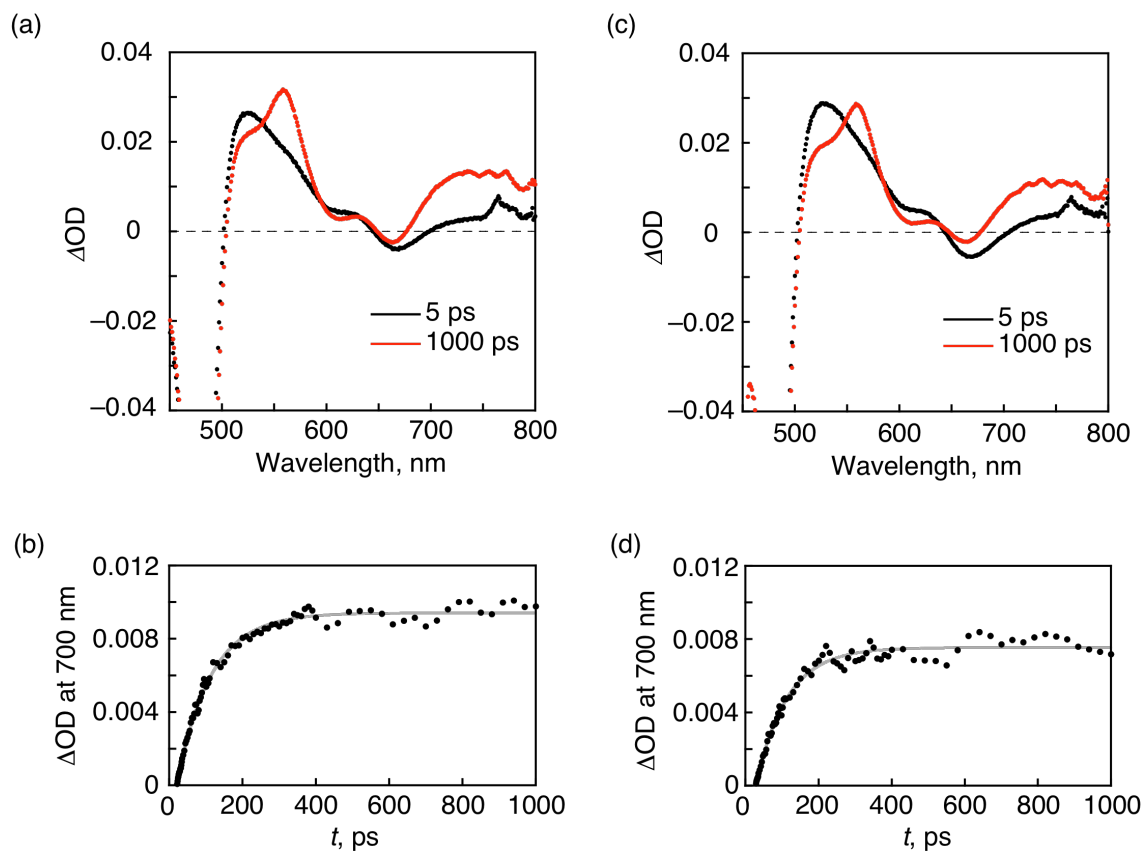
Figure S3. (a) Femtosecond transient absorption spectra of **1** (4.0×10^{-5} M) at 5 (black) and 1000 ps (red) after laser excitation at 430 nm and (b) time profile of ΔOD at 700 nm. (c) Femtosecond transient absorption spectra of **1** (4.0×10^{-5} M) with **3** (1.2×10^{-2} M) at 5 (black) and 1000 ps (red) after laser excitation at 430 nm and (b) time profile of ΔOD at 700 nm.