Supporting Information

Indan-C₆₀: From Crystalline Molecule to Photovoltaic Application

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**Experimental Section:**

1. **Synthesis of Indan-\( C_{60} \) and its derivatives**

Indan-\( C_{60} \) was synthesized by refluxing 1-indanone and \( p \)-toluenesulfonylhydrazone (1.2 equiv) in methanol with stirring for 12 h. The mixture was allowed to stand at room temperature for 1 day and the product was collected by filtration, washed with MeOH, and dried under vacuum. Methyl 4-benzoylbutyrate \( p \)-tosylhydrazone was synthesized according to the reported literature.\(^{51}\)

Indan-\( C_{60} \) was synthesized according to modification of the reported literature.\(^{51}\) Briefly, methyl 4-benzoylbutyrate \( p \)-tosylhydrazone and NaOMe were dissolved in dry pyridine, and then the mixture was stirred for 30 min. A solution of \( C_{60} \) in 1,2-dichlorobenzene (DClB) was added and was stirred at 120 °C for 24 h. Indan-\( C_{60} \) was isolated by high-performance liquid chromatography (HPLC) using Buckyprep column with toluene as the eluent. Indan-\( C_{60} \) was confirmed by matrix assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometry and \( ^1 \)H NMR spectroscopy. MALDI-TOF \( m/z \): 836. \( ^1 \)H NMR (CDCl\(_3\), 400 MHz): 3.46 (m, 4H), 7.54-7.40 (m, 3H), 8.35 (d, \( J = 8.2 \) Hz, 1H).

Indan-\( PC_{60} \)BM was synthesized by heating Indan-\( C_{60} \) and methyl 4-benzoylbutyrate \( p \)-tosylhydrazone with stirring at 120 °C for 24 h and the resulted bis-adducts were isolated by HPLC. The Indan-\( PC_{60} \)BM products contain a mixture of regioisomers and they were not further purified. Indan-\( PC_{60} \)BM was confirmed by the MALDI-TOF mass spectrometry and \( ^1 \)H NMR spectroscopy. MALDI-TOF \( m/z \): 1026. \( ^1 \)H NMR (CDCl\(_3\), 400 MHz): 2.12-2.17, 2.30-2.31, 2.42-2.60, and 2.89-2.93 (m, 6H); 3.57-3.75 (m, 7H); 7.44-7.47, 7.53-7.59, and 7.92-7.98 (m, 9H).

*Figure S1.* MALDI-TOF mass spectrum of Indan-\( C_{60} \). The peak at \( m/z \) 720 is attributed to \( C_{60} \) fragment formed by loss of the exohedral functional group under laser desorption condition.

*Figure S2.* MALDI-TOF mass spectrum of Indan-\( PC_{60} \)BM. The peaks at \( m/z \) 720, 836, and 910 are attributed to \( C_{60} \), Indan-\( C_{60} \), and \( PC_{60} \)BM fragments formed by loss of the exohedral functional groups under laser desorption condition, respectively.

*Figure S3.* HPLC profiles of purified (a) Indan-\( C_{60} \) and (b) Indan-\( PC_{60} \)BM (20×250 mm Buckyprep column; flow rate 3 mL/min; toluene as eluent).
2. Cyclic voltammograms of Indan-C₆₀ and its derivatives

Electrochemistry experiments were carried out in o-DCB solvent containing 0.05 M n-Bu₄NPF₆ with glassy carbon as the working electrode, and Pt wire and Ag wire as the counter and reference electrodes, respectively, at a scan rate of 100 mV s⁻¹. The potentials were reported with reference to the $E_{1/2}$ value of the Fe⁺²/Fe redox couple measured in the sample solution.

![Cyclic voltammograms](image)

**Figure S4.** Cyclic voltammograms of Indan-C₆₀, Indan-PC₆₁BM and PC₆₁BM.

3. UV-vis absorption spectra of Indan-C₆₀, Indan-PC₆₁BM, and PC₆₁BM

UV-vis absorption experiments were carried out in toluene with sample concentrations of $10^{-5}$ M.

![UV-vis absorption spectra](image)

**Figure S5.** UV-vis absorption spectra of Indan-C₆₀, Indan-PC₆₁BM and PC₆₁BM in toluene.
4. OPV device measurements of Indan-PC$_{61}$BM and PC$_{61}$BM

The OPV devices were fabricated in the configuration of ITO/PEDOT:PSS/P3HT:acceptor/Ca/Al. ITO glass substrates were sequentially cleaned with deionized water, acetone, and isopropanol for 10 min each and then were treated by oxygen plasma for 6 min. Then the PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate)) was spin-coated on the ITO-coated glass from a PEDOT:PSS aqueous solution (Baytron P VP AI 4083 from H.C. Starck) at 3000 rpm and annealed on a hotplate at 140 °C for 10 min in air. After that the active layer dissolved in CDB was spin-coated on the PEDOT:PSS layer in the N$_2$ glove box (1:0.7 wt ratio, 12 mg/mL for Indan-PC$_{61}$BM; 1:0.8 wt ratio, 12 mg/mL for PC$_{61}$BM) and thermally annealed at 110 °C for 10 min. A bi-layer cathode consisting of a calcium layer (25 nm) and subsequently an aluminium layer (80 nm) was deposited by thermal evaporation under vacuum. The $J$-$V$ characterization was measured in the N$_2$ glove box under a Newport 6279 NS solar simulator (100 mW cm$^{-2}$, AM 1.5G). The external quantum efficiency (EQE) measurements of the devices were performed in air (Oriel Instrument’s IQE-200).

![Figure S6](image)

**Figure S6.** External quantum efficiencies (EQE) of OPV devices based on P3HT:Indan-PC$_{61}$BM and P3HT:PC$_{61}$BM, respectively.
5. Microscopic characterizations of P3HT and Indan-PC_{61}BM blended film

![Figure S7](image1)

*Figure S7.* Optical microscope image of the P3HT: Indan-PC_{61}BM blends after heating at 110 °C for 10 min.

![Figure S8](image2)

*Figure S8.* AFM (5 μm × 5 μm) topography and phase images of the P3HT:Indan-PC_{61}BM blends after heating at 110 °C for 10 min.

6. SEM and XRD characterizations of Indan-C_{60} materials

![Figure S9](image3)

*Figure S9.* SEM image of Indan-C_{60} solids precipitated from toluene solution and left to stand for several days and its XRD pattern.
Figure S10. XRD pattern of Indan-C$_{60}$ microsheets prepared from o-DCB solution by solvent evaporation method.

Figure S11. XRD pattern of Indan-C$_{60}$ aloe-like micro-nano superstructures prepared from CHCl$_3$ solution by solvent evaporation method.

Figure S12. $^1$H NMR spectra of (a) Indan-C$_{60}$ and (b) Indan-PC$_{61}$BM.

Reference