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Supplementary Information for

Single *cis*-2 regioisomer of ethylene-tethered indene dimer–fullerene adduct as an electron-acceptor in polymer solar cells

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Experimental

Instruments. Fullerene derivative isomers separation was accomplished by Shimadzu Prominence Modular HPLC with Nacalai Tesque cosmosil buckyprep. ^{1}H NMR and ^{13}C NMR spectra were measured with a JEOL JNM-EX400 NMR spectrometer. High-resolution mass spectra were measured on a JEOL JMS-700 MStation spectrometer. Attenuated total reflectance (ATR) FT-IR spectra were recorded on a ThermoFisher Scientific Nicolet 6700 FT-IR. UV-Vis absorption spectra were obtained on a Perkin Elmer Lambda 900 UV/vis/NIR spectrometer. Single-crystal X-ray diffraction analysis data for compound *cis*-2-BIEC were collected at –150 °C on a Rigaku Saturn70 CCD diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71069 Å). The structures were solved by direct method (SHELXS-2014). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed using an ALS 630A electrochemical analyzer in *o*-dichlorobenzene/acetonitrile mixture (v:v=5:1) containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4PF_6) as a supporting electrolyte. Thermogravimetric analysis (TGA) measurements were conducted with a SHIMADZU DTG-60 under flowing nitrogen at a scan rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) analysis was made on a SHIMAZU DSC-60 under flowing nitrogen at a scan rate of 10 °C min^{-1}. Atomic force microscopy (AFM) analyses were carried out with an Asylum Technology MFP-3D-SA in the AC mode. Photoluminescence (PL) spectra were recorded with a HORIBA SPEX Fluoromax-3 spectrofluorometer.

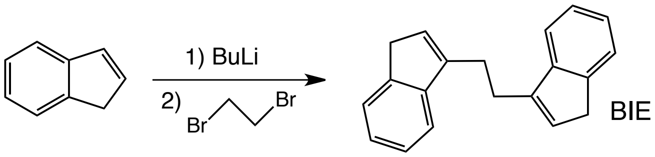
Grazing incidence wide-angle X-ray scattering (GI-WAXS) measurements were conducted at the SPring-8 on beamline BL46XU. The sample was irradiated at a fixed incident angle on the order of 0.12° through a Huber diffractometer with an X-ray energy of 12.40 keV (λ = 1

Å), and the GI-WAXS patterns were recorded with a 2-D image detector (Pilatus 300K). Samples for the X-ray measurements were prepared by spin-coating the P3HT:fullerene solution on the ITO/PEDOT:PSS substrate. Solvent and thermal annealing was cunducted after the spin-coating.

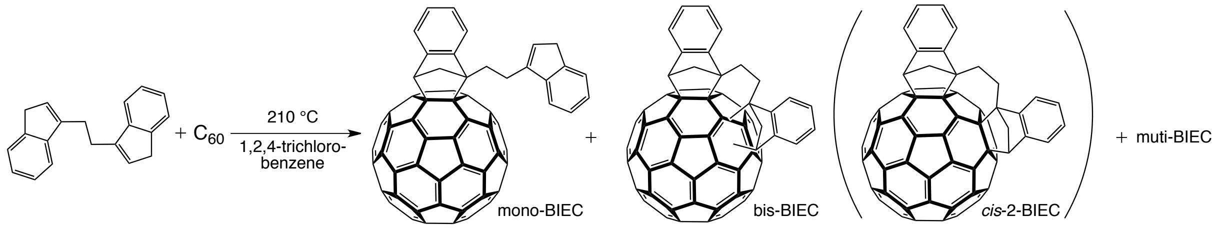
Photocurrent-voltage characteristics were measured by Keithley 2400 SourceMeter under an argon atmosphere and simulated solar light (100 mW cm^{-2}, AM1.5) with OTENTO-SUN III solar simulator (Bunkoukeiki). Photocurrent action spectra were recorded with CEP-2000RR (Bunkoukeiki). Current–voltage characteristics of the electron-only devices for space-charge-limited current (SCLC) measurements were conducted using Keithley 2400 SourceMeter under an argon atmosphere.

Materials. C_{60} (99.98%) was obtained from MTR Ltd. and used as-received. All other solvents and chemicals were of reagent-grade quality, purchased commercially, and used without further purification unless otherwise noted. Thin layer chromatography (TLC) and column chromatography were performed with Silica gel 60 F_{254} (Merck) and SiliaFlash F60 (230–400 mesh; SiliCycle Inc.), respectively.

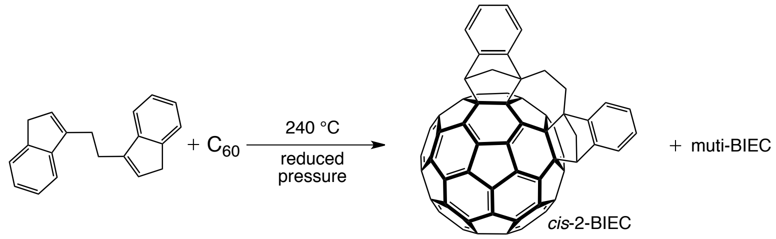
Synthesis.



1,2-Bis(3-indenyl)ethane (BIE): BIE was synthesized acrording to a literature procedure[S1] with slight modifications. 4Å molecular sieves (0.5 g) were add into 300-mL flask and activated with flame under vacuum. Then indene (13.9 g, 120 mmol) and dry THF (150 mL) were added via syringe under argon atmosphere and the mixture were cooled to –78°C. *n*-Butylllithium (1.6 M solution in hexane, 78 mL, 125 mmol) was injected dropwise. The solution turned orange and a precipitate formed. Neat 1,2-dibromoethane (4.8 mL, 55 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for 3 h. The reaction was quenched by adding aqueous NH_4Cl (50 mL). The mixture was filtrated and washed with petroleum ether. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. Crystallization from acetone and ethanol provided light yellow powder (6.6 g, 43%). ^{1}H NMR (acetone-d_6, 400 MHz): δ 7.46 (t, 4H), 7.29 (t, 2H), 7.19 (t, 2H), 6.36 (s, 2H), 3.34 (s, 4H), 2.97 (s, 4H). ^{13}C NMR (acetone-d_6, 400 MHz): δ 146.19, 145.30, 141.51, 128.81, 126.81, 125.37, 124.51, 119.68, 38.20, 26.96. IR (ATR): ν_{max}/cm^{-1} 3058, 3015, 2896, 2838, 1605, 1573, 1460, 1439, 1394, 1246, 1231, 1167, 1120, 1053, 1013, 965, 920, 799, 765, 735, 712. HRMS (APCI): calcd for $C_{20}H_{18}$[M+H] 259.1481, found 259.1479.



Bis(3-indenyl)ethane–C_{60} adducts (BIEC): BIE (0.80 g, 3.1 mmol) and C_{60} (2.4 g, 3.3 mmol) were dissolved in 1,2,4-trichlorobenzene (120 mL) and stirred at 210°C for 48 h under argon atmosphere. Subsequently, the reaction mixture was poured into CH_3OH (600 mL) and filtrated. The residue was dissolved with CS_2 and absorbed on silica gel. The unreacted C_{60}, mono-BIEC (57.4 mg, yield 2%), bis-BIEC (1.7 g, yield 58%), and multi-BIEC were eluented in this order by silica gel column chromatography with hexane/CS_2 = 2/1. bis-BIEC was a mixture of regioisomers and three components were further isolated by preparative HPLC equiped with Buckyprep columns. The ratio of the three fractions was 10 : 83 : 7 according to the sequence of elution. The second component was collected and characterized as *cis*-2-BIEC (1.4 g, yield 48%). The characterizations of the first and third components were not conducted due to the low yields.



cis-2-BIEC was also synthesized by a slovent-free procedure as follows. The vessel loaded with BIE (0.26 g, 1.0 mmol) and C_{60} (0.79 g, 1.1 mmol) was vacuumed and then heated at 240 °C for 2.5 h. The reaction mixture was cooled down and dissolved with CS_2. The unreacted C_{60}, *cis*-2-BIEC, and multi-BIEC were eluented in this order by silica gel column chromatography with hexane/toluene = 2/1. 95.8 mg of *cis*-2-BIEC was obtained (yield 10%).

cis-2-BIEC: ^{1}H NMR ($C_2D_2Cl_4$, 400 MHz): δ 7.58 (d, 1H), 7.29-7.08 (m, 7H), 4.47 (s, 1H), 4.26 (s, 1H), 3.45 (d, 1H), 3.36 (t, 1H), 3.11 (d, 1H), 3.06 (m, 1H), 2.93 (t, 1H), 2.79 (m, 1H), 2.47 (d, 1H), 2.29 (d, 1H). ^{13}C NMR ($C_2D_2Cl_4$, 400 MHz): δ 160.71, 159.94, 156.32, 149.76, 149.03, 148.77, 148.67, 148.06, 148.00, 147.92, 147.58, 147.46, 147.39, 147.24, 147.10, 147.01, 146.69, 146.56, 146.46, 146.13, 146.02, 145.91, 145.83, 145.74, 145.49, 145.31, 145.21, 145.12, 145.07, 144.96, 144.94, 144.83, 144.69, 144.46, 144.38, 144.15, 143.95, 143.88, 143.82, 143.70, 142.78, 142.67, 141.85, 141.11, 140.37, 139.81, 139.40, 135.81, 134.27, 133.69, 133.01, 131.33, 127.24, 127.05, 126.60, 126.47, 124.67, 123.03, 122.15, 120.82, 120.72, 120.18, 73.30, 73.22, 72.47, 71.67, 64.24, 64.02, 56.24, 54.36, 52.79, 48.51, 28.63, 25.26. IR (ATR): ν_{max}/cm^{-1} 2911, 2842, 1454, 1431, 1419, 1266, 1186, 1153, 1121, 1100, 1075, 1025, 968, 932, 860, 740. HRMS (ESI): calcd for $C_{80}H_{18}$[M+H] 979.1481, found 979.1470.

mono-BIEC: ^{1}H NMR ($C_2D_2Cl_4$, 400 MHz): δ 7.57 (d, 1H), 7.49 (d, 1H), 7.43-7.37 (m, 4H), 7.28 (t, 1H), 7.17 (t, 1H), 6.39 (s, 1H), 4.91 (s, 1H), 3.61 (d, 1H), 3.36 (m, 1H), 3.32 (s, 1H), 3.12-2.92 (m, 3H), 2.98 (d, 1H). ^{13}C NMR ($C_2D_2Cl_4$, 400 MHz): δ 156.94, 155.23, 154.14, 147.07, 146.64, 146.26, 146.17, 146.15, 146.01, 145.77, 145.74, 145.67, 145.32, 145.28, 145.24, 145.22, 145.17, 145.03, 145.02, 145.00, 144.90, 144.77, 144.52, 144.47, 144.45, 144.23, 144.19, 144.09, 142.94, 142.64, 142.54, 142.50, 142.36, 142.10, 142.08, 142.00, 141.96, 141.91, 141.87, 141.77, 141.59, 141.55, 140.01, 139.59, 139.54, 139.28, 137.52, 137.27, 137.19, 137.06, 128.39, 127.30, 127.26, 126.20, 124.78, 124.27, 124.00, 123.08, 118.99, 78.91, 77.11, 65.31, 56.68, 48.10, 37.81, 31.41, 28.97, 24.58, 22.52, 14.07. IR (ATR): ν_{max}/cm^{-1} 2914, 2848, 1509, 1457, 1424, 1391, 1284, 1181, 1152, 1037, 1011, 961, 931, 910, 761, 745, 710. HRMS (ESI): calcd for $C_{80}H_{18}$[M+H] 979.1481, found 979.1493.

Quantum Chemical Calculation. Geometry optimization and electronic structure calculations for the fullerene compounds were performed using density functional theory (DFT) at the RB3LYP/6-31G (d) level. The calculations were carried out with Gaussian 09 software package using a spin-restricted formalism.[S2]

Device Fabrication. The organic solar cells were fabricated as follows. An indium tin oxide (ITO) glass substrate with a sheet resistance of 5 Ω/sq (Geomatec) was used. The substrates were sonicated consecutively with detergent, deionized water, 2-propanol and ethanol for 15 min. After dried and UV-ozone treated, the substrates were spin-coated with poly(ethylene dioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS, Clevios P VP AI 4083) at 1000 rpm for 60 s and dried at 200 °C for 10 min. Afterwards, a mixed solution of P3HT

(15 mg mL^{-1}) and fullerene derivative (12 mg mL^{-1}) in *o*-dichlorobenzene was spin-coated at 1500 rpm for 60 s onto the PEDOT:PSS layer under an argon atmosphere. The blend films were put in the glass petridish to undergo solvent annealing, then on the 150 °C hotplate for 10 min to go through thermal annealing. Finally, 20 nm calcium and 100 nm Al layers were successively deposited under high vacuum (ca. 10^{-4} Pa). During the photovoltaic measurements, a non-reflective black aperture of 2 mm × 2 mm was attached to define the active area and avoid the scattering effect of incident light.

The electron-only devices were fabricated as follows. A 50 nm Al film was first thermally deposited onto the glass substrate. The P3HT:fullerene blend film with a thickness of 165 – 185 nm was spin-coated at 500 rpm for 90 s. Then, the active layer was capped by a 100 nm Al electrode.

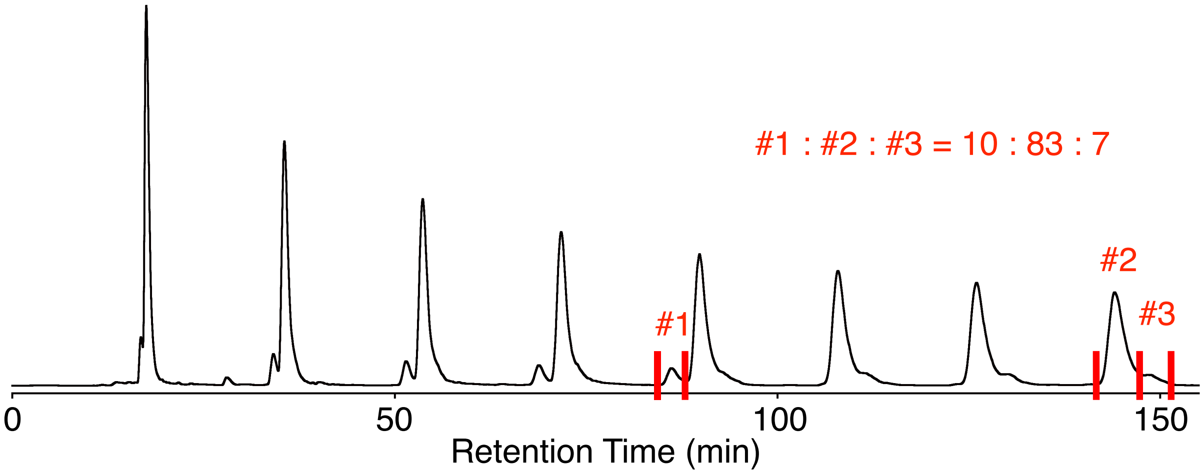


Fig. S1. HPLC profile of bis-BIEC. The ratio of the three fractions (#1 : #2 : #3) was 10 : 83 : 7. The second component was collected and characterized as the *cis*-2 isomer (*cis*-2-BIEC). The characterization of the first and third components could not be conducted due to the low yields.

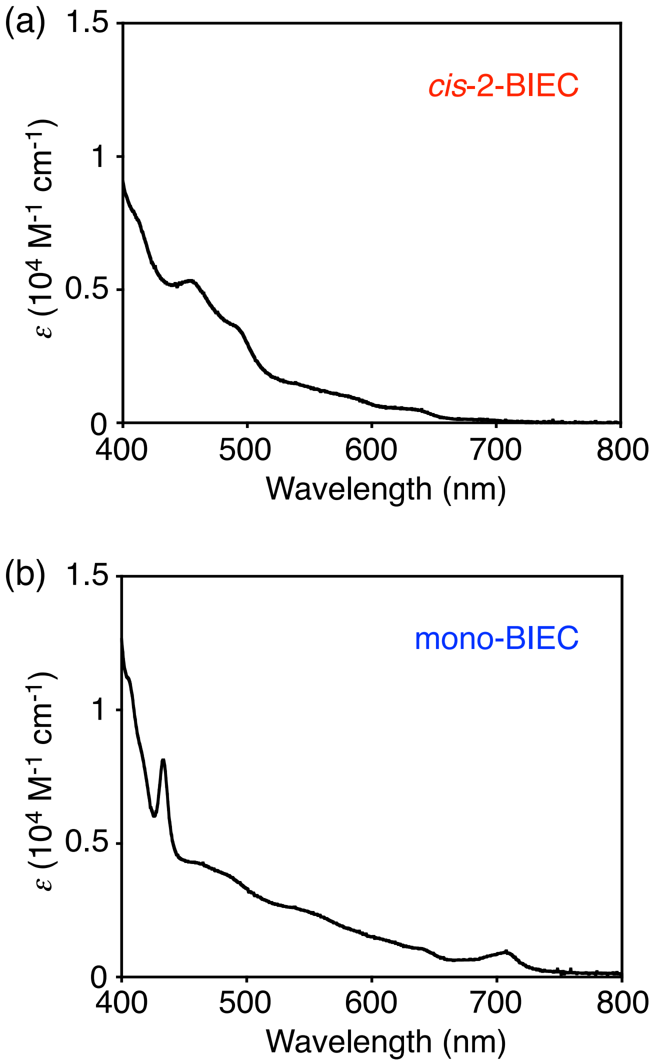


Fig. S2. UV-Vis-near infrared absorption spectra of (a) *cis*-2-BIEC and (b) mono-BIEC in *o*-dichlorobenzene. The spectral features are consistent with a literature.[S3]

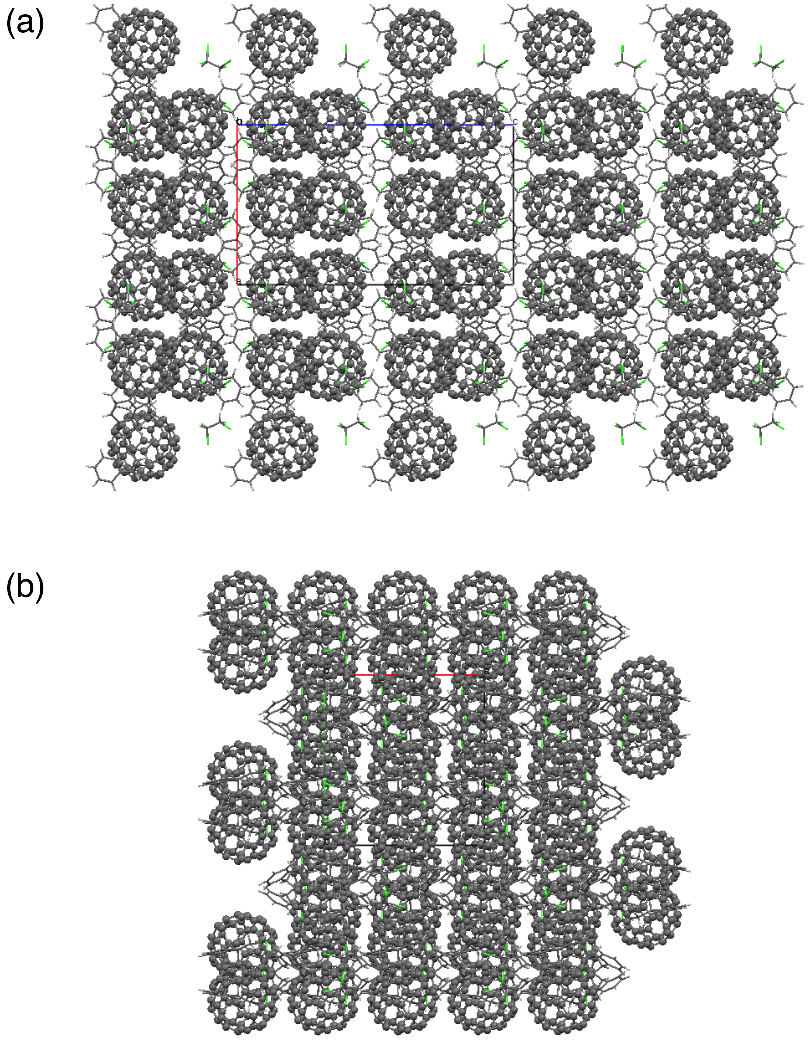


Fig. S3. X-ray crystal packing structure of *cis*-2-BIEC with solvent molecules along the (a) *b*-axis and (b) *c*-axis.

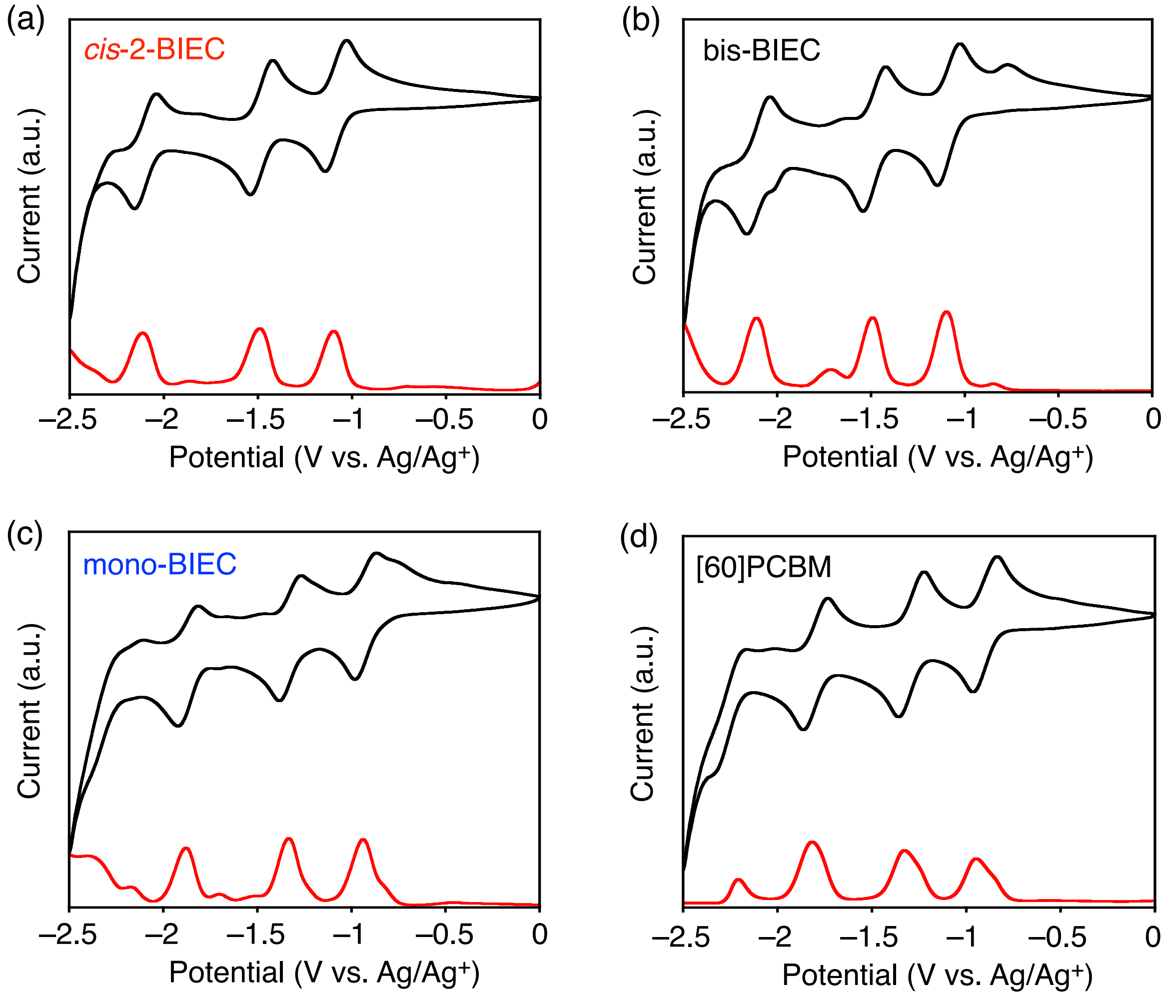


Fig. S4. Cyclic voltammograms (black) and differential pulse voltammograms (red) of (a) *cis*-2-BIEC, (b) bis-BIEC, (c) mono-BIEC and (d) [60]PCBM measured in *o*-dichlorobenzene/acetonitrile mixture (v:v=5:1) containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6). Sweep rate: 0.1 V s^{-1}; reference electrode, Ag/Ag+ (0.01 M $AgNO_3$, 0.09 M Bu_4PF_6 in acetonitrile).

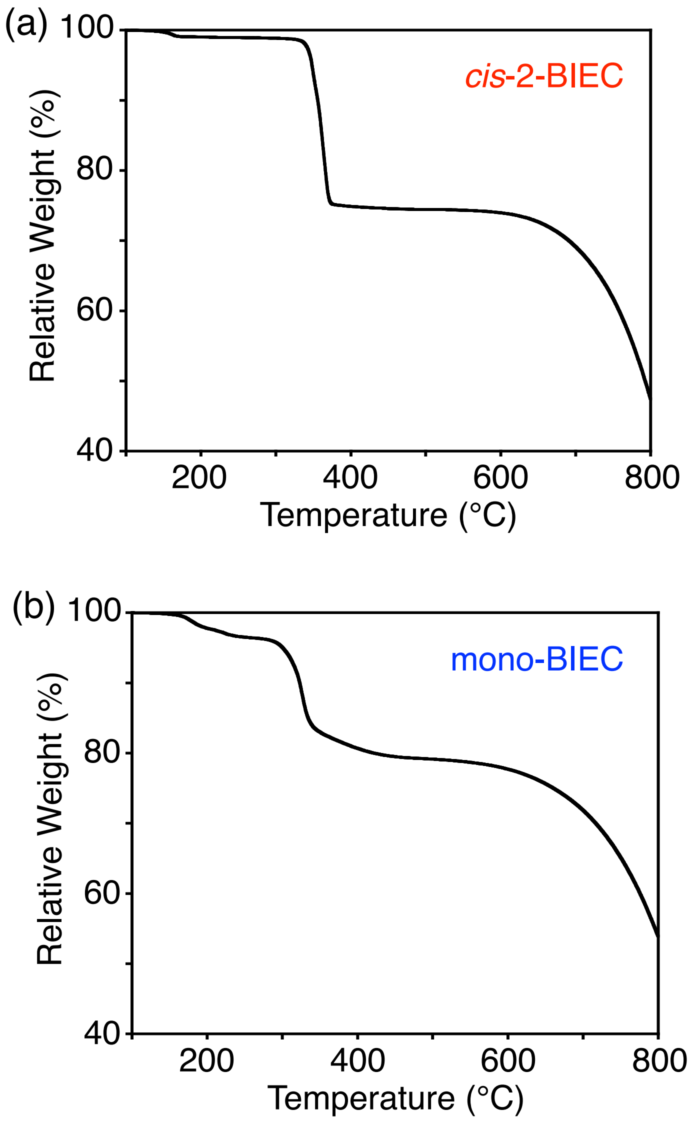


Fig. S5. TGA of (a) *cis*-2-BIEC and (b) mono-BIEC. The analyses were performed under flowing nitrogen at a scan rate of 10 °C min^{-1}.

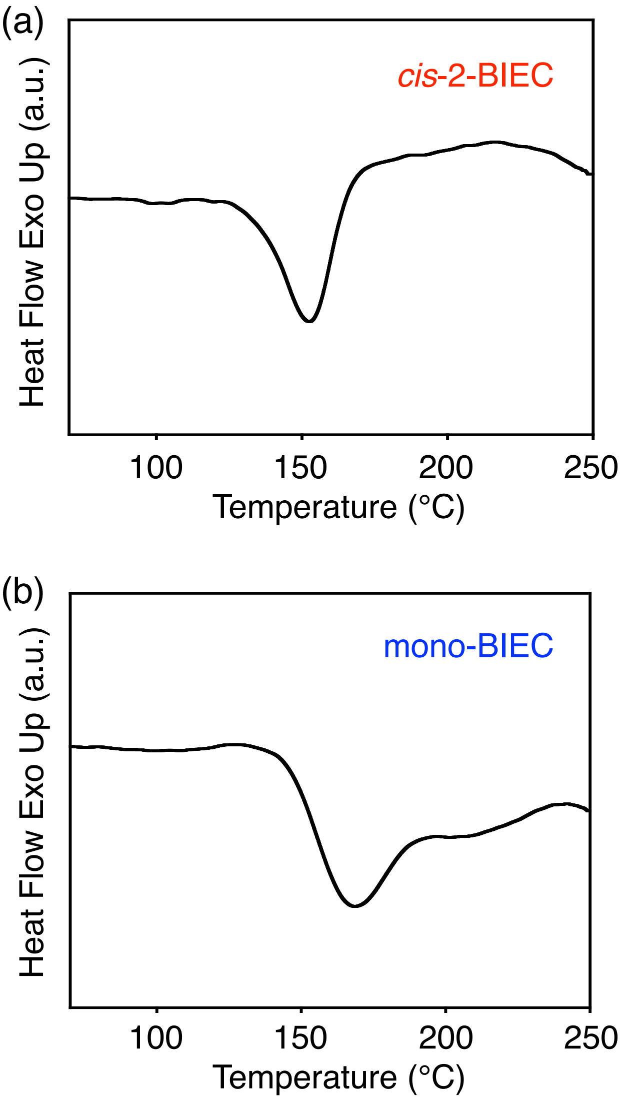


Fig. S6. DSC curves of (a) *cis*-2-BIEC and (b) mono-BIEC. The analyses were performed under flowing nitrogen at a scan rate of 10 °C min^{-1}.

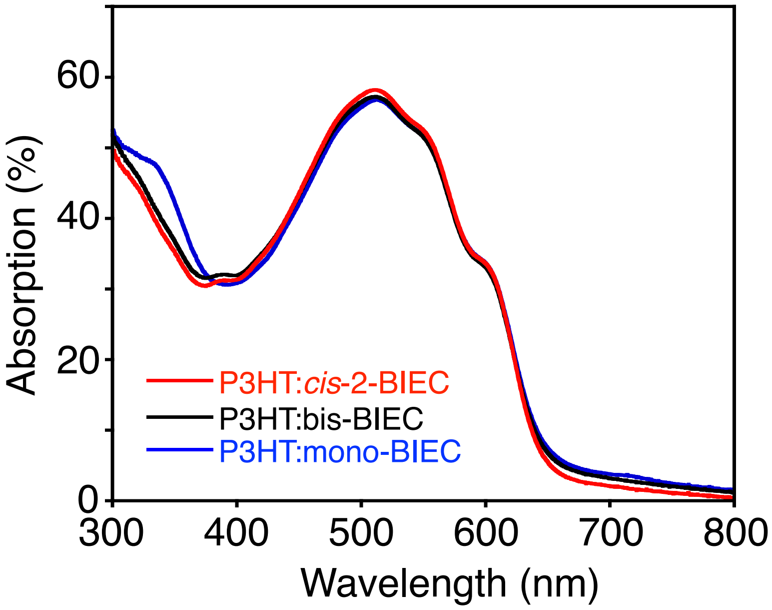


Fig. S7. UV-visible-near infrared absorption spectra of P3HT:*cis*-2-BIEC (red), P3HT:bis-BIEC (black), and P3HT:mono-BIEC (blue) films on ITO/PEDOT:PSS substrate.

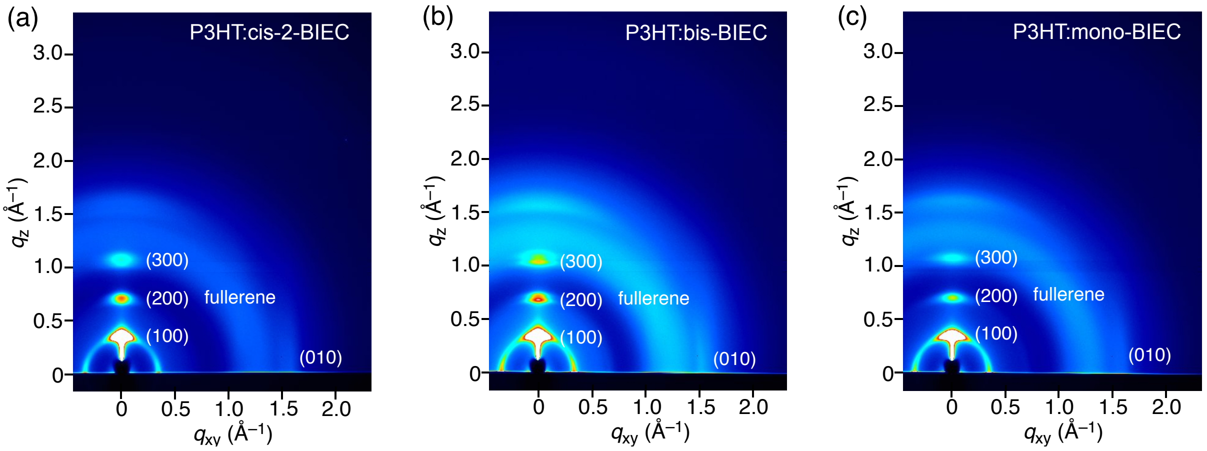


Fig. S8. Two dimensional GIWAXS plots of (a) P3HT:*cis*-2-BIEC, (b) P3HT:bis-BIEC, and (c) P3HT:mono-BIEC films on ITO/PEDOT:PSS substrates.

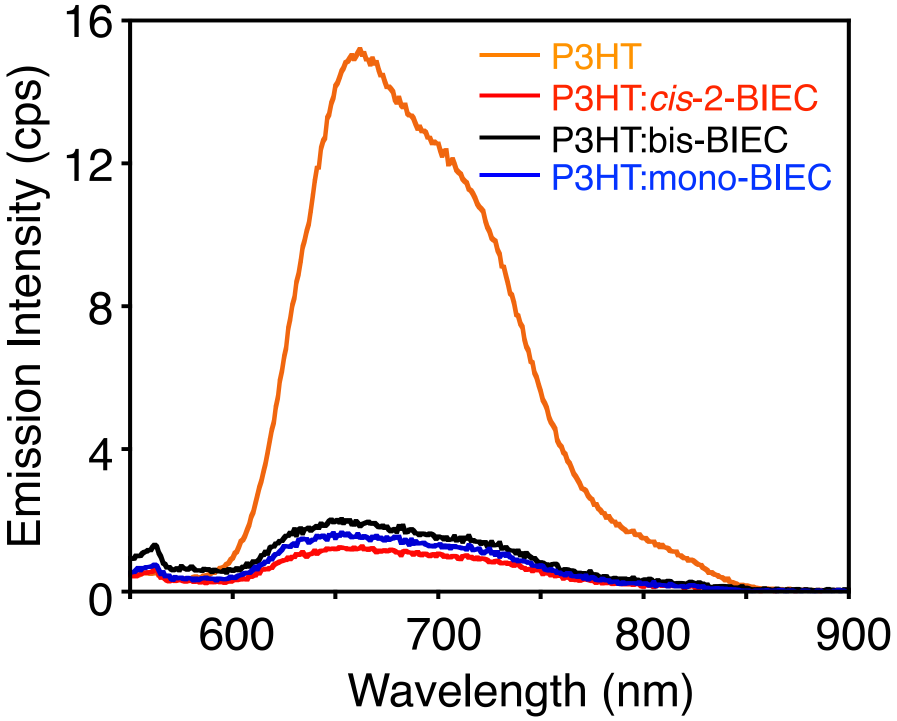


Fig. S9. Normalized photoluminescence spectra of pristine P3HT (orange), P3HT:*cis*-2-BIEC (red), P3HT:bis-BIEC (black), and P3HT:mono-BIEC (blue) films excited at the absorption maxima. The emission intensities were normalized by that of the P3HT film considering the difference in the absorbances of the P3HT:fullerene isomer films at the excitation wavelengths. The measurements were conducted three times and the averaged spectra are shown.

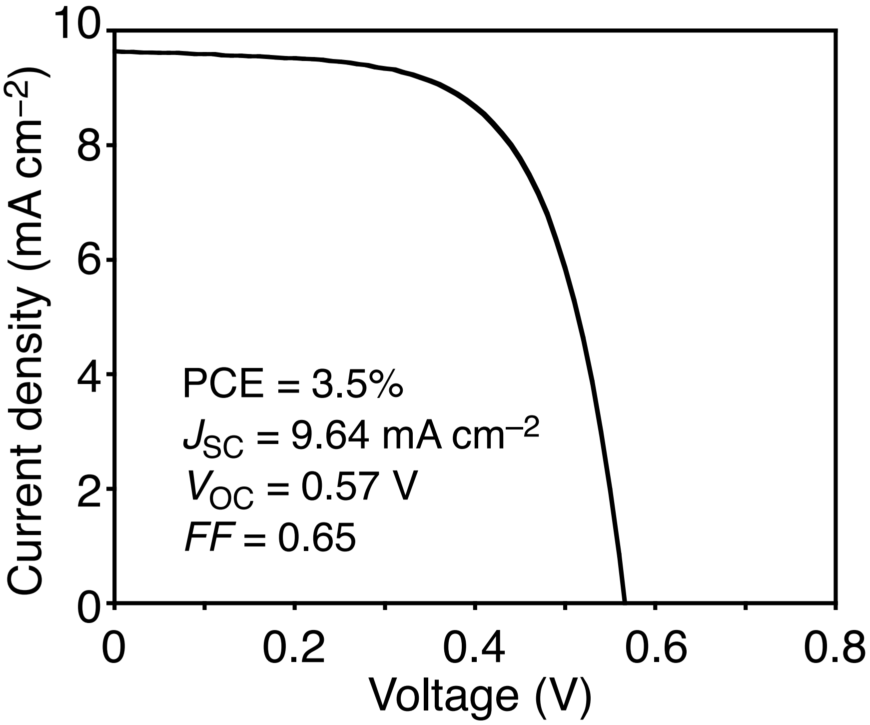


Fig. S10. Current density-voltage curve under illumination of the PSC device based on P3HT:[60]PCBM fabricated with a spin-coating solution of P3HT:[60]PCBM ([P3HT] = [[60]PCBM] = 25 mg mL^{-1}) in *o*-dichlorobenzene. The PSC device parameters are also shown as the inset.

References

S1. R. B. Grossman, R. A. Doyle and S. L. Buchwald, *Organometallics*, 1991, **10**, 1501.

S2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Gaussian, Inc., Wallingford CT, 2009.

S3. K. Kordatos, T. D. Ros, M. Prato, R. V. Bensasson and S. Leach, *Chem. Phys.*, 2003, **293**, 263.