

Supporting Information

Single Crystalline of Indene-C₆₀ Bisadduct – Isolation and Application in Polymer Solar Cells

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General experimental details

Indene (99%) was purchased from Sigma-Aldrich Co.. C₆₀ (95%) was purchased from Yongxin Co. (China). *o*-dichlorobenzene was purchased from Alfa-Aesar Co.. P3HT (4002-E) was purchased from Rieke Metals Inc.

Flash chromatography purification was performed following standard chromatographic methods. Analytical and preparative HPLC was carried out on LC908-C60 (Jai CO., LTD.). A Cosmosil® Buckyprep-D column (4.6 ID × 250 mm) and COSMOSIL 5PBB column (10 x 250 mm) were used with toluene as eluent (3 mL/min) and UV detection was recorded at 350 nm.

¹H NMR spectra were measured on a Bruker DMX-400 spectrometer. ¹³C NMR were performed on a Bruker DMX-600 spectrometer. Chemical shift was reported in ppm relative to the singlet of CDCl₃ at 7.26 ppm for ¹H NMR and 77.63 ppm for ¹³C NMR. High resolution mass spectra were measured by MALDI-FT MS. Absorption spectra were taken on a Hitachi U-3010 UV-vis spectrophotometer. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere on Shimadzu thermogravimetric analyzer (model DTG-60) at heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurement was recorded on METTLER differential scanning calorimeter (DSC822e) under nitrogen at heating rate of 10 °C/min. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation. A Pt disk was taken as the working electrode, Pt wire as the counter electrode, and Ag/Ag⁺ electrode (0.01 M AgNO₃, 0.09 M NBu₄PF₆ in acetonitrile) as the reference electrode. A solution of *o*-dichlorobenzene: acetonitrile (V:V = 5:1) with 0.1 M tetrabutylammonium hexafluorophosphate (NBu₄PF₆) was used as electrolyte, and the scan rate was fixed at 100 mV s⁻¹. The optical microscope images were taken on polarized optical microscope (POM) OLYMPUS BX51.

Synthesis and separation of IC₆₀BA isomers

Indene (2.32 g, 20 mmol) and C₆₀ (1.44 g, 2 mmol) were dissolved in 60 mL of *o*-dichlorobenzene. Then the solution was heated to 180 °C and refluxed for 12 h. Subsequently, the reaction mixture was subjected to silica column. The unreacted C₆₀, indene-C₆₀ monoadduct (IC₆₀MA), and IC₆₀BA were separated and purified by silica gel column chromatography with 10% toluene in hexane several times. A total of 410 mg IC₆₀MA (yield 22%) and 680 mg IC₆₀BA mixture (yield 35.6%) were obtained. Then the obtained IC₆₀BA mixture was subjected to HPLC with Cosmosil® Buckyprep-D column (4.6 ID × 250 mm) and COSMOSIL 5PBB column (10 x 250 mm), getting fraction 1 (F1, trans-2, 10mg), F2 (trans-2, 25mg), F3 (trans-2, 20mg), F4 (trans-3, 120mg), F5 (trans-4, 80mg), F6 (e, 40mg). The six fractions were further purified with COSMOSIL 5PBB column (10 x 250 mm) column under recycle mode. However, only F6 was successfully separated into e1 (18mg) and e2 (18mg). The isomers in other fractions were too close to separate from each other.

UV-Vis absorption spectra of IC₆₀BA isomers

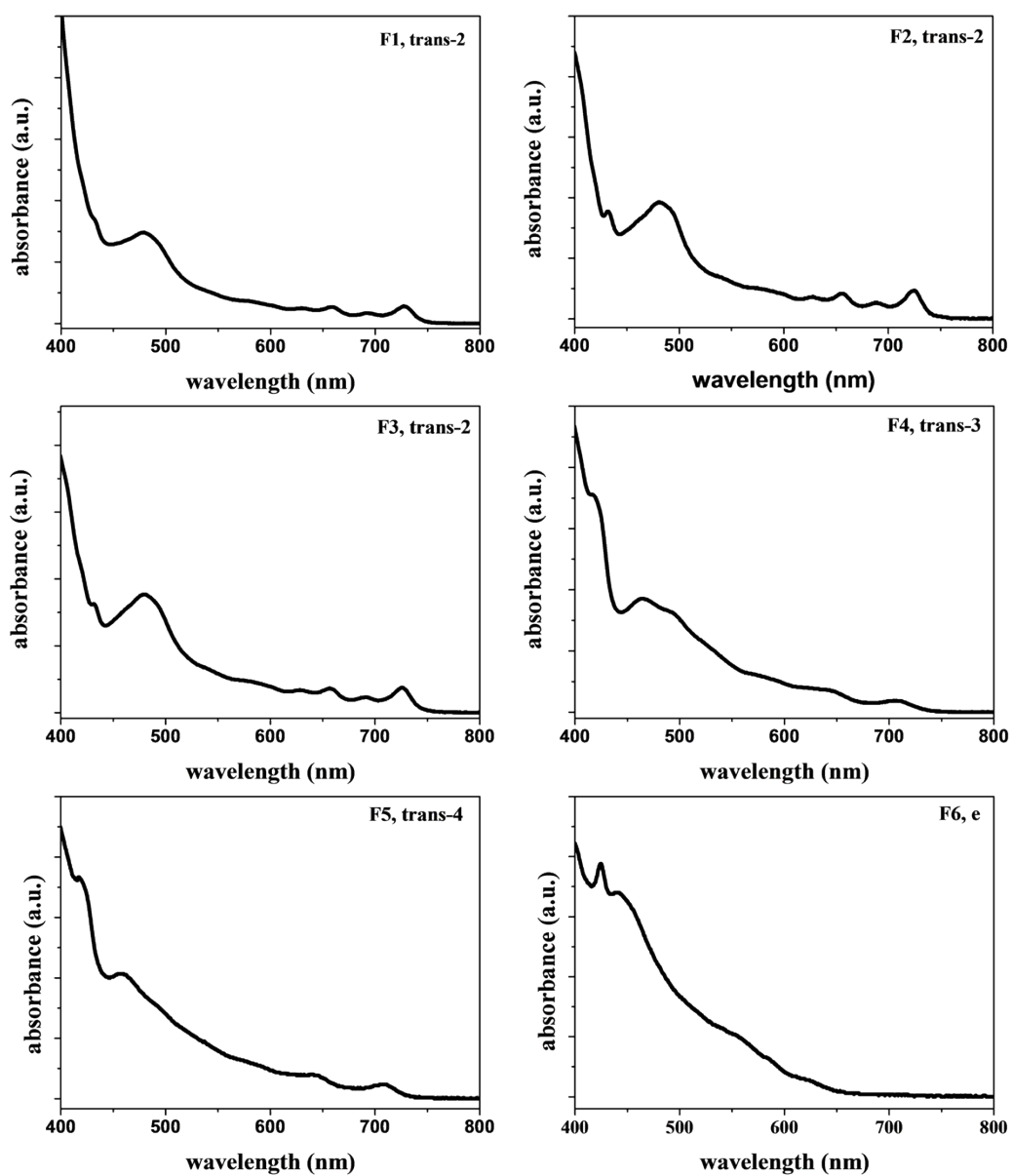


Figure S1 UV-Vis absorption spectra of IC₆₀BA isomers in toluene (10⁻⁴ mol/L).

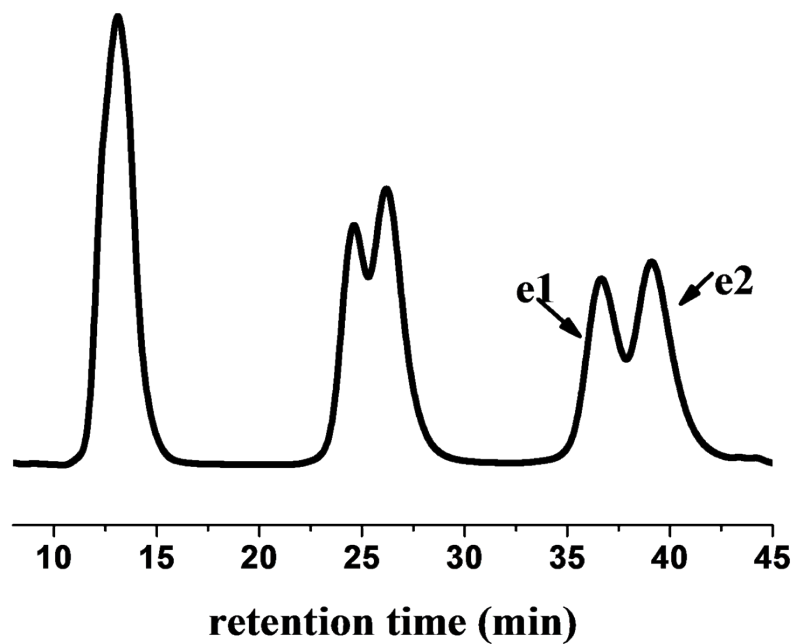


Figure S2 HPLC chromatography of e1 and e2. Conditions: COSMOSIL 5PBB column (10 x 250 mm); eluent, toluene; flow rate, 3 mL min⁻¹; detection, UV 350 nm; recycle, three times.

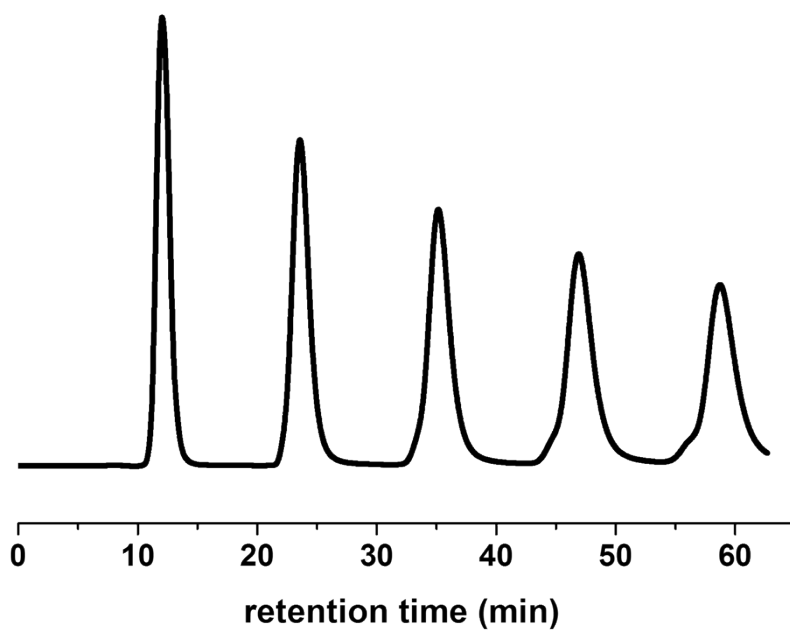


Figure S3 HPLC chromatography of trans-3. Conditions: COSMOSIL 5PBB column (10 x 250 mm); eluent, toluene; flow rate, 3 mL min⁻¹; detection, UV 350 nm; recycle, five times.

Characterization data for e1

^1H NMR (400 MHz, CDCl_3 , δ): 7.26-7.47 (m, 8H, Ar), 4.58 (d, $J = 1.15$ Hz, 1H, CH), 4.58 (d, $J = 1.15$ Hz, 1H, CH), 4.52 (d, $J = 1.13$ Hz, 1H, CH), 4.00 (d, $J = 0.87$ Hz, 1H, CH), 3.55 (d, $J = 9.99$ Hz, 1H, CH_2), 3.32 (d, $J = 9.95$ Hz, 1H, CH_2), 2.69 (d, $J = 9.99$ Hz, 1H, CH_2), 2.50 (d, $J = 9.96$ Hz, 1H, CH_2). ^{13}C NMR (600 MHz, CDCl_3 , δ): 161.25, 159.79, 155.16, 154.36, 154.30, 154.24, 154.07, 153.75, 149.94, 149.38, 148.27, 148.19, 148.08, 147.73, 147.47, 147.32, 147.20, 146.93, 146.85, 146.53, 146.39, 146.25, 146.19, 145.61, 145.28, 145.11, 144.89, 144.22, 143.89, 143.77, 143.70, 143.56, 143.18, 142.96, 142.77, 142.65, 141.86, 141.68, 141.56, 140.59, 137.54, 137.40, 137.24, 131.15 (forest of peaks belonging to sp^2 carbons on the fullerene cage, Figure S5), 129.63, 128.82, 128.30, 127.79, 127.73, 127.67, 124.50, 124.41 (sp^2 carbons on the indene addends), 75.40, 75.26, 74.93, 74.83, 58.66, 58.46, 57.81, 47.07, 45.92 (sp^3 carbons on the indene addends and C_{60} cage). MALDI-FT-MS (m/z): calcd. for $\text{C}_{78}\text{H}_{16}$, 952.125749; found M^+ , 952.126065.

Characterization data for e2

^1H NMR (400 MHz, CDCl_3 , δ): 7.30-7.54 (m, 8H, Ar), 4.61 (s, 1H, CH), 4.56 (s, 1H, CH), 4.51 (s, 1H, CH), 4.43 (s, 1H, CH), 3.48 (d, $J = 11.12$ Hz, 1H, CH_2), 3.26 (d, $J = 9.83$ Hz, 1H, CH_2), 2.62-2.67 (m, 2H, CH_2). ^{13}C NMR (600 MHz, CDCl_3 , δ): 161.34, 159.82, 155.66, 155.47, 154.12, 153.40, 153.16, 150.32, 149.55, 148.68, 148.52, 148.44, 148.23, 147.92, 147.74, 147.57, 147.17, 147.05, 146.94, 146.79, 146.58, 146.56, 146.38, 146.24, 146.17, 146.06, 145.77, 145.52, 145.47, 145.25, 145.15, 145.10, 144.97, 144.72, 144.30, 143.83, 143.54, 143.49, 143.45, 143.09, 143.05, 142.85, 142.65, 142.56, 142.19, 142.04, 141.84, 140.80, 140.72, 137.41, 137.21, 136.76, 136.67 (forest of peaks belonging to sp^2 carbons on the fullerene cage, Figure S7), 129.64, 128.83, 127.69, 127.56, 127.50, 127.42, 125.90, 124.40, 124.32, 124.22 (sp^2 carbons on the indene addends), 75.32, 75.20, 74.60, 74.49, 58.82, 58.76, 58.55, 57.65, 47.68, 45.80 (sp^3 carbons on the indene addends and C_{60} cage), MALDI-FT-MS (m/z): calcd. for $\text{C}_{78}\text{H}_{16}$, 952.125749; found M^+ , 952.125845.

Characterization data for trans-3

^1H NMR (400 MHz, CDCl_3 , δ): 7.17-8.19 (m, 8H, Ar), 4.47-5.13 (m, 4H, CH), 3.80 (t, $J = 10$ Hz, 1H, CH_2), 3.34 (dd, $J = 76.5, 9.9$ Hz, 1H, CH_2), 2.85 (dd, $J = 28.2, 21.4$ Hz, 1H, CH_2), 2.66 (dd, $J = 31.1, 9.6$ Hz, 1H, CH_2). ^{13}C NMR (600 MHz, CDCl_3 , δ): 160.49-133.09 (forest of peaks belonging to sp^2 carbons on the fullerene cage, Figure S9), 129.64, 128.82, 127.89, 127.73, 127.67, 127.57, 125.90, 124.76, 124.73, 124.59, 124.56, 124.22, 124.16, 124.12 (sp^2 carbons on the indene addends), 75.31, 75.03, 58.85, 58.63, 57.80, 46.62 (sp^3 carbons on the indene addends and C_{60} cage), MALDI-FT-MS (m/z): calcd. for $\text{C}_{78}\text{H}_{16}$, 952.125749; found M^+ , 952.126043.

^1H NMR and ^{13}C NMR spectra of e1, e2 and trans-3

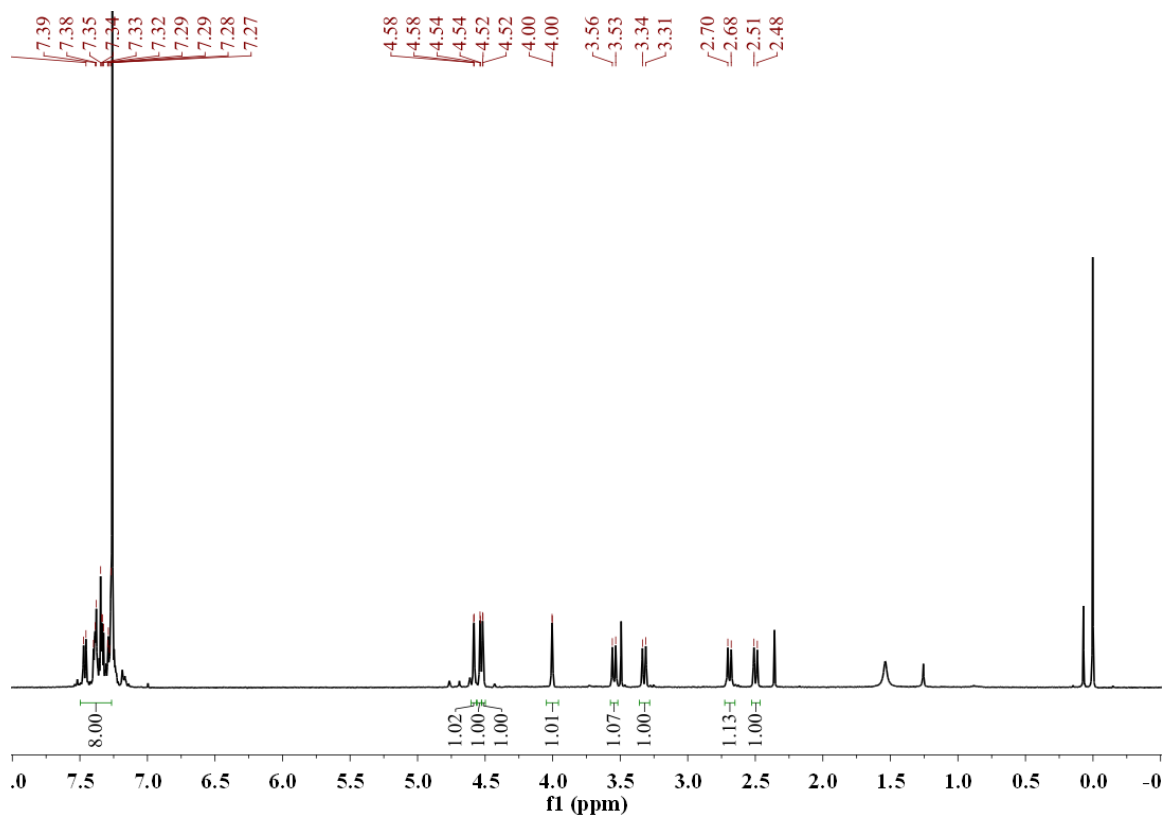


Figure S4 ^1H NMR spectrum of e1 in CDCl_3 .

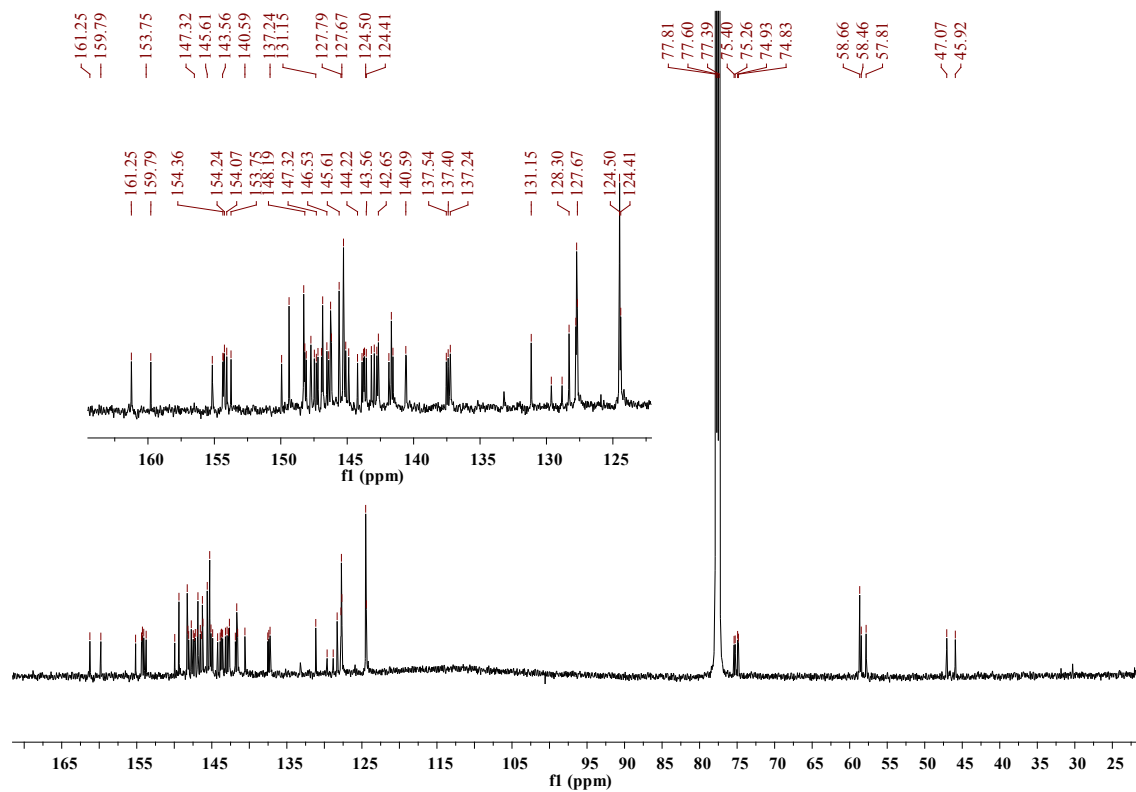


Figure S5 ^{13}C NMR spectrum of e1 in CDCl_3 .

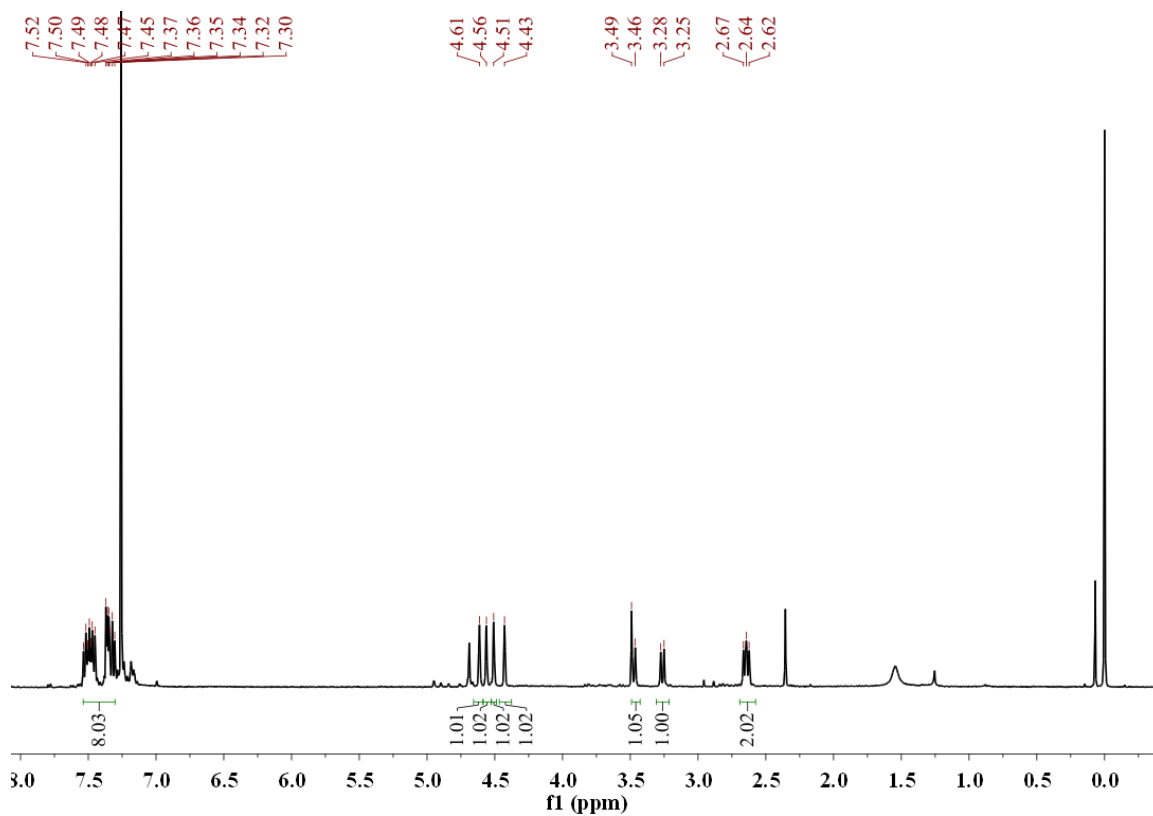


Figure S6 ^1H NMR spectrum of e2 in CDCl_3 .

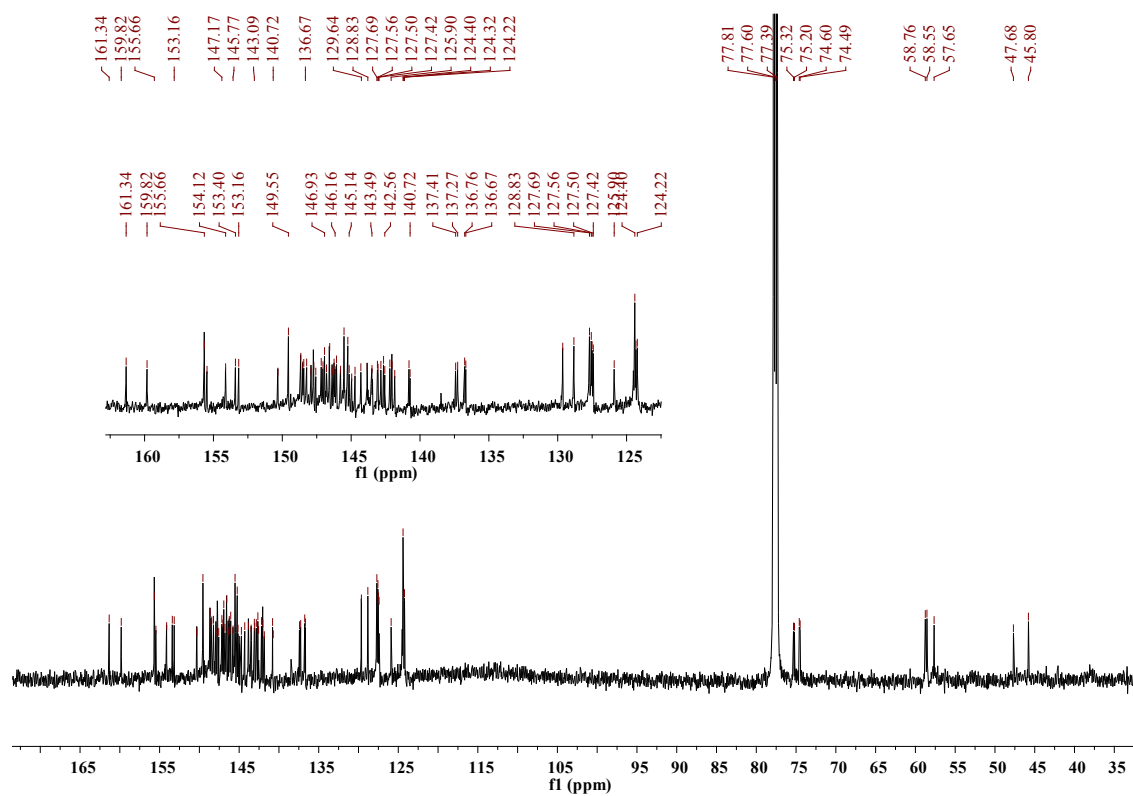


Figure S7 ^{13}C NMR spectrum of e2 in CDCl_3 .

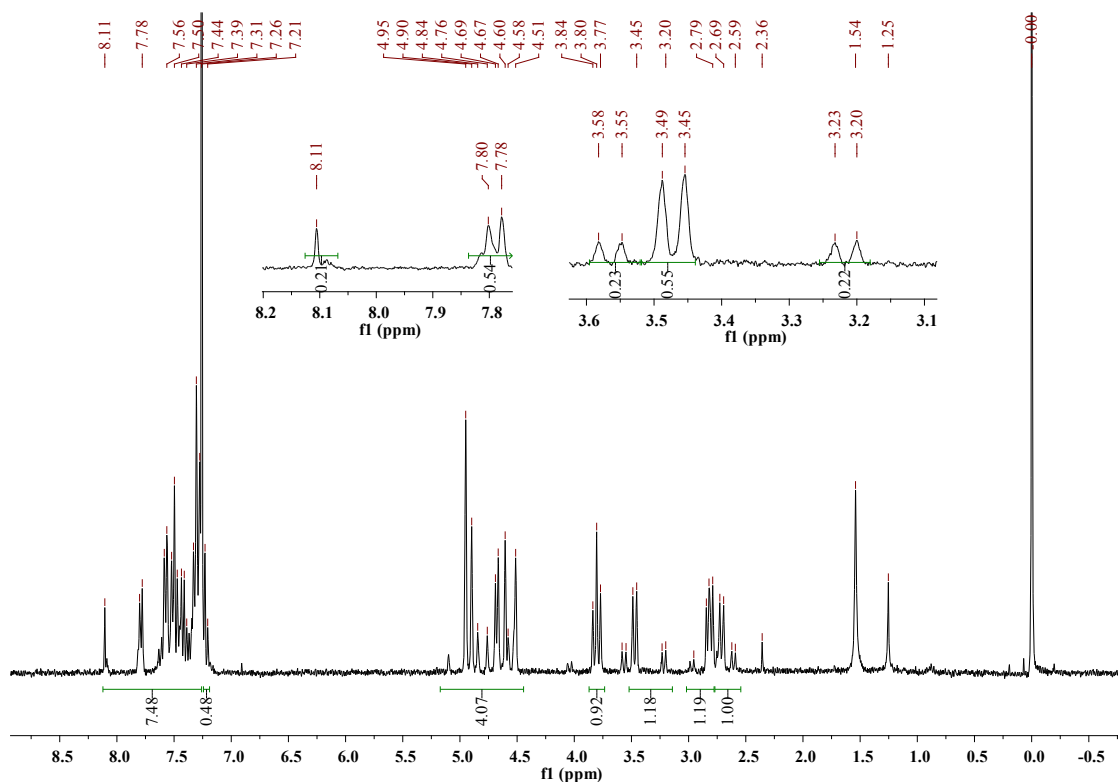


Figure S8 ^1H NMR spectrum of trans-3 in CDCl_3 .

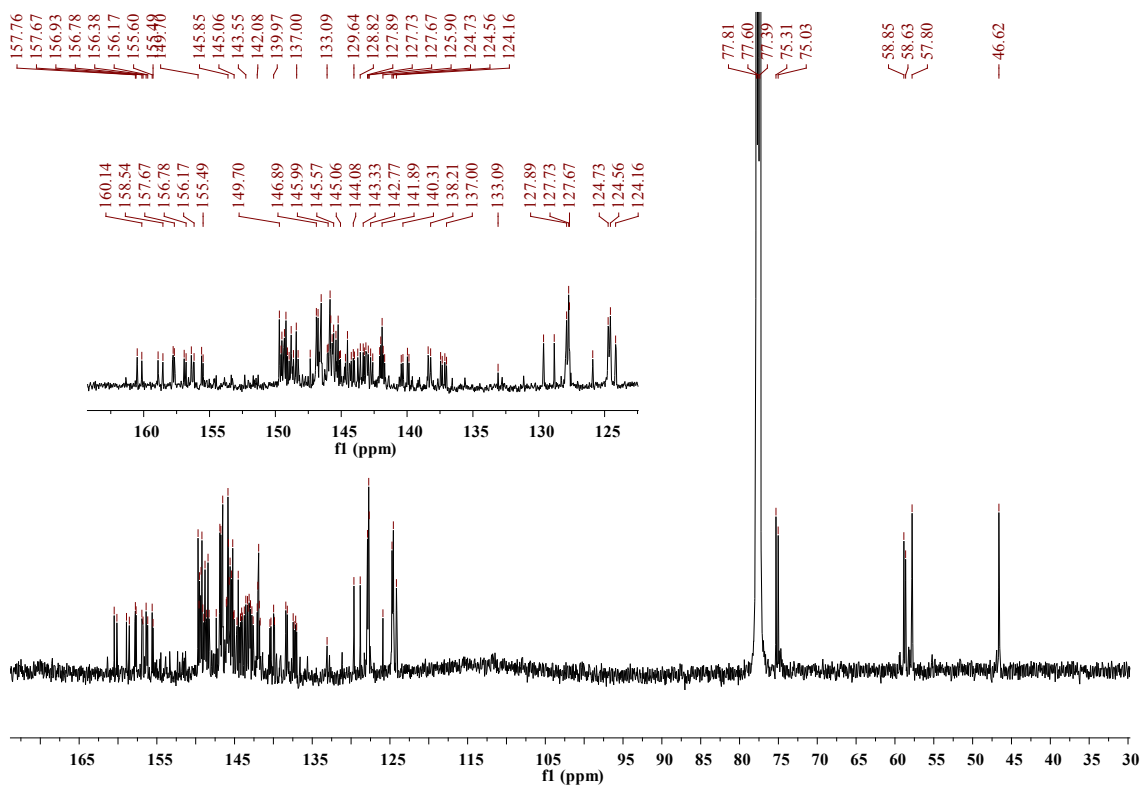


Figure S9 ^{13}C NMR spectrum of trans-3 in CDCl_3 .

Mass spectra of e1, e2 and trans-3

MALDI(N),E1,20150524

Analysis Info

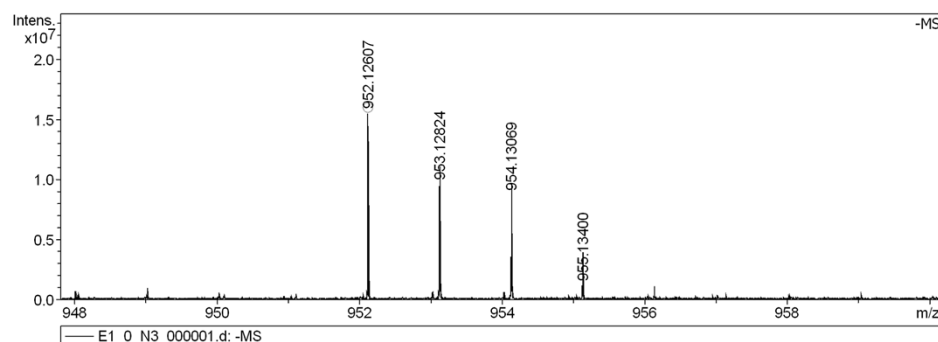
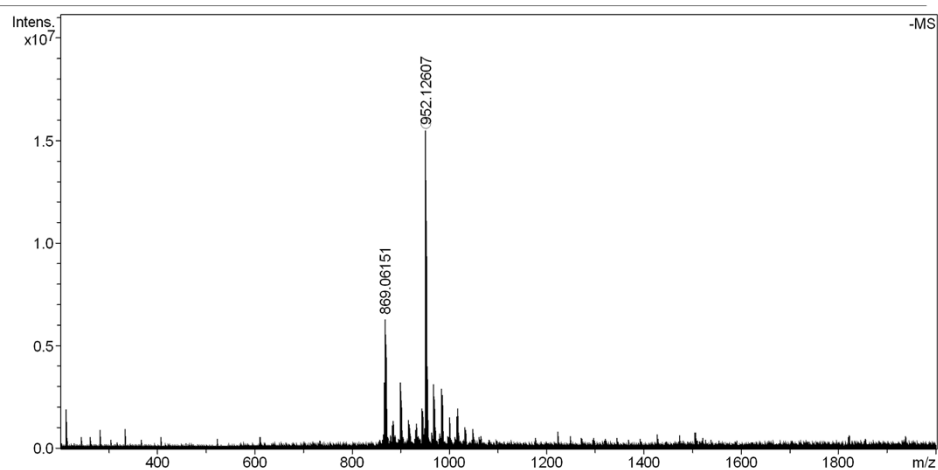
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Operator
Instrument solarix

Acquisition Parameter

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Broadband High Mass	2000.0 m/z	Laser Power	27.6 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
952.126065	1	C78H16	100.00	952.125749	0.3	0.4	115.9	71.0	odd	ok

Figure S10 High resolution MALDI mass spectrum of e1.

MALDI(N),E2,20150524

Analysis Info

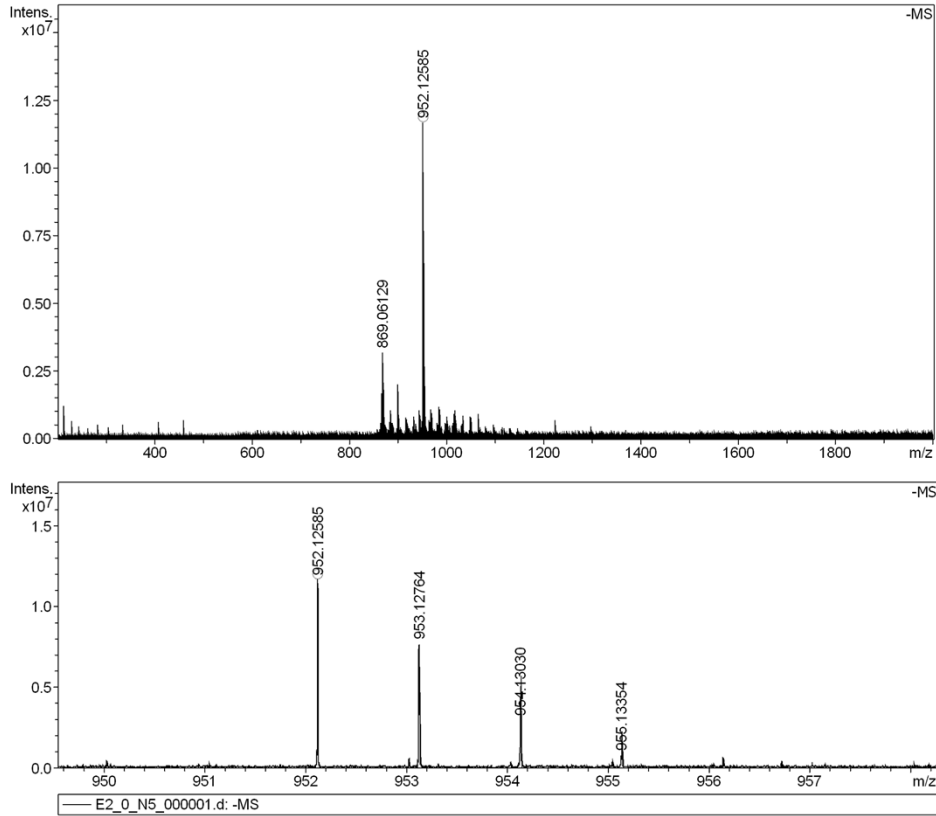
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Operator
Instrument solariX

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Broadband High Mass	2000.0 m/z	Laser Power	27.6 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule	
952.125845	1	C78H16	100.00	952.125749	-0.1		0.8	96.2	71.0	odd	ok

Figure S11 High resolution MALDI mass spectrum of e2.

MALDI(N),Tran-3,20150524

Analysis Info

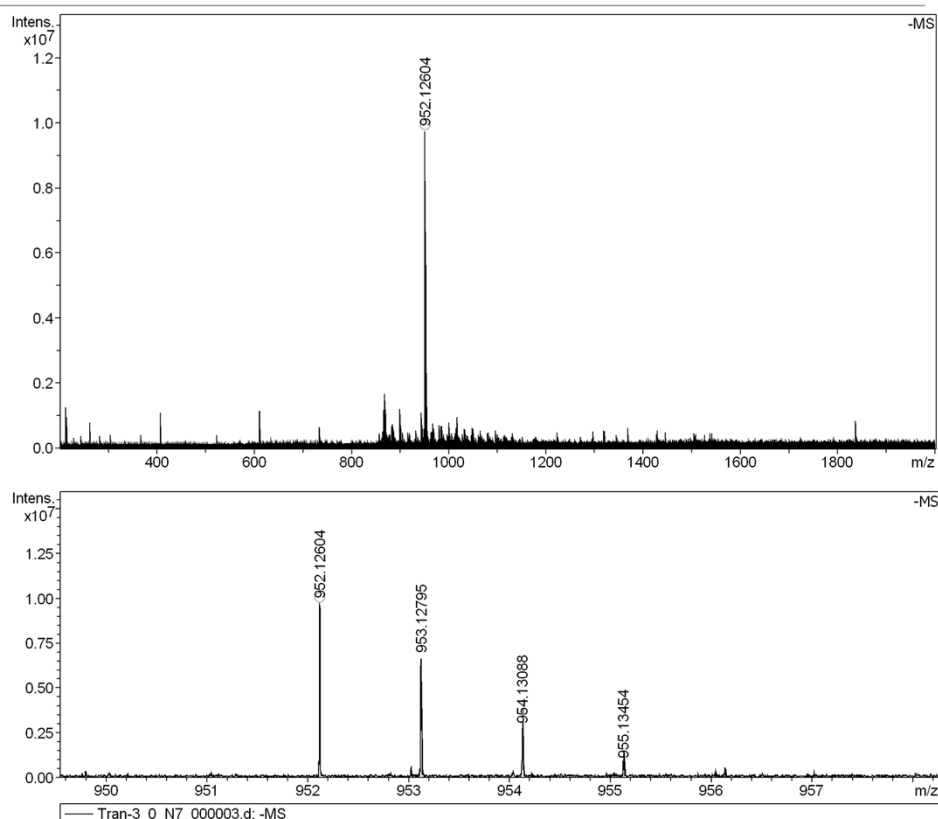
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Comment

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Operator
Instrument solarix

Acquisition Parameter

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Broadband High Mass	2000.0 m/z	Laser Power	28.4 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
952.126043	1	C ₇₈ H ₁₆	100.00	952.125749	0.3	0.5	78.4	71.0	odd	ok

Figure S12 High resolution MALDI mass spectrum of trans-3.

Experimental and data for X-ray crystallography

Intensity data were collected with Saturn724+ CCD diffractometer using Mo-K α radiation, the temperature during data collection was maintained at 173.1500 K.

Crystal data for e1 IC₆₀BA, C₇₈H₁₆, M=952.91, T=173.1500 K, λ =0.71073 Å, Monoclinic, Space group C 2/c, a = 25.122(5) Å, b = 18.297(3) Å, c = 21.244(5) Å, α = 90°, β = 114.378(3)°, γ = 90°, V=8894(3) Å³, Z=8, D(cal)= 1.423 mg/m³, F(000)= 3872, Crystal size 0.34 x 0.34 x 0.07 mm³, 32560 reflections collected, 10148 Independent reflections (R(int) = 0.0617) and the final R was 0.0824 [$I > 2\sigma(I)$] and wR(F2) was 0.1088 (all data).

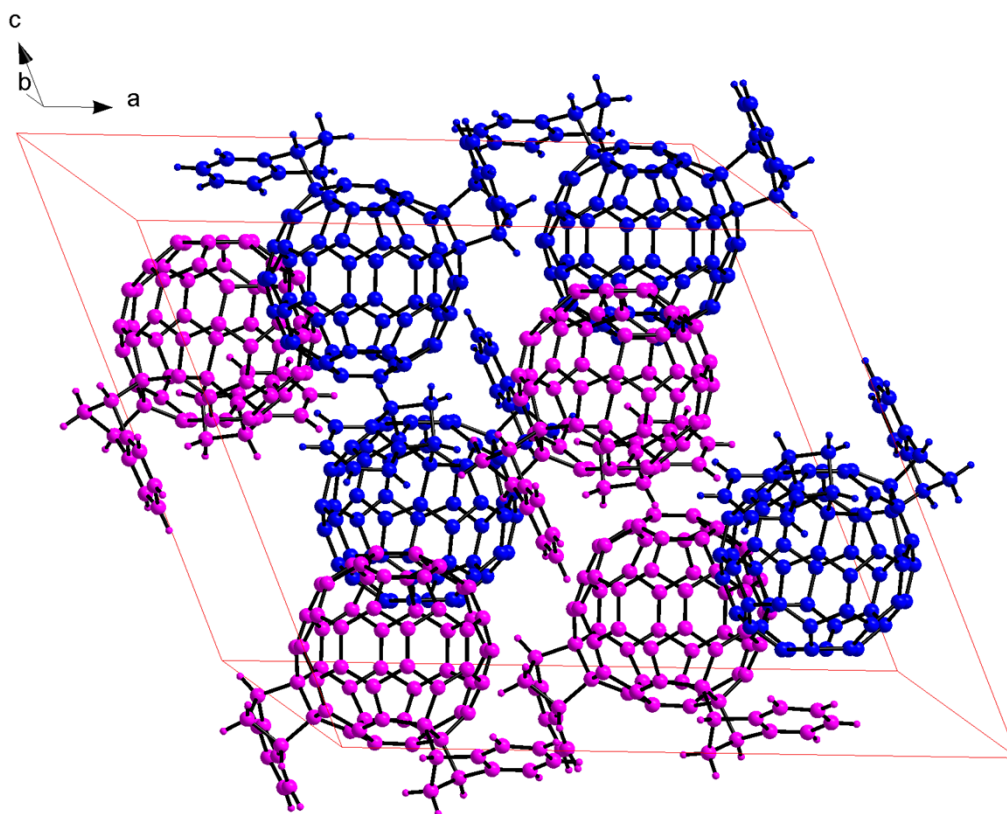


Figure S13 Single crystal cell of e1 (blue molecules are L while red are R).

The measured TGA and DSC curves of e1, e2 and trans-3

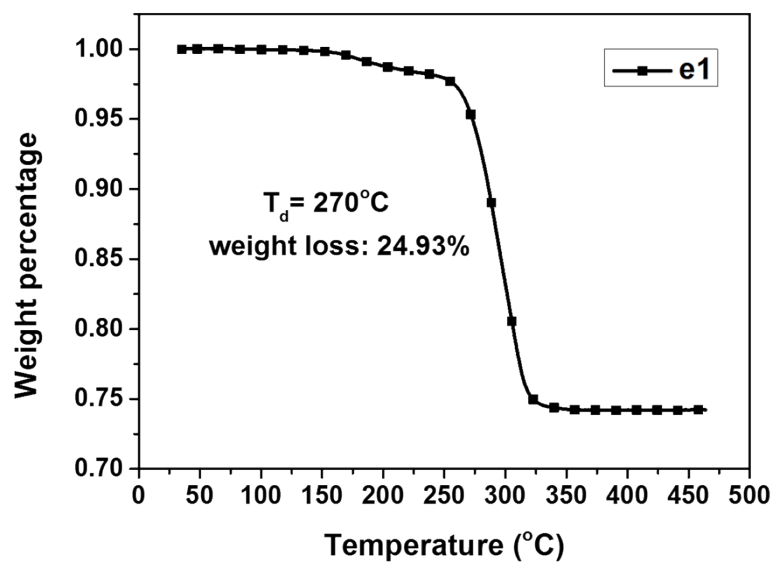


Figure S14 The measured TGA curve of e1.

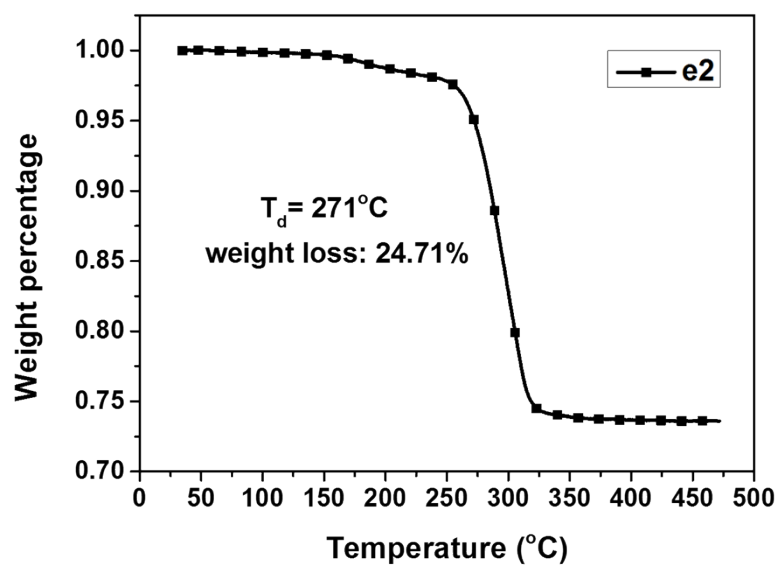


Figure S15 The measured TGA curve of e2.

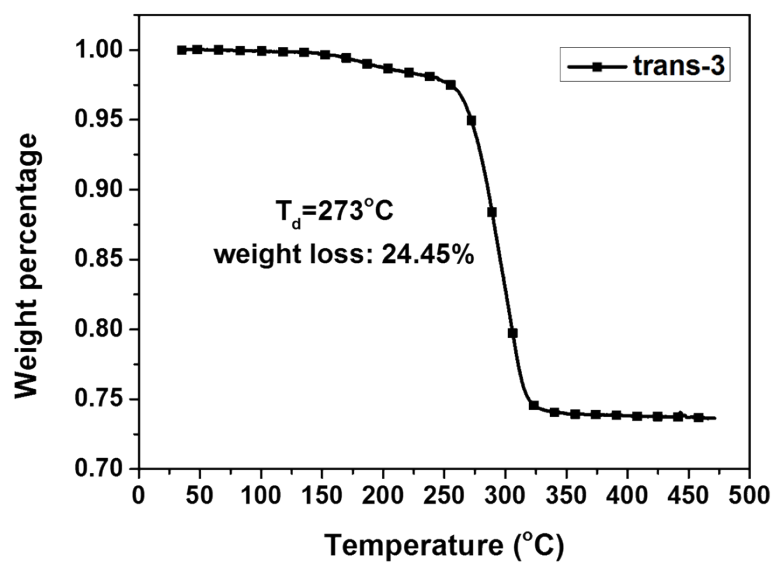


Figure S16 The measured TGA curve of trans-3.

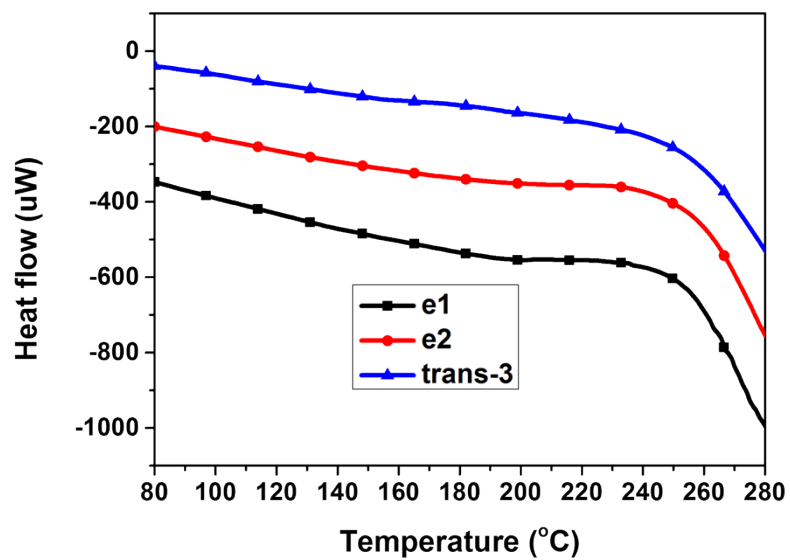


Figure S17 The measured DSC curve of e1, e2 and trans-3.

Electrochemical data

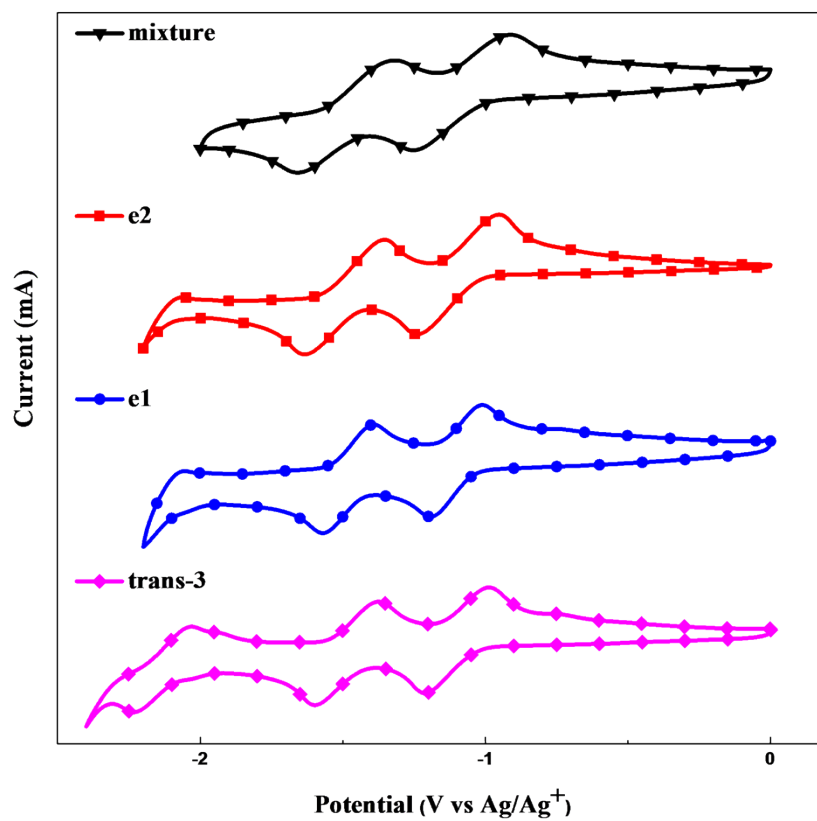


Figure S18 Cyclic voltammetry of the IC₆₀BA isomers in *o*-dichlorobenzene: acetonitrile (V:V = 5:1) with 0.1 M NBu₄PF₆ at 100 mV s⁻¹.

Device fabrication and characterisation

Fabrication and Characterization of PSCs: The PSCs were fabricated in the configuration of the traditional sandwich structure ITO/PEDOT:PSS/P3HT:IC₆₀BA/Ca/Al. 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 PVPAl4083, Germany) was filtered through a 0.45 μm filter and spin coated at 2500 rpm for 35 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 *o*-dichlorobenzene (ODCB) (total concentration is 34 mg mL⁻¹, weight ratio of P3HT: acceptor is 1:1) was spin-coated on the PEDOT:PSS layer. The blend films were then put into glass petridishes while still wet to undergo solvent annealing process. The thickness of the photoactive layer was estimated by Surface Profiler in the range of 180–240 nm. The device was annealed at 150 °C for 10 min. 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. 10⁻⁵ Pa. The device active area of the PSCs is ca. 4 mm². 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 AM 1.5G 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 500 W xenon lamp. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

The space charge limited current (SCLC) of IC₆₀BA isomers were studied using electron-only devices to find the charge-transport properties. The electron-only devices, consisting of active layer sandwiched between a ZnO coated ITO electrode and LiF/Al counter-electrode as the hole-blocking contact, were fabricated. From the current density as a function of voltage data, the electron mobility in the trap-free space-charge limited current (SCLC) region can be estimated using the Mott-Gurney equation:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3}$$

where ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the material, μ is the charge-carrier mobility, V is the effective voltage, $V = V_{\text{appl}} - V_{\text{bi}}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential which results from the difference in the work function of the anode and the cathode, and d is the sample thickness. Using this expression, the electron mobility of the IC₆₀BA isomers were calculated.

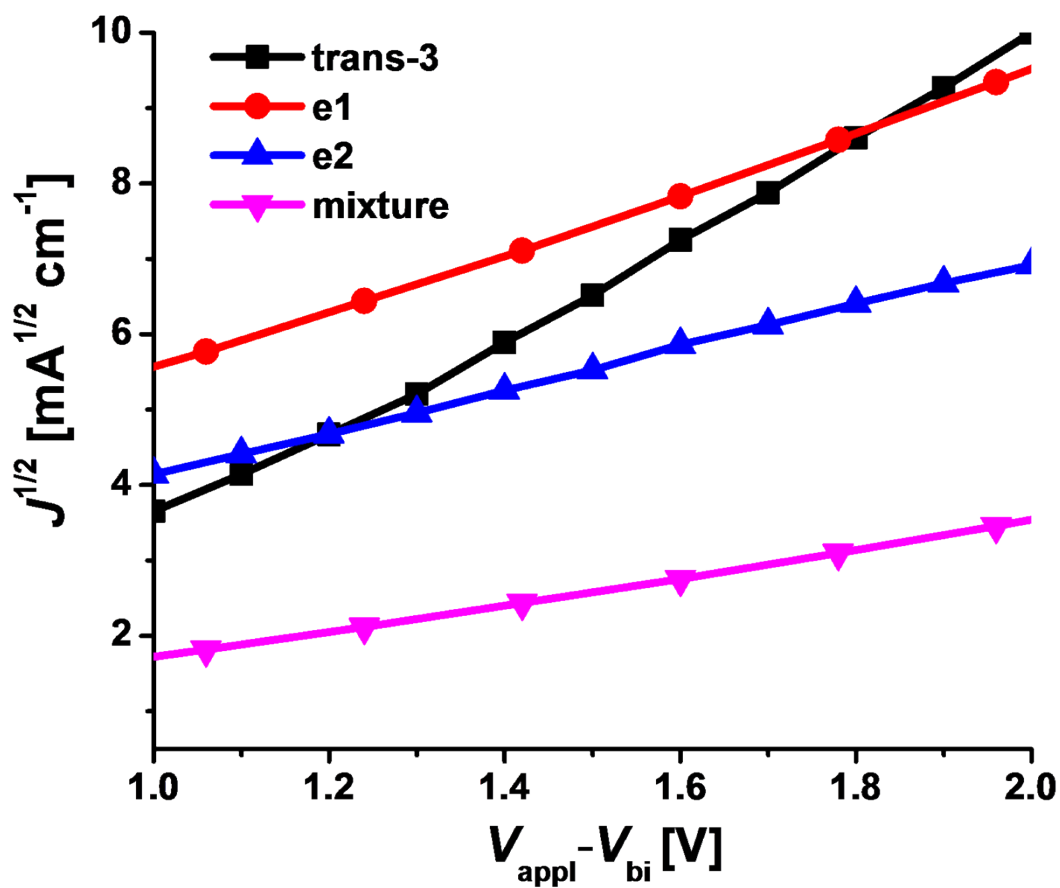


Figure S19 the $J^{1/2}$ - V curves for electron-only devices of P3HT:IC₆₀BA isomers.

Table S1 Space charge limited current (SCLC) mobility of IC₆₀BA measured in electron-only devices.

	Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
trans-3	3.1×10^{-4}
e1	7.7×10^{-5}
e2	8.2×10^{-5}
mixture	4.5×10^{-5}

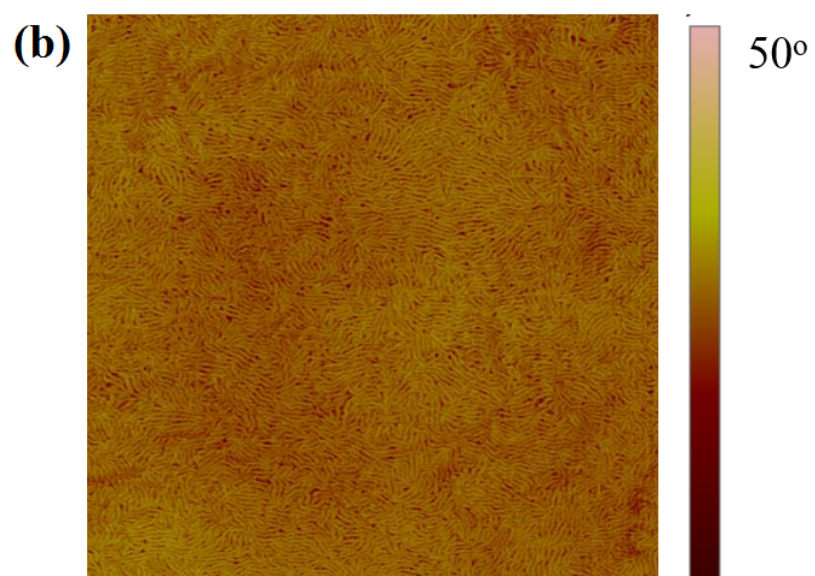
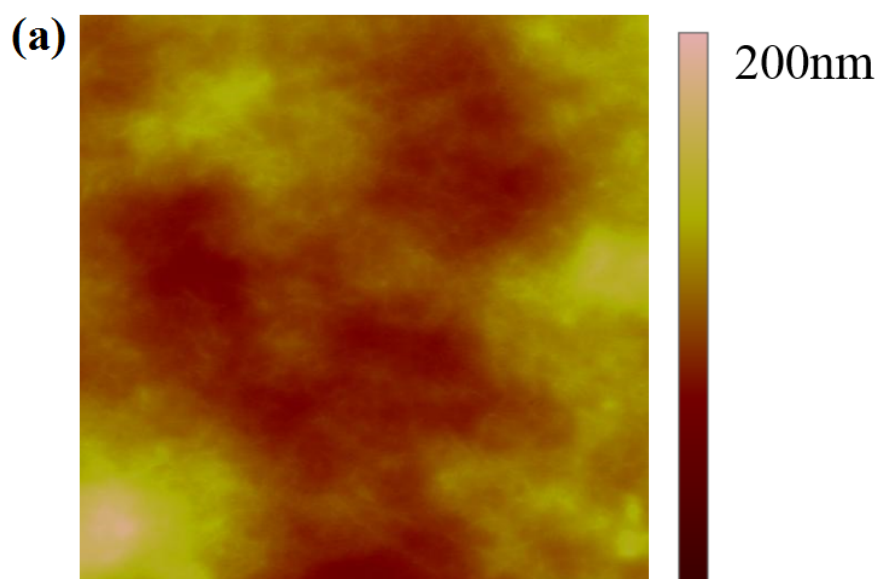


Figure S20 AFM height images (a) and phase images (b) of P3HT:mixture blend film ($3\mu\text{m} \times 3\mu\text{m}$).