

Supporting Information

Dihydronaphthyl-based [60]fullerene bisadducts for efficient and stable polymer solar cells

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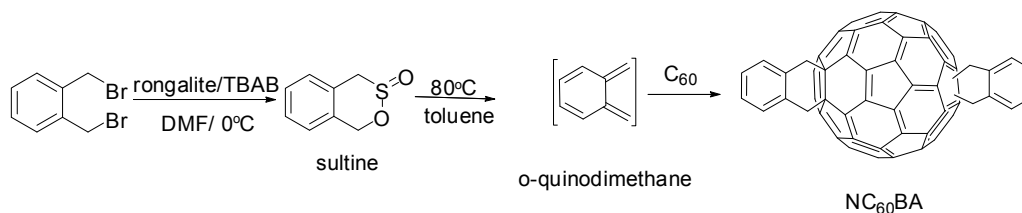
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Experimental Section

Materials: Chemicals were purchased from commercial sources and used without further purification unless otherwise noted. All solvents were purified and freshly distilled prior to use according to literature procedures.

Measurements: ^1H NMR and ^{13}C NMR spectra were measured on Bruker DMX-400 or Bruker DMX-600 spectrometer. Chemical shifts of NMR were reported in ppm relative to the singlet of CDCl_3 at 7.26 ppm for ^1H NMR and 77.6 ppm for ^{13}C NMR. Splitting patterns were designated as s (singlet), d (doublet), t (triplet), m (multiplet) and br (broaden). Absorption spectra were taken on a Hitachi U-3010 UV-vis spectrophotometer. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation. A Pt disk as the working electrode, Pt wire as the counter electrode, and Ag/Ag^+ electrode (0.01 M AgNO_3 , 0.09 M Bu_4NPF_6 in acetonitrile) as the reference electrode was used in a mixed solution of o-dichlorobenzene/acetonitrile (v:v=5:1) with 0.1M tetrabutylammonium hexafluorophosphate (NBu_4PF_6) at 100 mV/s. The differential scanning calorimetry (DSC) analysis of fullerene derivatives was performed under a nitrogen atmosphere on a TA Instruments Q-100 at heating rates of $10^\circ\text{C min}^{-1}$. Thermogravimetric analysis (TGA) was recorded on TA Q-50 under nitrogen atmosphere at a heating rate of $20^\circ\text{C min}^{-1}$. The optical microscopy images were measured by Olympus Fluoview Fv1000. High performance liquid chromatography (HPLC) analysis was performed on LC908-C60(Jai CO., LTD.) equipped with a Cosmosil Buckyprep column ($\Phi 20\text{mm}\times 250\text{ mm}$, Nacalai USA) using toluene as eluent.

Synthetic procedure 1



Synthesis of Sultine. Sodium hydroxymethanesulfinate (rongalite, 402.8 mg, 3.4136 mmol) and tetrabutylammonium bromide (TBAB, 82.5 mg, 0.2561 mmol) were added to DMF (15 ml) solution of 1,2-bis(bromomethyl)benzene (225.3 mg, 0.8534 mmol). The mixture was stirred at 0°C under argon atmosphere for 4 h. Afterwards, water was added and the mixture was extracted with CH₂Cl₂. The organic extracts were dried over NaSO₄, and the solvent was evaporated at 25°C to give colorless oil. The crude product was subjected to the next reaction without further purification. ¹H NMR (400 MHz, CDCl₃): δ(ppm) 7.19-7.42 (m, 4H), 5.31 (d, 1H), 4.97 (d, 1H), 4.42 (d, 1H), 3.55 (d, 1H).

Synthesis of NC₆₀BA. To a solution of C₆₀ (217.4 mg, 0.302 mmol) in toluene (250 mL) was added the sultine (152.4 mg, 0.906 mmol). The mixture was heated to 80°C under argon atmosphere for 15 h. After cooling down, water was added and the mixture was extracted with toluene. The organic extracts were dried over NaSO₄, and concentrated under reduced pressure. The crude product was first purified by a silica gel column using toluene as eluent. Further purification by preparative HPLC equipped with a Buckyprep column using toluene as eluent afforded brown powder. Fig. S1 shows HPLC curve of the reaction mixture. Yield: 72%. ¹H NMR (400 MHz, CDCl₃): δ(ppm) 7.13-7.85 (m, 8H), 3.45-4.96 (m, 8H). ¹³C NMR (200 MHz, CDCl₃): δ(ppm) 162.46, 156.32, 155.87, 150.02, 149.00, 147.55, 147.11, 146.79, 146.36, 146.26, 146.03, 145.81, 145.61, 145.41, 144.59, 143.51, 143.27, 143.07, 142.37, 142.12, 139.25, 138.89, 138.62, 128.88, 128.61, 78.77, 65.90, 65.61, 65.29, 65.18, 64.63, 46.11, 45.86. MALDI-TOF MS: calcd. 928.13; found 928.04.

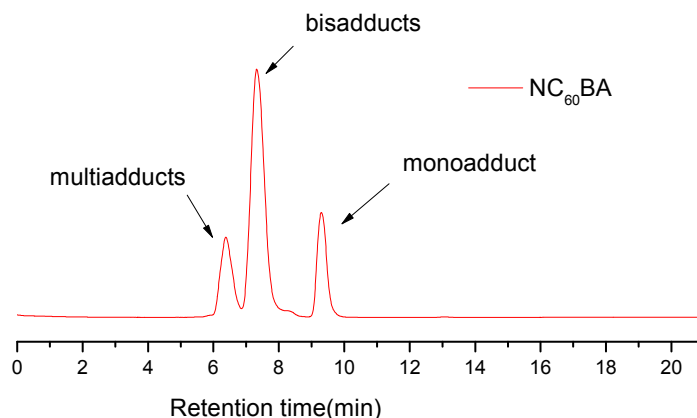


Fig. S1. HPLC curve of the reaction mixture ($\Phi 20 \times 250$ mm Buckyprep column; flow rate 12 mL/min; toluene as eluent).

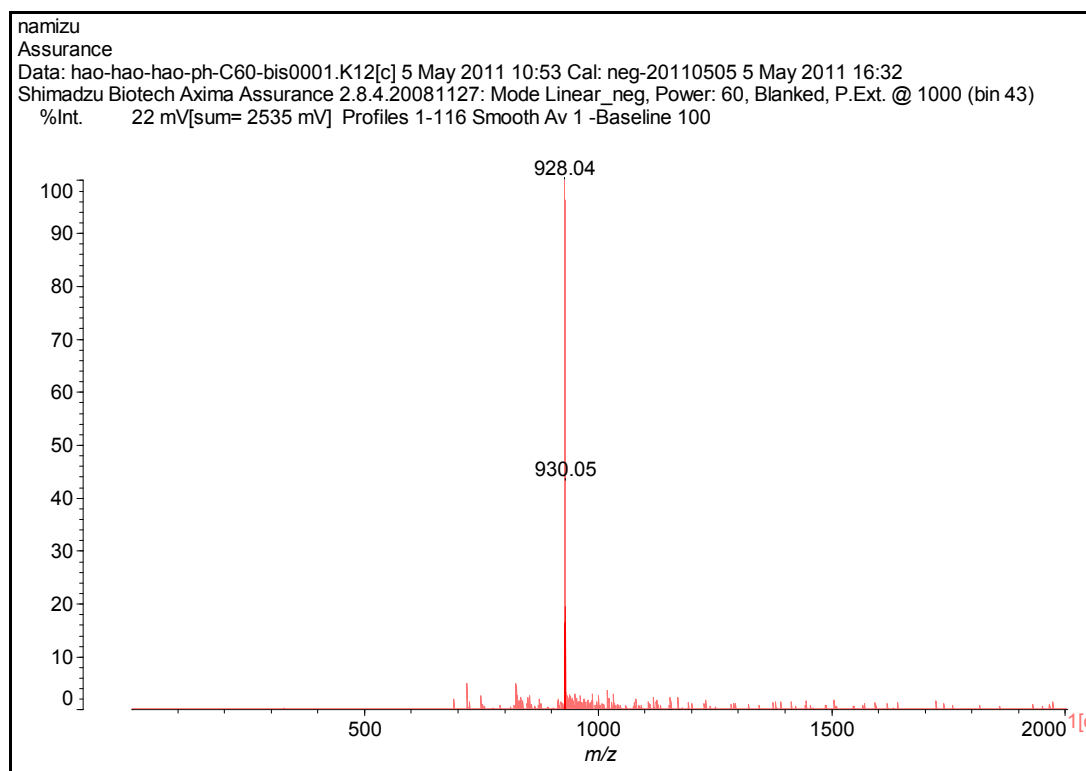
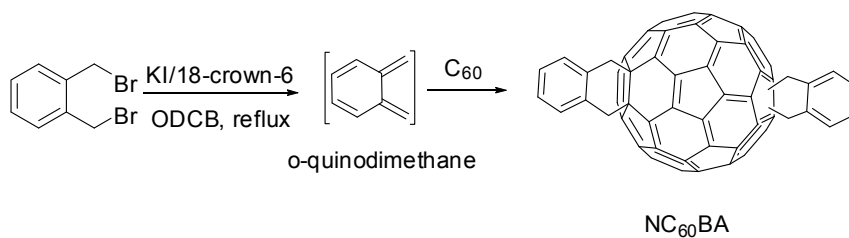


Fig. S2. MALDI-TOF MS of the product from Synthetic procedure 1

Synthetic procedure 2



To a mixture of [60]fullerene (720 mg, 1.0 mmol), KI (1.66 g, 10 mmol), and 18-crown-6 (2.64 g, 10 mmol) in o-dichlorobenzene (400 mL) was added 1,2-bis(bromomethyl)benzene (660 mg, 2.5 mmol). The mixture was refluxed in the dark for 24 h. After cooled to room temperature, the mixture was washed with 5% KCl aq, 5% Na₂S₂O₃ aq, and water successively, and dried over NaSO₄. After the solvent was evaporated under reduced pressure, the crude product was first purified by a silica gel column using toluene as the eluent. Further purification by preparative HPLC equipped with a Buckyprep column using toluene as eluent afforded brown powder. **Yield: 65%.**

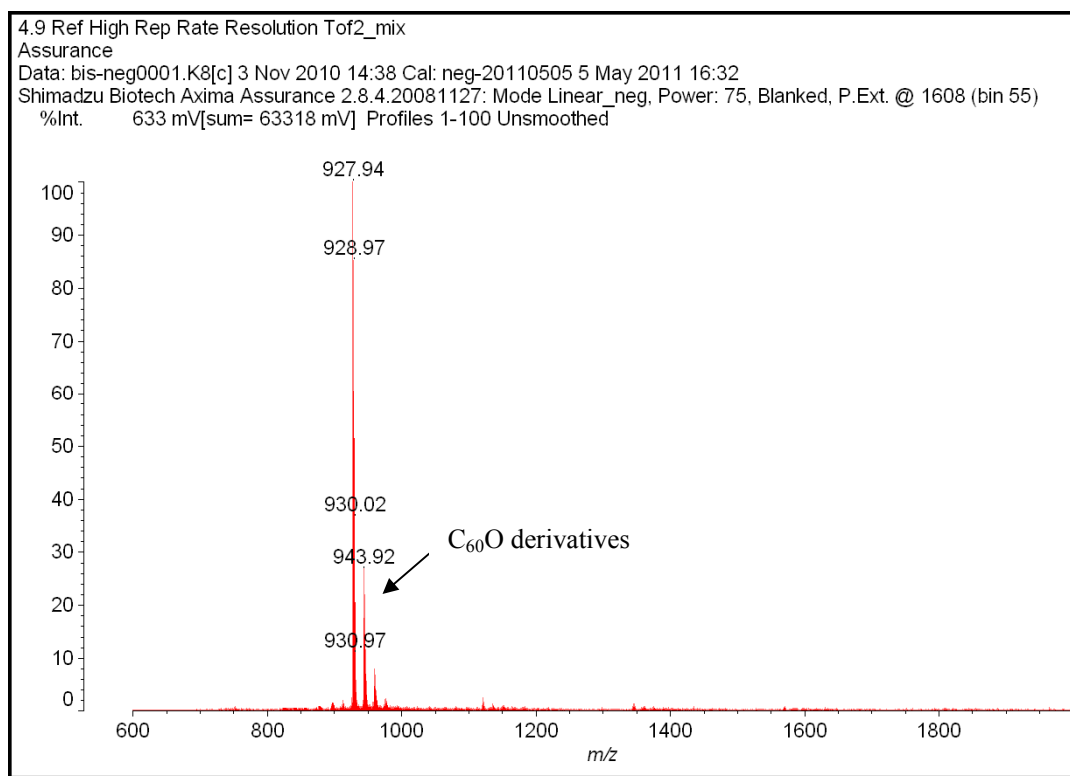


Fig. S3. MALDI-TOF MS of the product from Synthetic procedure 2

Fabrication and Characterization of PSCs. Conventional PSCs structures based on ITO/PEDOT:PSS/P3HT:NC₆₀BA(or PCBM)/Ca/Al were used. The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropanol, and then treated in an ultraviolet-ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company, USA) for 20 min. Then PEDOT:PSS (poly (3,4-ethylene dioxythiophene):poly(styrene sulfonate)) (Baytron PVPAl 4083, Germany) was filtered through a 0.45 μm filter and spin coated at 4000 rpm for 60 s on the ITO electrode. Subsequently, the PEDOT: PSS film was baked at 150°C for 20 min in the air. The blend solution of P3HT and different fullerene derivative acceptors in dichlorobenzene (DCB) (17 mg/mL for each chemical) was then spin-coated (800 rpm for 20 s) on top of the PEDOT:PSS layer. The blend films were then put into glass petridishes directly to undergo solvent annealing process. The thickness of the photoactive layer was estimated by Surface Profiler in the range of 180–220 nm. The device was annealed at 120°C for 10 min. The thermal stability of the P3HT:PC₆₁BM and P3HT:NC₆₀BA based devices were subjected to sustained heating at 150 °C for different times. A bilayer cathode consisted of Ca (20 nm) capped with Al (100 nm) was thermal-evaporated under a shadow mask in a base pressure of ca. 10⁻⁴ Pa. The device active area of the PSCs is 4mm². The J–V measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. Device characterization was done in glovebox under simulated AM1.5G irradiation (100 mW cm⁻²) using a xenon-lamp-based solar simulator (from Newport Co., LTD.). The EQE measurements of the PSCs were performed by Stanford Research Systems model SR830 DSP lock-in amplifier coupled with WDG3 monochromator and 500W xenon lamp. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

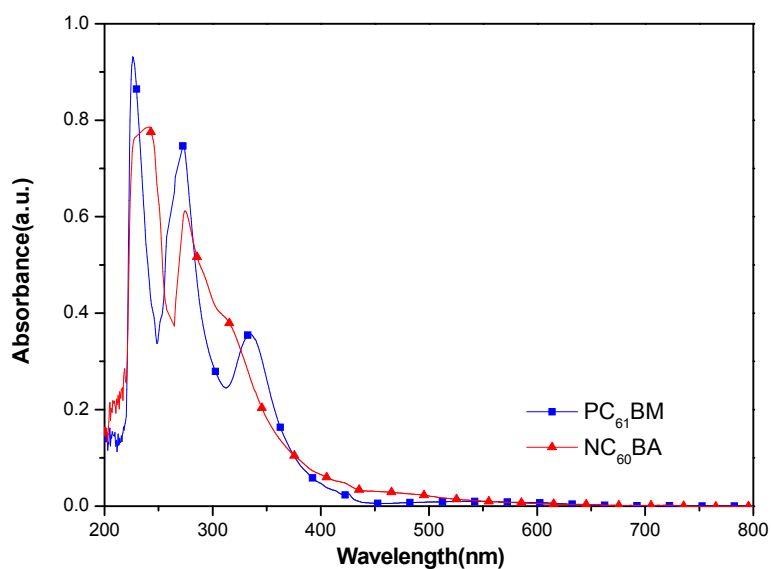


Fig. S4. UV-vis absorption spectra (200 nm to 800 nm) of fullerene derivatives in THF solutions (10^{-5} mol/L)

Table S1. Photovoltaic performance of the P3HT: NC₆₀BA (1:1, w/w) PSCs with different annealing times.

Annealing time	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
0 h	0.82	9.84	0.641	5.17
5 h	0.83	8.97	0.627	4.67
10 h	0.82	9.00	0.626	4.62
20 h	0.82	8.91	0.623	4.55

Table S2. Photovoltaic performance of the P3HT:PC₆₁BM (1:1, w/w) PSCs with different annealing times.

Annealing time	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
0 h	0.59	10.31	0.70	4.27
5 h	0.61	8.79	0.66	3.52
10 h	0.61	6.98	0.69	2.98
20 h	0.63	5.04	0.61	1.94

Organic Field-Effect Transistor. Fullerene-based field-effect transistor was fabricated through the top-contact and bottom-gate configuration. Si/SiO₂ (500nm) substrate was cleaned by sequential ultrasonic treatment in acetone and isopropyl alcohol for 15 min followed by N₂ blowing treatment. The fullerene films were spin-coated from a 15 mg/ml chloroform solution at 2000 rpm. Source and drain electrodes Al (60 nm) were evaporated under high vacuum (10⁻⁶ mbar) through a shadow mask with length-to-width ratio (L/W) of ca.1/20. Electrical measurements were performed at room temperature in glove box with N₂ atmosphere using Keithley 4200-SCS. The field-effect mobility was calculated in the saturation regime from the linear fit of (I_{DS})^{1/2} vs V_{GS}. The threshold voltage (V_T) was estimated as the 13 V intercept of the linear section of the plot of (I_{DS})^{1/2} vs V_{GS}. The sub threshold swing is about 1.58×10⁻⁹, which was calculated by taking the inverse of the slope of log(I_{DS}) vs V_{GS} in the region of exponential current increase. The calculated electron mobility of NC₆₀BA is 2.4×10⁻³ cm² V⁻¹ s⁻¹.

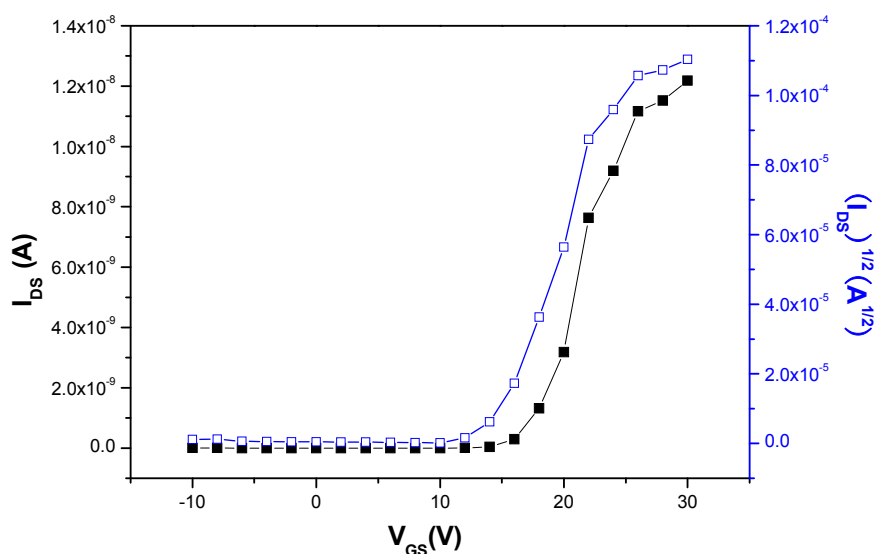


Fig. S5. Transfer characteristic of NC₆₀BA

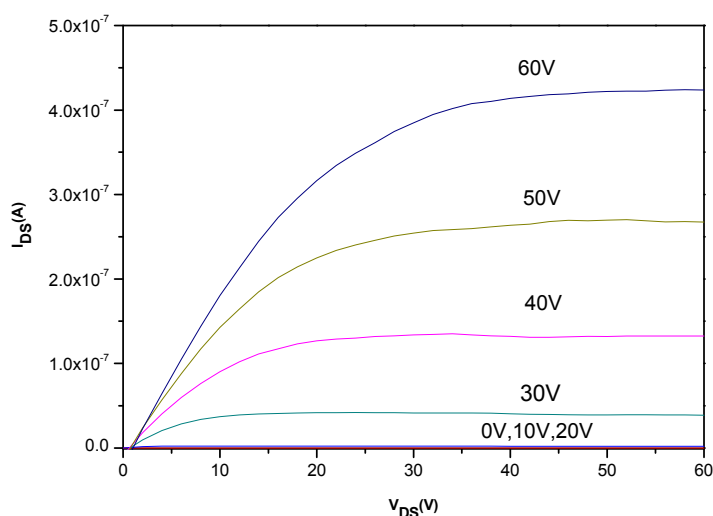


Fig. S6. Output current-voltage characteristic of NC₆₀BA

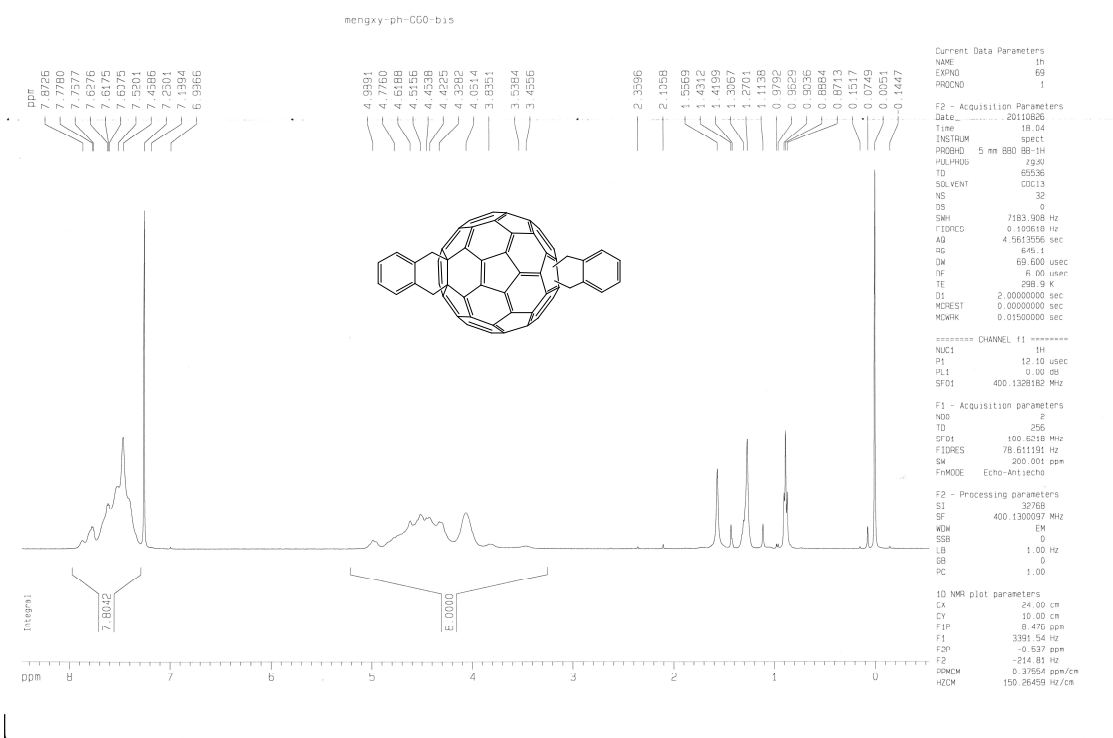


Fig. S7. ^1H NMR spectrum of NC_{60}BA

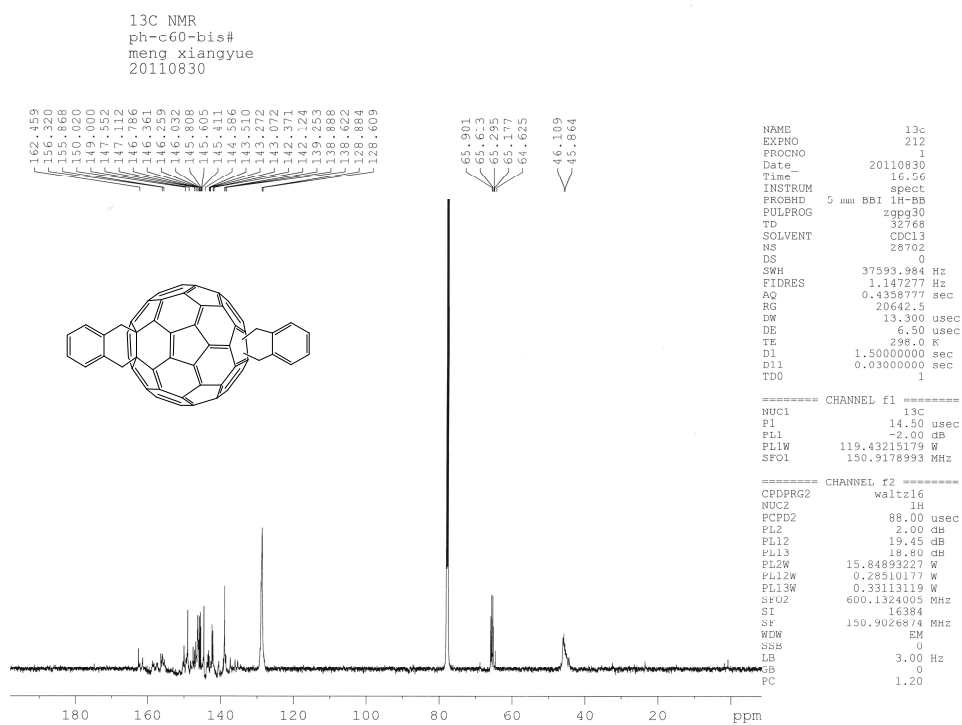


Fig. S8. ^{13}C NMR spectrum of NC_{60}BA