

Supporting Information for

Intermolecular packing and charge transfer in metallofullerene/porphyrin cocrystals

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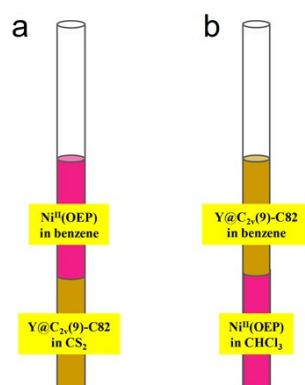
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Experimental details

Materials. $Y@C_{2v}(9)-C_{82}$ was synthesized by the direct-current arc-discharging method and purified by multi-step high performance liquid chromatographic separations.³⁵ NiP (97%) was purchased from Sigma-Aldrich Corporation. HPLC grade solvents were used as received.

Characterization. Single-crystal X-ray data of **1** were collected at 173 K using a Bruker D8 QUEST machine equipped with a CMOS camera (0.71073 Å). Single-crystal X-ray data of **2** were collected at 100 K using synchrotron radiation (0.65250 Å) with a MarCCD detector at beamline BL17B of the Shanghai Synchrotron Radiation Facility. A multi-scan method (SADABS) was used for absorption corrections. The structures were solved with direct methods and were refined with SHELXL-2016.³⁶ Steady state absorption spectra were obtained using Perkin Elmer Lambda2 UV/vis two-beam spectrophotometer using a slit width of 2 nm and a scan rate of 480 nm/ min. All spectra were recorded in the solid state by squeezing the samples in the middle of two quartz glass sheets. Femtosecond transient absorption spectra were obtained with a Ti:sapphire laser system CPA-2101 (Clark-MXR), Inc.) in combination with a Helios TAPPS-transient absorption pump probe spectroscopy detection unit from Ultrafast Inc. The initial laser output wavelength is 775 nm with a pulse width of 150 fs and 1 kHz repetition. The excitation wavelength was generated using a NOPA noncollinear optical parametric amplifier. Transient absorption spectra were measured in the solid state by squeezing the samples in the middle of two quartz glass sheets. Finally, spectra were acquired with a HELIOS (Ultrafast Systems) transient absorption spectrometer.

Preparation of Cocrystals. Black cocrystals **1** were produced by the slow diffusion of a benzene solution of NiP (P is the dianion of octaethylporphyrin) into a CS_2 solution of $Y@C_{2v}(9)-C_{82}$. Black cocrystals **2** were generated by slow diffusion of a benzene solution of $Y@C_{2v}(9)-C_{82}$ into a $CHCl_3$ solution of NiP (Scheme S1).



Scheme S1. Preparation of (a) **1** and (b) **2**. The glass tubes were stilled under dark for a period of one month.

Crystal data of 1. $2(YC_{82}) \cdot 2(C_{36}H_{44}N_4Ni) \cdot 3(C_6H_6) \cdot 2(CS_2)$, black block, $0.04 \times 0.04 \times 0.02$ mm, monoclinic, space group $C2/m$, $a = 26.7012(15)$ Å, $b = 17.2044(10)$ Å, $c = 17.8379(10)$ Å, $\beta = 107.076(2)^\circ$, $V = 7833.1(8)$ Å³, $Fw = 3716.96$, $\lambda = 0.71073$ Å, $Z = 2$, $D_{calc} = 1.576$ Mg m⁻³, $\mu = 1.099$ mm⁻¹, $T = 173$ K, $R_1[7691$ reflections with $I > 2\sigma(I)] = 0.1346$, wR_2 (all 58599 data) = 0.3993, GOF (on F^2) = 1.138. The maximum residual electron density is 1.304 eÅ⁻³. Crystallographic data has been deposited in the Cambridge Crystallographic Data Center (CCDC number: 1888173).

Crystal data of 2. $YC_{82} \cdot C_{36}H_{44}N_4Ni \cdot 2(C_6H_6)$, black block, $0.30 \times 0.30 \times 0.20$ mm, monoclinic, space group $C2/m$, $a = 25.3135(5)$ Å, $b = 15.1618(4)$ Å, $c = 19.8648(5)$ Å, $\beta = 95.0350(10)^\circ$, $V = 7594.7(3)$ Å³, $F_w = 1821.40$, $\lambda = 0.65250$ Å, $Z = 4$, $D_{calc} = 1.593$ Mg m⁻³, $\mu = 0.862$ mm⁻¹, $T = 100$ K, $R_1[9190$ reflections with $I > 2\sigma(I)] = 0.0691$, wR_2 (all 68528 data) = 0.2022, GOF (on F^2) = 1.052. The maximum residual electron density is 1.295 eÅ⁻³. Crystallographic data has been deposited in the Cambridge Crystallographic Data Center (CCDC number: 1876677).

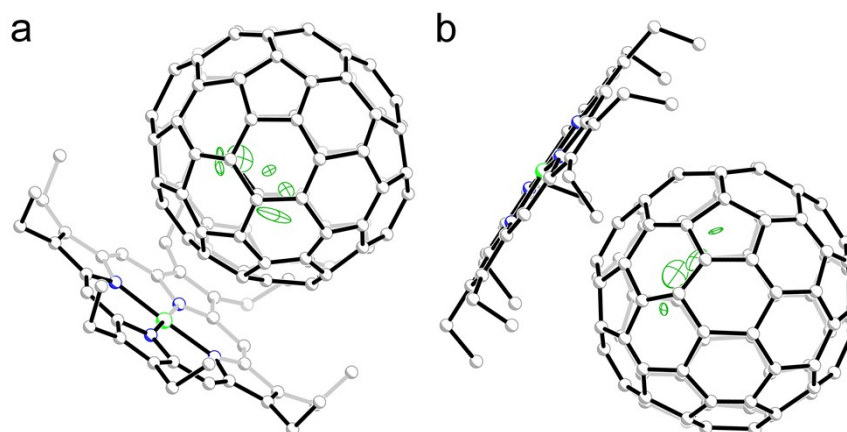


Fig. S1. Drawings depict the relative orientation of $Y@C_{2v}(9)-C_{82}$ to NiP and the positions of internal Y atom in (a) **1** and (b) **2**. The orientation of $Y@C_{2v}(9)-C_{82}$ moiety is set to be same for the ease of comparison. H atoms and solvent molecules are omitted.

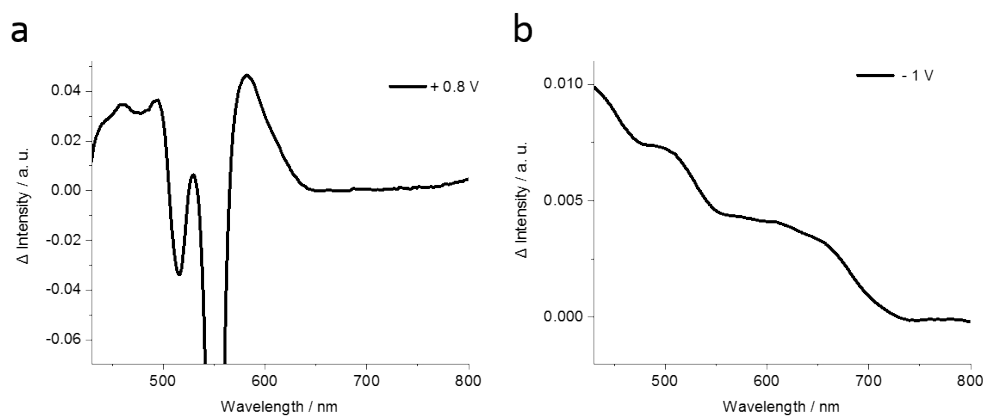


Fig. S2. Differential absorption spectra obtained upon electrochemical redox of NiP with an applied potential of (a) +0.8 V in 1,2-dichlorobenzene/acetonitrile (v/v: 5/1) and $Y@C_{2v}(9)-C_{82}$ with an applied potential of (b) -1 V in 1,2-dichloroethane with 0.1 M TBAPF₆ vs. Ag-wire.

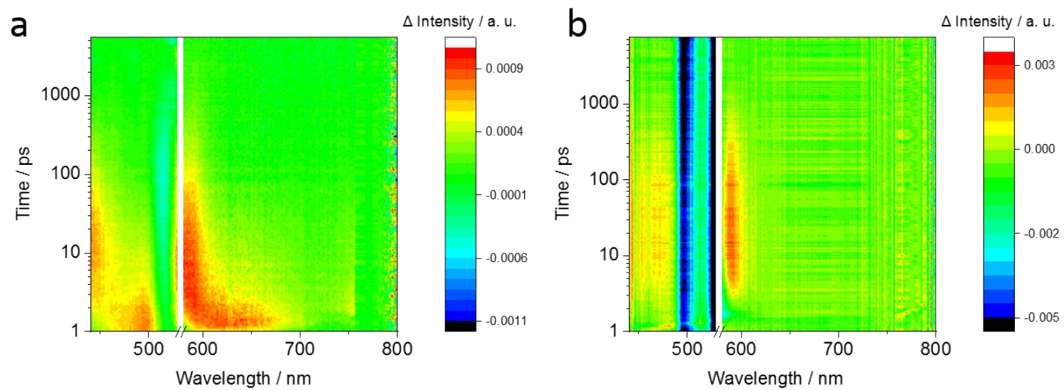


Fig. S3. (a) Differential absorption spectra changes obtained upon femtosecond pump-probe experiments upon 550 nm excitation of **1**. (b) Differential absorption spectra changes obtained upon femtosecond pump-probe experiments upon 550 nm excitation of **2**.