Supplementary Information

Novel fullerene-porphyrin-fullerene triad linked by metal axial coordination: Synthesis, X-ray crystal structure, and spectroscopic characterizations of *trans*-bis([60]fullerenoacetato)tin(IV) porphyrin

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Synthesis. To a suspension of [60]fullerenoacetic acid **2** (54.4 mg, 0.070 mmol) in CH$_2$Cl$_2$/THF (1:2 v/v, 20 mL), the solution of *trans*-dihydroxo[*meso*-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]tin(IV) **1** (40 mg, 0.032 mmol) in CH$_2$Cl$_2$ (4 mL) was added. The reaction mixture was stirred for 24 hr at room temperature, after which the solvent was evaporated to dryness under reduced pressure. The residue was dissolved in CHCl$_3$ and filtered through a Celite pad. After evaporating the filtrate, the product was recrystallized from CHCl$_3$/CH$_3$CN to afford crystalline solid of *trans*-bis([60]fullerenoacetato)[*meso*-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]tin(IV) **3** (75.4 mg, 86%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 9.32 (s, 8H, β-pyrrolic H), 8.09 (s, 8H, *o*-Ph), 7.82 (s, 4H, *p*-Ph), 2.32 (s, 2H), 1.50 (s, 72H, *t*-butyl). UV-vis (toluene, nm): λ_{max}(log ε) 324(4.62), 430(4.93), 520(3.51), 564(3.82), 604(3.68). IR (KBr, cm^{-1}): ν_{CO} 1667. MS (MALDI-TOF): *m/z* 1956.8 [(*M* – C$_{60}$CHCOO)$^+$ requires 1956.64]. Anal. Calcd. for C$_{200}$H$_{94}$N$_4$O$_4$Sn·3H$_2$O: C, 86.11; H, 3.61; N, 2.01. Found: C, 86.18; H, 3.63; N, 1.80.

X-ray crystal structure determination. Single crystals of **3** suitable for X-ray crystallography were grown from the slow diffusion of CH$_3$CN into the 1:1 CHCl$_3$/CH$_2$Cl$_2$ solution of **3**. A dark violet plate crystal covered with Paraton-N hydrocarbon oil on a glass fiber was mounted on a Siemens SMART diffractometer equipped with a graphite monochromated Mo Kα (λ = 0.71073 Å) radiation source and a CCD detector. Three sets of fifteen frames of two-dimensional diffraction images were collected and processed to deduce a cell parameter and orientation matrix. Data collection was performed at 100(2) K. A total of 1265 frames were collected with a scan width of 0.3° in ω with an exposure time of 10 s/frame. The frames were integrated with the SAINT software package with a narrow frame algorithm. The integration of the data using monoclinic unit cell yielded a total of 46436 reflections of which 18033 were independent and 9592 were greater than 2σ(*I*). The final cell constants were refined with 7069 reflections with 2.18° $\leq$ θ $\leq$ 25.79°. Analysis of the data showed negligible decay during data collection. Semi-empirical absorption correction was applied by using SADABS. Crystallographic data and additional details of

data collection and refinement are summarized in Table S1 for **3**.   The structure was solved by direct methods and the subsequent difference Fourier syntheses and refined with the SHELX-TL software package, using the monoclinic space group *C*2/*c* with *Z* = 4.   The porphyrin ring sits on the inversion center and the position of the central metal ion, Sn(1) is coincident with Wyckoff position *a*.   One of the four unique tertiary butyl groups in the porphyrin was disordered over two sites (C(17) and C(17')) with a half-occupancy factor respectively.   There were $2.5CHCl_3$, $1CH_2Cl_2$, and 1.5 water molecules in the asymmetric unit as the co-crystallized solvents.   A $CHCl_3$ (C(3S), Cl(7), Cl(8)) sit on the special position with site symmetry 2 at the Wyckoff position *e*.   The carbon atom of the CH_2Cl_2 was disordered over two sites (C(4S) and C(4S')).   An isolated peak close to the disordered butyl group was assigned as O(2W).   All non-hydrogen atoms were refined anisotropiclly.   All hydrogen atoms except for the lattice water molecules, O(1W) and O(2W) were included in calculated positions with isotropic thermal parameters 1.2 times those of attached atoms. Final full matrix least-squares refinement on F^2 converged to $R1 = 0.1052$ and $wR2 = 0.2785$ ($I > 2\sigma(I)$) with GOF = 1.052.

Sheldrick, G. M. SHELX-TL, v. 5.10; Bruker Analytical X-ray, Madison, WI, 1997.

Sheldrick, G. M. SADABS.   Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen: Gottingen, Germany, 1996.

Saint Plus, v. 6.01, Bruker Analytical X-ray, Madison, WI, 1999.

Time-resolved fluorescence lifetime measurements. A picosecond time-correlated single photon counting (TCSPC) system was employed for time-resolved fluorescence and fluorescence anisotropy decay measurements.[1] The system was consisted of a self-mode-locked and cavity-dumped femtosecond Ti:sappahire laser pumped by a cw Nd-YAG laser (Spectra-Physics, Millennia). The full width at half maximum of the instrument response function was 53 ps. The fluorescence decays were measured with magic angle emission polarization.

Femtosecond transient absorption measurements. The dual-beam femtosecond time-resolved transient absorption spectrometer consisted of a self-mode-locked femtosecond Ti:sapphire laser (Coherent, MIRA), a Ti:sapphire regenerative amplifier (Clark MXR, CPA-1000) pumped by a Q-switched Nd:YAG laser (ORC-1000), a pulse stretcher/compressor, OPG-OPA system, and an optical detection system.[2] A femtosecond Ti:sapphire oscillator pumped by a cw Nd:YVO4 laser (Coherent, Verdi) produced a train of 60 fs mode-locked pulses with an averaged power of 600 mW at 800 nm. The seed pulses from the oscillator were stretched (~250 ps) and sent to a Ti:sapphire regenerative amplifier pumped by a Q-switched Nd:YAG laser operating at 1 kHz. The femtosecond seed pulses and Nd:YAG laser pulses were synchronized by adjusting an electronic delay between Ti:sapphire oscillator and Nd:YAG laser. Then, the amplified pulse train inside the Ti:sapphire regenerative amplifier cavity was cavity-dumped by using Q-switching technique, and about 30 000-fold amplification at 1 kHz was obtained. After recompression, the amplified pulses were color-tuned by optical parametric generation and optical parametric amplification (OPG-OPA) technique. The resulting laser pulses had a pulse width of ~150 fs and an average power of 5-30 mW at 1 kHz repetition rate in the range 550-700 nm. The pump beam was focused to a 1 mm diameter spot, and laser fluence was adjusted less than ~1.0 mJ cm^{-2} by using a

variable neutral-density filter. The fundamental beam remaining in the OPG-OPA system was focused onto a flowing water cell to generate white light continuum, which was again split into two parts. The one part of the white light continuum was overlapped with the pump beam at the sample to probe the transient, while the other part of the beam was passed through the sample without overlapping the pump beam. The time delay between pump and probe beams was controlled by making the pump beam travel along a variable optical delay. The white continuum beams after sample were sent to a 15 cm focal length spectrograph (Acton Research) through each optical fiber and then detected by the dual 512 channel photodiode arrays (Princeton Instruments). The intensity of the white light of each 512 channel photodiode array was processed to calculate the absorption difference spectrum at the desired time delay between pump and probe pulses. To obtain the time-resolved transient absorption difference signal at the specific wavelength, the monitoring wavelength was selected by using an interference filter. By chopping the pump pulses at 43 Hz, the modulated probe pulses as well as the reference pulses were detected by two separate photodiodes. The output current was amplified with a homemade fast preamplifier, and then the resultant voltage signals of the probe pulses were gated and processed by a boxcar averager. The resultant modulated signal was measured by a lock-in amplifier and then fed into a personal computer for further signal processing.

References

1. I.-W. Hwang, H. S. Cho, D. H. Jeong, D. Kim, A. Tsuda, T. Nakamura and A. Osuka, *J. Phys. Chem. B*, 2003, **107**, 9977.

2. H. S. Cho, N. W. Song, Y. H. Kim, S. C. Jeoung, S. Hahn, D. Kim, S. K. Kim, N. Yoshida and A. Osuka, *J. Phys. Chem. A*, 2000, **104**, 3287.

Table S1. Crystal data and structure refinement for **3**.

Empirical formula	$C_{207}H_{109}N_4O_7Cl_{19}Sn$
	$C_{200}H_{94}N_4O_4Sn \cdot 5CHCl_3 \cdot 2CH_2Cl_2 \cdot 3H_2O$
Formula weight	3556.22
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 40.6082(17)$ Å $\quad \alpha = 90°$
	$b = 13.5086(6)$ Å $\quad \beta = 106.771(1)°$
	$c = 29.0086(12)$ Å $\quad \gamma = 90°$
Volume	$15236.1(11)$ Å^3
Z	4
Density (calculated)	1.550 mg/m^3
Absorption coefficient	0.571 mm^{-1}
$F(000)$	7232
Crystal size	0.30 x 0.30 x 0.05 mm^3
Theta range for data collection	1.05 to 28.32°.
Index ranges	$-37 \leq h \leq 54, -17 \leq k \leq 17, -38 \leq l \leq 31$
Reflections collected	46436
Independent reflections	18033 [R(int) = 0.0809]
Completeness to theta = 28.32°	95.0 %
Absorption correction	SADABS
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	18033 / 6 / 1120
Goodness-of-fit on F^2	1.052
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.1052, wR2 = 0.2785$
R indices (all data)	$R1 = 0.1906, wR2 = 0.3423$
Extinction coefficient	0.00124(15)
Largest diff. peak and hole	2.307 and -1.831 e.Å^{-3}

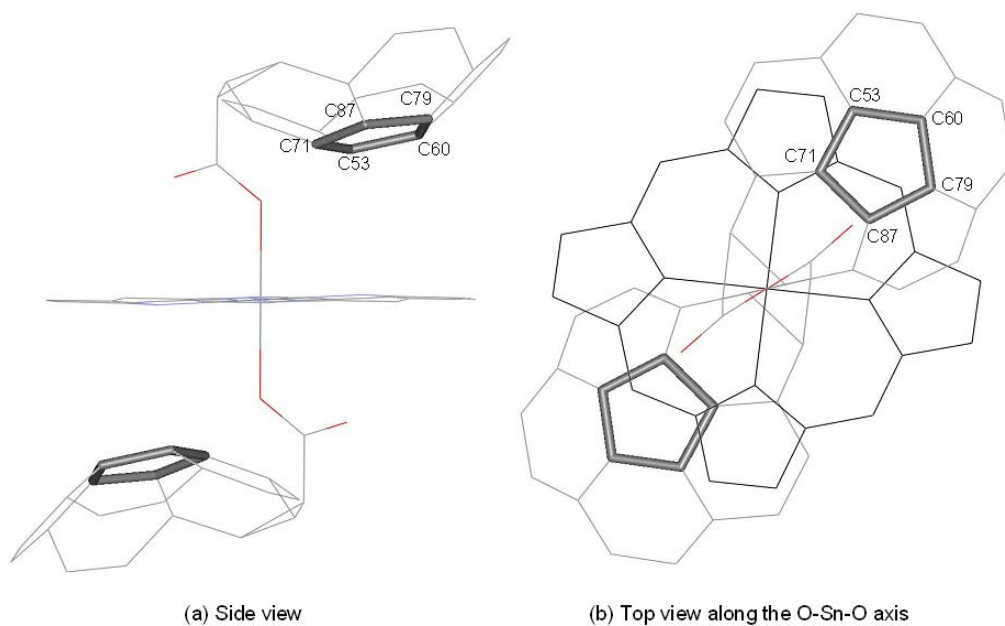(a) Side view   (b) Top view along the O-Sn-O axis

Figure S1. Views representing the close proximity between the porphyrin plane and the fullerene moieties. The distances from the porphyrin mean plane to each carbon atoms of the closest 5-membered rings in the fullerene moiety: C71, 3.324(7); C87, 3.212(8); C79, 3.522(8); C60, 3.845(8); C53, 3.725(7) Å. The dihedral angle between the two planes is estimated to be 15.8(4)º.
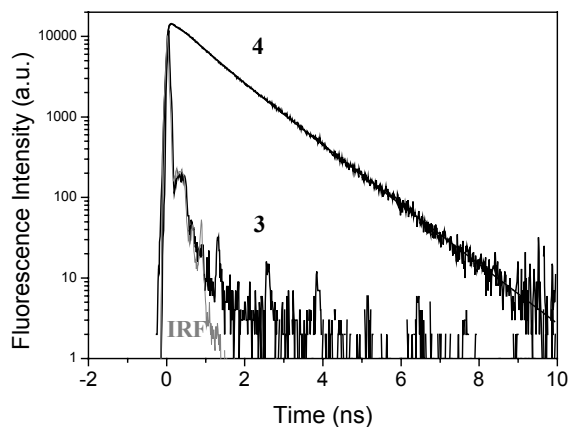
Figure S2. Fluorescence decay curves of **3** and **4** observed at 607 nm by the time-correlated single-photon counting method. IRF denotes the instrumental response function with 53 ps (fwhm). The excitation wavelength is 430 nm.
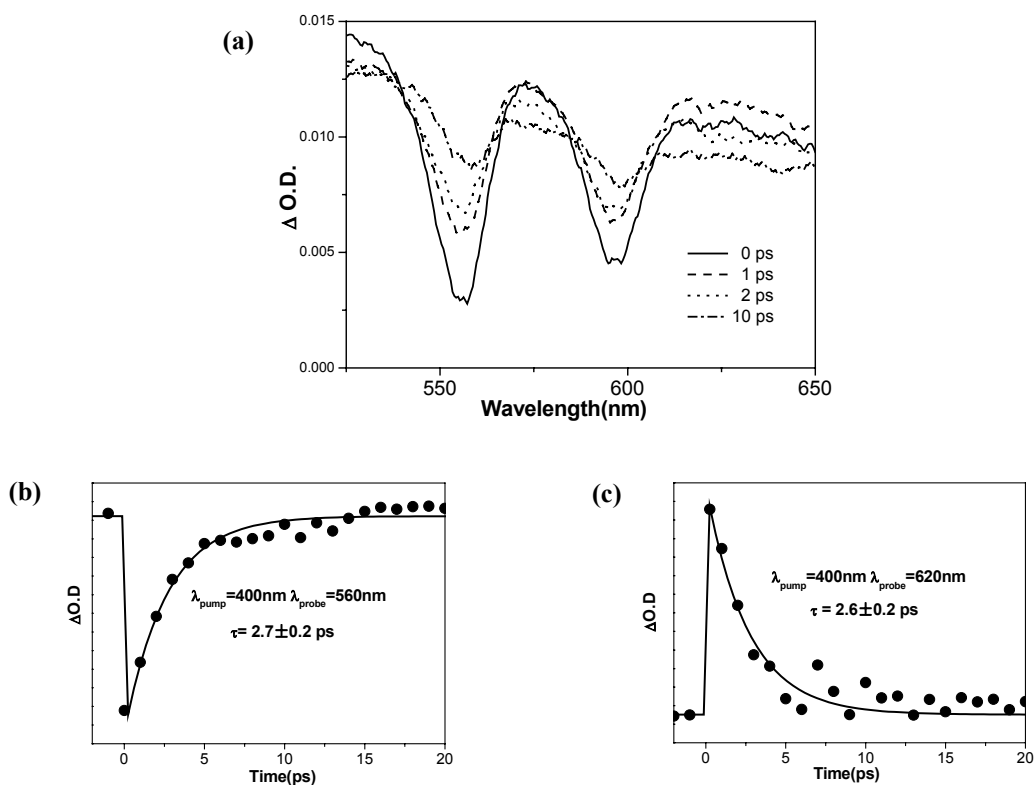

Figure S3. Transient absorption spectra (a) and temporal profiles at 560 nm (b) and 620 nm (c) of **3** in toluene after photoexcitation at 400 nm.

(a) ΔO.D. vs Wavelength(nm)

Legend:
— 0 ps
-- 1 ps
····· 2 ps
-·-· 10 ps

(b) ΔO.D vs Time(ps)

λ_{pump} = 400nm λ_{probe} = 560nm

τ_1 = 450±50 fs

τ_2 = 3±0.2 ps

(c) ΔO.D vs Time(ps)

λ_{pump}=400nm λ_{probe}=670nm
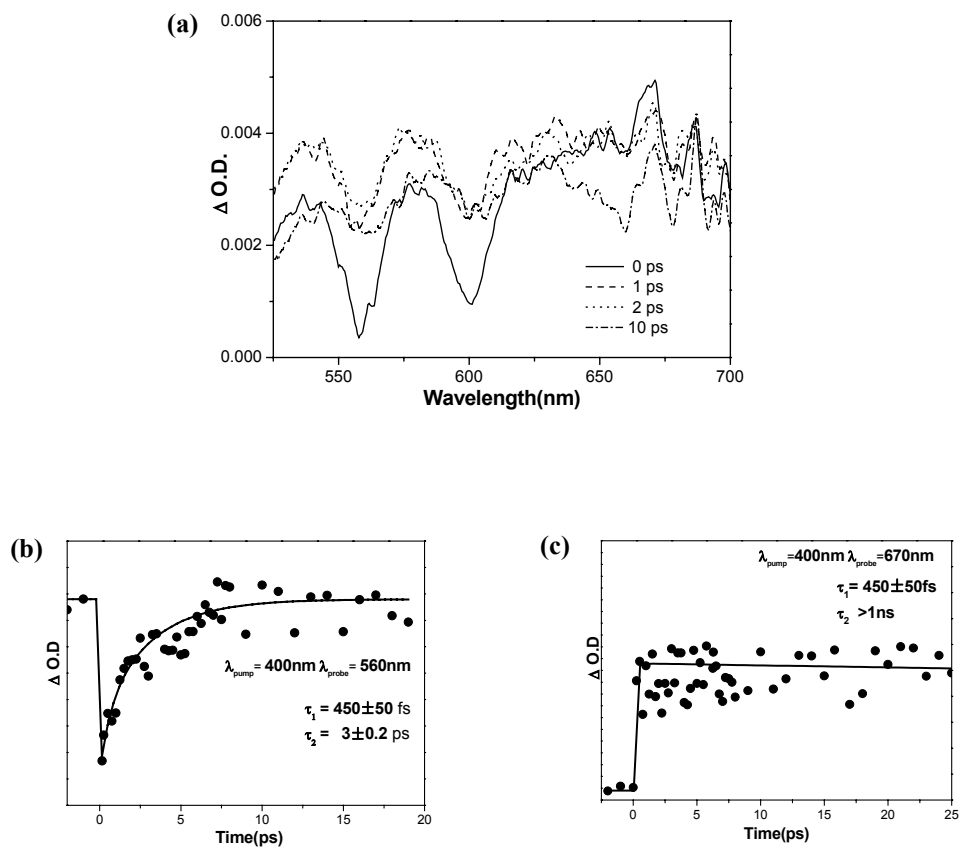
τ_1= 450±50fs

τ_2 >1ns

Figure S4. Transient absorption spectra (a) and time profiles at 560 nm (b) and 670 nm (c) of **3** in benzonitrile after photoexcitation at 400 nm.