Supporting Information

Semiconducting Single-Wall Carbon Nanotube and Covalent Organic Polyhedron-C_{60} Nanohybrids for Light Harvesting

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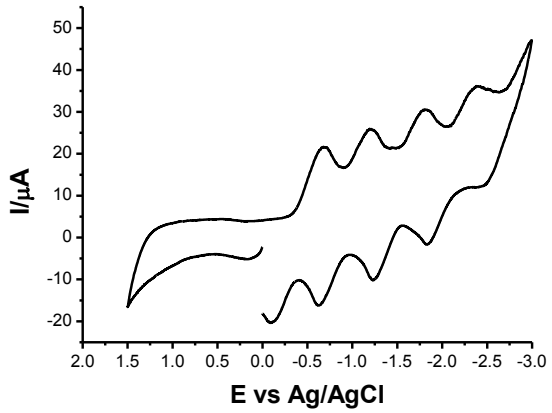
Experimental Details

1. Methods

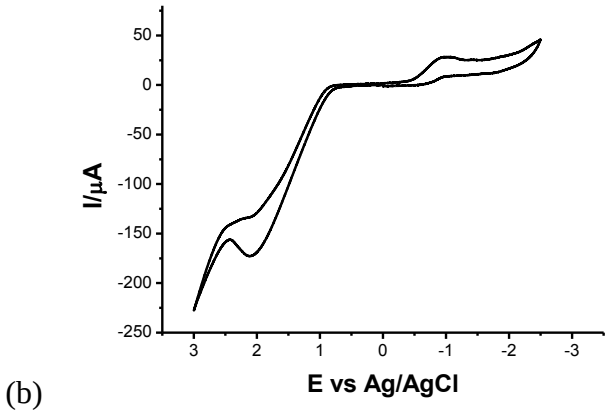
1.1 Electrochemical measurement

Cyclic voltammetry (CV) measurements were carried out under argon in anhydrous solvents with a BAS 100 Electrochemical Analyzer at a potential scan rate of 50 mV/s. The cell used three electrodes: a saturated silver chloride reference electrode (0.222 V vs. SHE), a glassy carbon working electrode, and a platinum counter electrode. The experiments were performed in a mixed solvent of toluene and dimethylformamide (2/1, v/v) with tetrabutylammoniumhexafluorophosphate (0.1 M) as electrolyte. The concentrations of the analytes were at 0.50-1.0 mmol.

The onset potentials of the n-doping and p-doping can be used to determine the LUMO and HOMO energy levels of the analytes, and the potential difference can be used to estimate the energy gap of the analytes.[1] E_{LUMO}=-(E_{red}+4.4) eV, E_{HOMO}=-(E_{ox}+4.4) eV, where E_{LUMO} is the LUMO energy level, E_{HOMO} is the HOMO energy level, and all electrode potential values are vs. SCE as the reference electrode.



(a)



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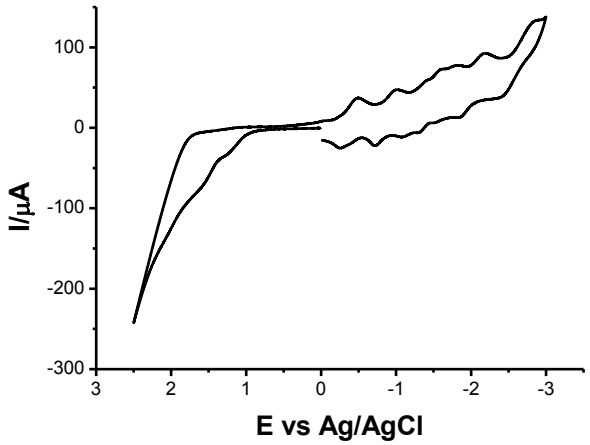

(c)

Figure S1. Cyclic Voltammetry of C_{60} (a), cage COP-5 (b), and C_{60}@COP complex (c).

Table S1. Calculated HOMO and LUMO energy levels of the analytes.

	Oxidation potential (V vs. Ag/AgCl)	Reduction potential (V vs. Ag/AgCl)	Energy Level		Band Gap
			HOMO	LUMO	
Cage	0.88	-1.01	-5.26	-3.37	1.89eV
C60	N/A	-0.35		-4.03	
Cage-C60	0.94(C60)	-0.26(cage)	-5.32	-4.12	1.20eV

1.2 Modelling and Structural Characterization

The Amber 11.0 molecular dynamics program package[2] was used to optimize the structure of the fullerene, the cage, the CNT, the cage/fullerene binding complexes, and the three-component binding complexes. The force field used was the general Amber force field (GAFF field)[3] with the charge parameters computed by AM1-BCC method.[4] For each structure optimization run, the molecule was first minimized for 1000 steps using the conjugate gradient method, and then it

was further optimized by simulated annealing method for 150 picosecond with a time-step of 1 femtosecond. During the simulated annealing, the system temperature was first raised up to 1000 K for 50 picoseconds and then gradually cooled to 0 K for another 100 picoseconds. Finally, the annealed structure was minimized again for another 1000 conjugate gradient steps and the final energy was recorded. The non-bonded interactions during the simulation were computed directly with a cutoff distance of 25 Å. A dielectric constant of 4.8 was assumed during the simulation, which is a typical value for organic solvents.

A FEI Tecnai F20 XT FEG electron microscope operated at 200 kV was used for transmission electron microscopy (TEM). Surface morphology of the organic solar cell devices was investigated using Digital Instruments Dimension 3000 atomic force microscope (AFM) operating in tapping mode. The C_{60}@COP binds to SWCNT surface through π-π interaction (Figure S2a), which forms a type-II heterojunction for nanohybrid solar cells. By mixing the C_{60}, COP-5 and SWCNT three components together, it is possible that the COP-5 directly binds onto the SWCNT surface without the C_{60} bound inside (Figure S2b), which makes the C_{60}/COP-5/SWCNT system is not efficient due to the lack of crucial C_{60}@COP complex.

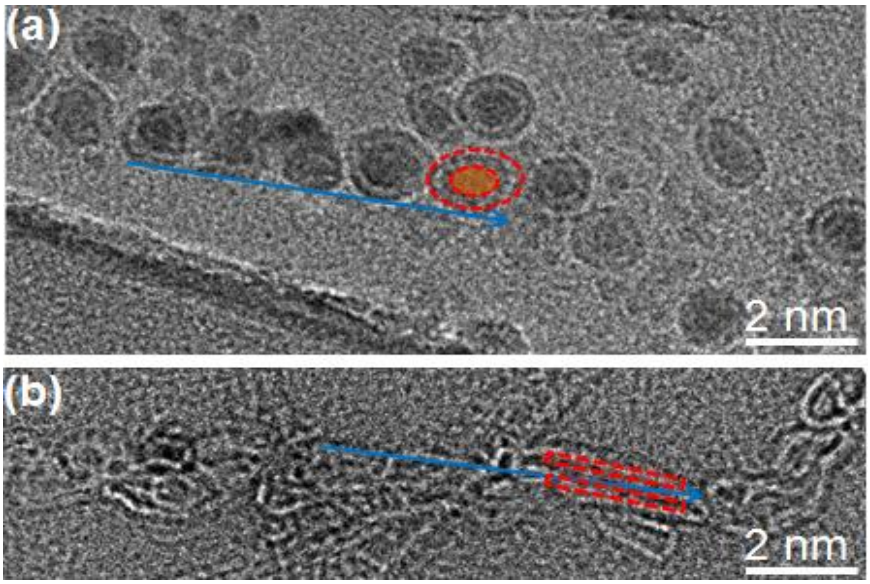

Figure S2. The TEM images of C_{60}@COP/SWCNT and C_{60}/COP-5/SWCNT, (a) and (b), respectively. The blue arrow indicates the direction of SWCNT, and red dashed line and orange shaded area represents the the COP shell and C_{60} core in (a); and red dashed line shows the COP-5 shell coating onto SWCNT in (b).

1.3 J-V Characterization of Solar Cell Devices

The effect of porphyrin COP-5 and C_{60} in combination with SWCNT on the photovoltaic properties of bulk heterojunction solar cells was demonstrated by the DC current density (J)–voltage (V) (Figure S3). As shown in Figure S3, the solar device shows a very small photoresponse from COP-5/SWCNT and C_{60}/SWCNT. This result further supports the tunable band level by the formation of C_{60}@COP complex, which makes a more effective photovoltaic system (C_{60}@COP/SWCNT). The solar cell performance is highly dependent on the sequence of the three component mixing (COP-5, C_{60} and SWCNT) in solution, which is presumably due to the effect of SWCNT on the COP-C_{60} complex binding: the initial π-π stacking between COP-5 and SWCNT may impede the further C_{60} binding. The photovoltaic performance indicates that the COP-5 preferentially binds with SWCNT to form a shell coating (Figure S2), which increase the fill factor of nanohybrid solar cell; however, the COP-5 coated SWCNT and C_{60} leads to a low performance. By blending COP-5 and C_{60} first, the preformed C_{60}/COP-5 complex and SWCNT nanohybrids confirm a type-II heterojunction, as shown in the main text.

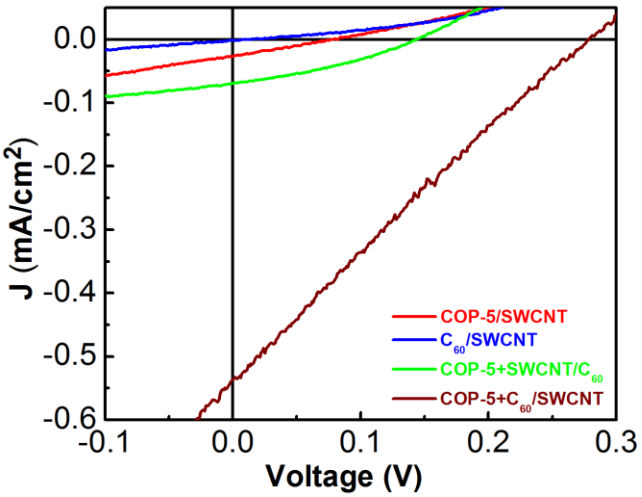

Figure S3. J-V characteristics of solar cells(Red: COP-5/SWCNT;Blue: C_{60}/SWCNT; Green: COP-5 mixed with SWCNT (1 wt%) for 1 hour, followed by blending with C_{60}(1:1 weight ratio between COP-5 and C_{60}); Brown: COP-5 mixed with C_{60} for 1 hour(1:1 weight ratio between COP-5 and C_{60}), followed by blending with 1wt% SWCNT) measured with incident light intensities from 100 mW/cm^2 AM 1.5 solar simulator.

Table S2. Photovoltaic Properties of Solar Cell Devices with Different Photoactive Nanohybrids and Nanotube Loading Under AM1.5 Solar Illumination (100 mW/cm^2)

Solar Cell Devices	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	Efficiency (%)
C_{60}@COP	0.0262	0.08	19	0.0004
C_{60}@COP/SWCNT (1wt%)	1.4	0.47	24	0.16
C_{60}@COP/SWCNT (3wt%)	2.34	0.49	14	0.16
C_{60}/COP-5/SWCNT (1wt%)	0.0275	0.1	25	0.0007

References:

[1] D.M. de Leeuw, M.M.J. Simenon, A.R. Brown, R.E.F. Einerhand, *Synth. Met.* **1997**, *87*, 53.
[2] D. A. Case, T. A. Darden, et al. (2010), AMBER 11, University of California, San Francisco.
[3] J. Wang, R. Wolf, J. Caldwell, P. Kollman, D. Case, *J. Comput. Chem.* **2004**, *25*, 1157.
[4] A. Jakalian, B. Bush, D. Jack, C. Bayly, *J. Comput. Chem.* **2000**, *21*, 132.