Supplementary Information for

Effects of dihydronaphthyl-based [60]fullerene bisadduct isomers on polymer solar cell performance

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Experimental

Instruments. ^{1}H 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 (ESI). Elemental analysis was performed at the Kyoto University Elemental Analysis Center. UV-visible absorption spectra were obtained on a Perkin Elmer Lambda 900UV/vis/NIR spectrometer. Atomic force microscopy (AFM) analyses were carried out with an Asylum Technology MFP-3D-SA in the AC mode. Thermogravimetric analysis (TGA) measurements were conducted with a SHIMADZU TG-60 under flowing nitrogen at a scan rate of 20 □ min^{-1}. Differential scanning calorimetry (DSC) analysis was made on a SHIMADZU DSC-60 at a scan rate of 10 □ min^{-1}. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed using an ALS 630A electrochemical analyzer in ODCB/acetonitrile mixture (v:v=5:1) containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Bu_4PF_6) as a supporting electrolyte. Photocurrent-voltage characteristics were measured by PECK2400-N with PEC-L11 solar simulator (Peccell Technologies) under standard two-electrode conditions (100 mW cm^{-2}, AM1.5). Photocurrent action spectra were recorded with CEP-2000RR (BUNKOUKEIKI). Fullerene bisadduct isomers separation was accomplished by Japan Analytical Industry LC-908 with Nacalai Tesque cosmosil buckyprep.

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 of NC_{60}BA.

Synthesis of **2** : **1**[1] (1.43 g, 6.5 mmol), *n*-hexanol (6.75 mL, 52.5 mmol) and sulfuric acid (0.15 mL) were stirred in 9 mL of toluene, and then the solution was refluxed 18 h. The reaction mixture was washed with saturated $NaHCO_3$ solution, water, and saturated NaCl solution and dried over anhydrous Na_2SO_4 and evaporated. Purification by column chromatography on silica gel using mixed solvent (hexane:ethyl acetate = 20:1) as eluent yielded **2** (2.17 g, 6.01 mmol, 92%) as colorless oil. ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.38 (s, 2H), 4.26 (t, 4H, *J* = 6.59 Hz), 3.23 (s, 4H), 1.71 (m, 4H), 1.40-131 (m, 12H), 0.89 (t, 6H, *J* = 5.21 Hz). Anal. Calcd for $C_{22}H_{32}O_4$: C, 73.30%; H, 8.95%; O, 17.75%. Found: C, 73.54%; H, 9.00%; O, 17.74%. IR (ATR): ν_{max}/cm^{-1} 2956, 2932, 2858, 1724, 1587, 1467, 1407, 1388, 1338, 1262, 1190, 1176, 1103, 998, 893, 782. HRMS (ESI): calcd for $C_{22}H_{33}O_4$[M+H] 361.2373, found 361.2368.

Synthesis of NC_{60}MA and NC_{60}BA :[2] **2** (2.17 g, 6.01 mmol) and C_{60} (2.16 g, 3.0 mmol) were dissolved in 216 mL of *o*-dichlorobenzene, and then the solution was heated to 220 ˚C and refluxed for 48 h. Subsequently, the reaction mixture was evaporated. After the solvents were removed, the unreacted C_{60} and NC_{60}MA were separated and purified from reaction mixture by silica gel column chromatography with toluene. Then, NC_{60}BA was separated and purified from residue by preparative GPC with toluene. A total of 876 mg of NC_{60}MA (yield 27%) and 1.87 g of NC_{60}BA (yield 43%) were obtained.

NC_{60}MA : ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.03 (s, 2H), 4.81 (m, 2H), 4.55 (m, 2H), 4.39 (t, 4H, *J* = 6.83 Hz), 1.81 (m, 4H), 1.48-1.35 (m, 12H), 0.91 (t, 6H, J = 7.07 Hz). Anal. Calcd for $C_{82}H_{32}O_4$: C, 91.10%; H, 2.98%; O, 5.92%. Found: C, 91.32%; H, 2.95%; O, 5.78%. IR (ATR): ν_{max}/cm^{-1} 2951, 2921, 2852, 1722, 1702, 1616, 1569, 1462, 1429, 1397, 1374, 1334, 1290, 1244, 1224, 1203, 1178, 1128, 1035, 978, 905, 789, 767, 731, 698, 670, 580, 573, 553, 527, 506. HRMS (ESI): calcd for $C_{82}H_{33}O_4$[M+H] 1081.2373, found 1081.2364.

$NC_{60}BA$: ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.22-7.51 (m, 4H), 5.01-3.91 (m, 16H), 1.82 (m, 8H), 1.42-1.25 (m, 24H), 0.90 (m, 12H). Anal. Calcd for $C_{104}H_{64}O_8$: C, 86.65%; H, 4.47%; O, 8.88%. Found: C, 84.21%; H, 4.43%; O, 8.64%. IR (ATR): ν_{max}/cm^{-1} 2951, 2927, 2855, 1722, 1616, 1573, 1456, 1414, 1379, 1330, 1279, 1218, 1167, 1122, 1040, 896, 789, 766, 725, 696, 670, 575, 526. HRMS (ESI): calcd for $C_{104}H_{65}O_8$[M+H] 1441.4674, found 1441.4664.

Separation and purification of $NC_{60}BA$ isomers.

Separation and purification were accomplished with a Buckyprep column at 50 ˚C.

trans-1 isomer: ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.12 (s, 4H), 4.99 (m, 4H), 4.80 (m, 4H), 4.41 (t, 8H, *J* = 6.83 Hz), 1.84 (m, 8H), 1.48-1.36 (m, 24H), 0.92 (t, 12H, *J* = 6.83 Hz). IR (ATR): ν_{max}/cm^{-1} 2951, 2926, 2854, 1722, 1616, 1573, 1538, 1451, 1424, 1415, 1379, 1330, 1280, 1222, 1198, 1168, 1121, 1046, 1020, 897, 762, 702, 671, 642, 282, 552, 532, 490. HRMS (ESI): calcd for $C_{104}H_{65}O_8$[M+H] 1441.4674, found 1441.4640.

trans-2 isomer: ^{1}H NMR ($C_2D_2Cl_4$, 393 K, 400MHz): δ 8.13 (s, 2H), 8.07 (s, 2H), 4.92 (d, 2H, *J* = 14.15 Hz), 4.74 (d, 4H, *J* = 14.15 Hz), 4.63 (d, 2H, *J* = 14.16 Hz), 4.45 (m, 8H), 1.90 (m, 8H), 1.59-1.39 (m, 24H), 0.99 (m, 12H). IR (ATR): ν_{max}/cm^{-1} 2952, 2928, 2856, 1723, 1616, 1574, 1558, 1538, 1495, 1464, 1456, 1431, 1415, 1378, 1331, 1280, 1221, 1203, 1168, 1122, 1086, 1040, 900, 790, 767, 737, 696, 671, 577, 561, 542, 528. HRMS (ESI): calcd for $C_{104}H_{65}O_8$[M+H] 1441.4674, found 1441.4640. ^{13}C NMR ($C_2D_2Cl_4$, 373 K, 100MHz): δ 167.22, 160.37, 154.24, 154.08, 153.64, 147.63, 147.03, 146.85, 146.62, 146.57, 146.06, 145.87, 145.55, 145.39, 145.14, 144.69, 144.15, 143.99, 143.55, 142.67, 142.46, 142.43, 142.01, 141.47, 141.37, 141.14, 141.03, 139.71, 139.22, 133.99, 132.98, 132.16, 128.32, 128.28, 65.90, 65.89, 63.90, 63.76, 44.84, 44.42, 31.24, 31.22, 28.47, 28.45, 25.45, 25.43, 22.23, 22.21, 13.61.

trans-3 isomer: ^{1}H NMR ($C_2D_2Cl_4$, 393 K, 400MHz): δ 8.11 (s, 2H), 7.88 (s, 2H), 4.77 (d, 2H, *J* = 14.15 Hz), 4.68 (d, 2H, *J* = 14.15 Hz), 4.47-4.31 (m, 12H), 1.91-1.79 (m, 8H), 1.59-1.32 (m, 24H), 1.03-0.91(m, 12H). IR (ATR): ν_{max}/cm^{-1} 2951, 2926, 2855, 1717, 1616, 1571, 1555, 1456, 1431, 1412, 1378, 1331, 1280, 1213, 1331, 1280, 1213, 1195, 1166, 1119, 895, 725, 696, 670, 576, 548, 521. HRMS (ESI): calcd for $C_{104}H_{65}O_8$[M+H] 1441.4674, found 1441.4643. ^{13}C NMR ($C_2D_2Cl_4$, 373 K, 100MHz): δ 167.18, 167.16, 159.47, 156.77, 156.72, 155.62, 149.27, 149.14, 148.48, 148.24, 148.01, 145.66, 145.55, 145.31, 145.28, 145.21, 145.19, 144.66, 143.98, 143.78, 143.59, 142.72, 141.57, 141.32, 141.18, 140.94, 140.82, 139.58, 135.95, 134.73, 132.06, 132.02, 128.23, 128.08, 65.90, 65.84, 64.46, 64.22, 45.00, 43.66, 31.25, 31.20, 28.46, 28.40, 25.45, 25.40, 22.24, 22.19, 13.66, 13.61.

trans-4 isomer: ^{1}H NMR ($C_2D_2Cl_4$, 393 K, 400MHz): δ 7.98 (s, 2H), 7.86 (s, 2H), 4.58 (d, 2H, *J* = 14.15 Hz), 4.50 (d, 2H, *J* = 14.15 Hz), 4.45-4.35 (m, 12H), 1.87 (m,8H), 1.55-1.37 (m, 24H), 0.99 (m, 12H). IR (ATR): ν_{max}/cm^{-1} 2952, 2927, 2855, 1717, 1616, 1573, 1453, 1377, 1330, 1278, 1217, 1165, 1121, 697, 538, 524, 506, 491, 469 457, 418. HRMS (ESI): calcd for $C_{104}H_{65}O_8$[M+H] 1441.4674, found 1441.4641.

e isomer: ^{1}H NMR ($C_2D_2Cl_4$, 393 K, 400MHz): δ 7.92 (s, 1H), 7.90 (s, 2H), 7.84 (s, 1H), 4.44-4.31 (m, 14H), 4.09 (b, 2H), 1.85 (m, 8H), 1.56-1.42 (m, 24H), 0.97 (m, 12H). IR (ATR): ν_{max}/cm^{-1} 2952, 2926, 2855, 1723, 1570, 1458, 1412, 1373, 1330, 1279, 1219, 1198, 1170, 1122, 1026, 889, 552, 526. HRMS (ESI): calcd for $C_{104}H_{65}O_8$[M+H] 1441.4674, found 1441.4638.

cis-2 and *cis*-3 isomers (mixture): ^{1}H NMR ($C_2D_2Cl_4$, 393 K, 400MHz): δ 8.00 (s, 2H, A), 7.88 (s, 2H, B), 7.76 (s, 2H, A), 4.50-4.01 (m, 16H), 1.85 (m, 8H), 1.57-1.40 (m, 24H), 0.98 (m, 12H) (A and B are *cis*-2 and *cis*-3 or *cis*-3 and *cis*-2 respectively. A:B = 2:3.). IR (ATR): ν_{max}/cm^{-1} 2952, 2925, 2854, 1719, 1653, 1570, 1558, 1541, 1522, 1507, 1457, 1457, 1427, 1383, 1329, 1278, 1201, 1163, 1121, 638, 569, 551, 524, 488. HRMS (ESI): calcd for $C_{104}H_{65}O_8$[M+H] 1441.4674, found 1441.4638.

Device fabircation and evaluation.

The organic solar cells were fabricated as follows.[3,4] Indium tin oxide (ITO) on a glass substrate with a sheet resistance of 5 Ω/ sq (Geomatec) was used. The substrates were sonicated consecutively with acetone and ethanol for 10 min. After blow-drying and UV-ozone treatment, the substrates were spin-coated at 1000 rpm with poly(ethylene dioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS, Clevios P) and dried with a hot plate at 200 °C for 10 min. For the fabrication of the active layer with bulk heterojunction structure, a mixed solution of P3HT (15 mg mL^{-1}) and fullerene (13.5 mg mL^{-1}) in *o*-dichlorobenzene was spin-coated at 1500 rpm for 1 min onto the ITO/PEDOT:PSS. Then, Al was deposited to obtain the device with the composite film of P3HT and PCBM (denoted as ITO/PEDOT:PSS/P3HT:fullerene/Al). After deposition, thermal annealing of active layer was acocomplished at 150 °C for 15 min. P3HT:fullerene films had the thicknesses of 90 nm.

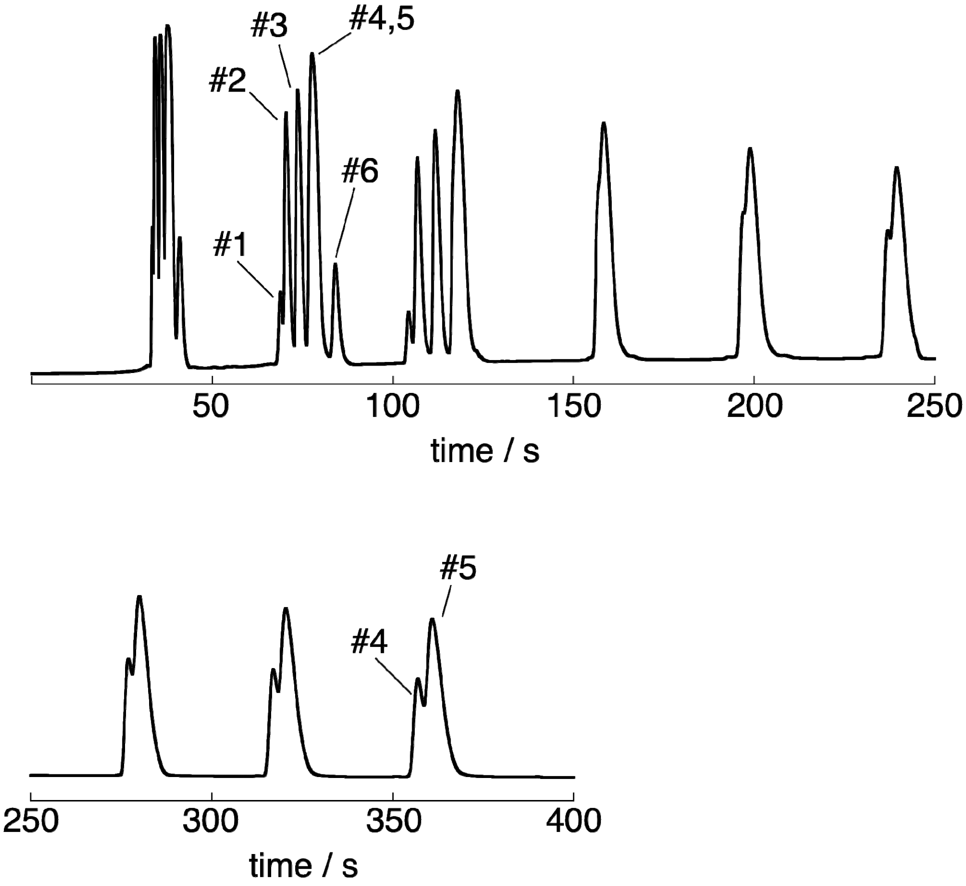

Fig. S1. HPLC chraomatography of regioisomeric mixture of the NC$_{60}$BA bisadducts. Conditions: Buckyprep column (20 x 250 mm); eluent, toluene; flow rate, 4 mL min^{-1}; detection, 350 nm. The peaks arising from the NC$_{60}$BA bisadducts were assigned as *trans*-1 (#1), *trans*-2 (#2), *trans*-3 (#3), *trans*-4 (#4), *e* (#5) and *cis*-2+*cis*-3 isomers (mixture, #6), respectively. The fraction of peaks #1-3 and #6 was collected by three cycles, whereas that of peaks #4 and #5 was collected by more than nine cycles. *cis*-2+*cis*-3 isomers could not be separated and used as a mixture.

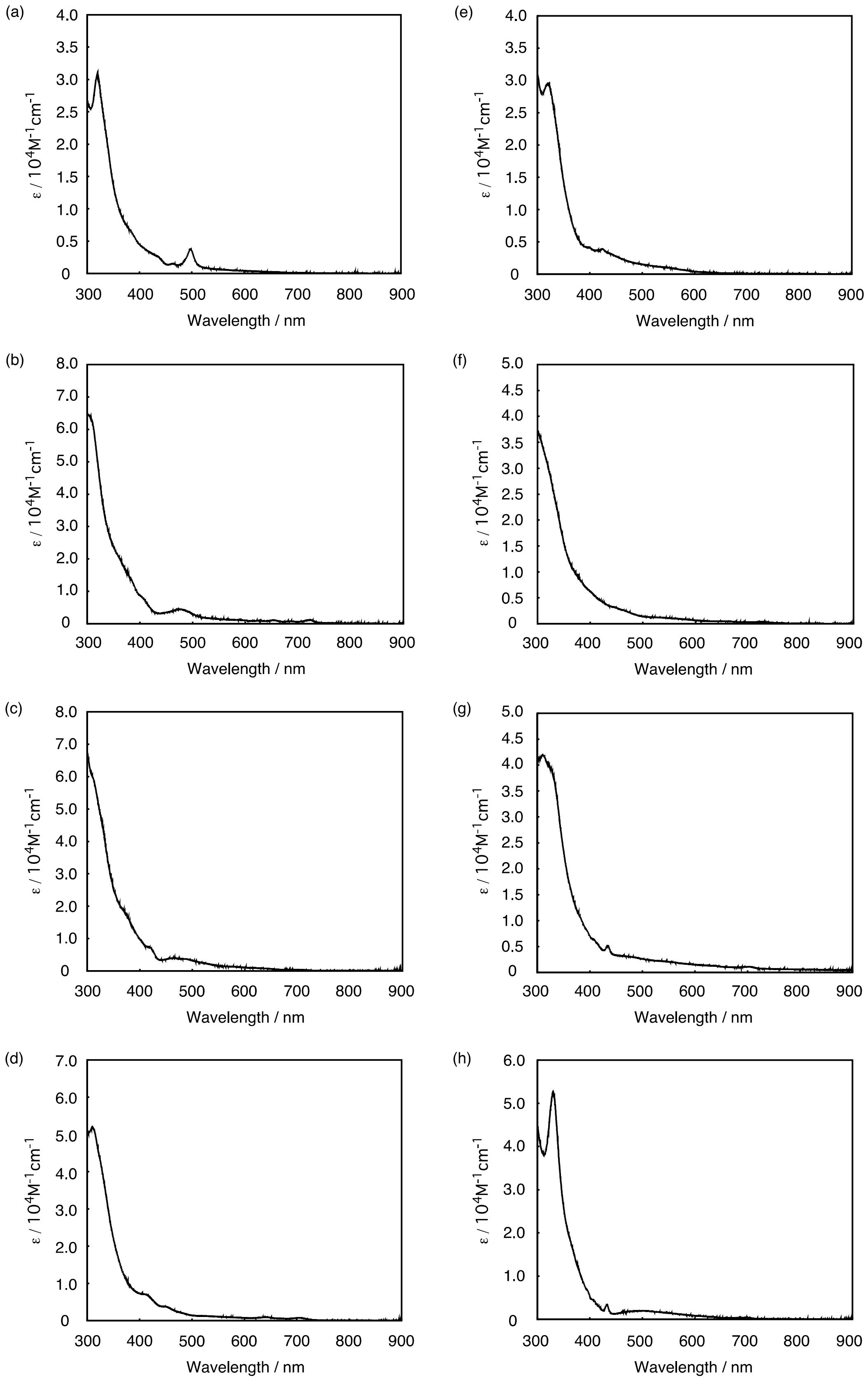

Fig. S2. UV-Vis absorption spectra of (a) *trans*-1, (b) *trans*-2, (c) *trans*-3, (d) *trans*-4, (e) *e*, (f) *cis*-2+*cis*-3 (mixture) isomers, (g) $NC_{60}MA$ and (h) [60]PCBM in *o*-dichlorobenzene.

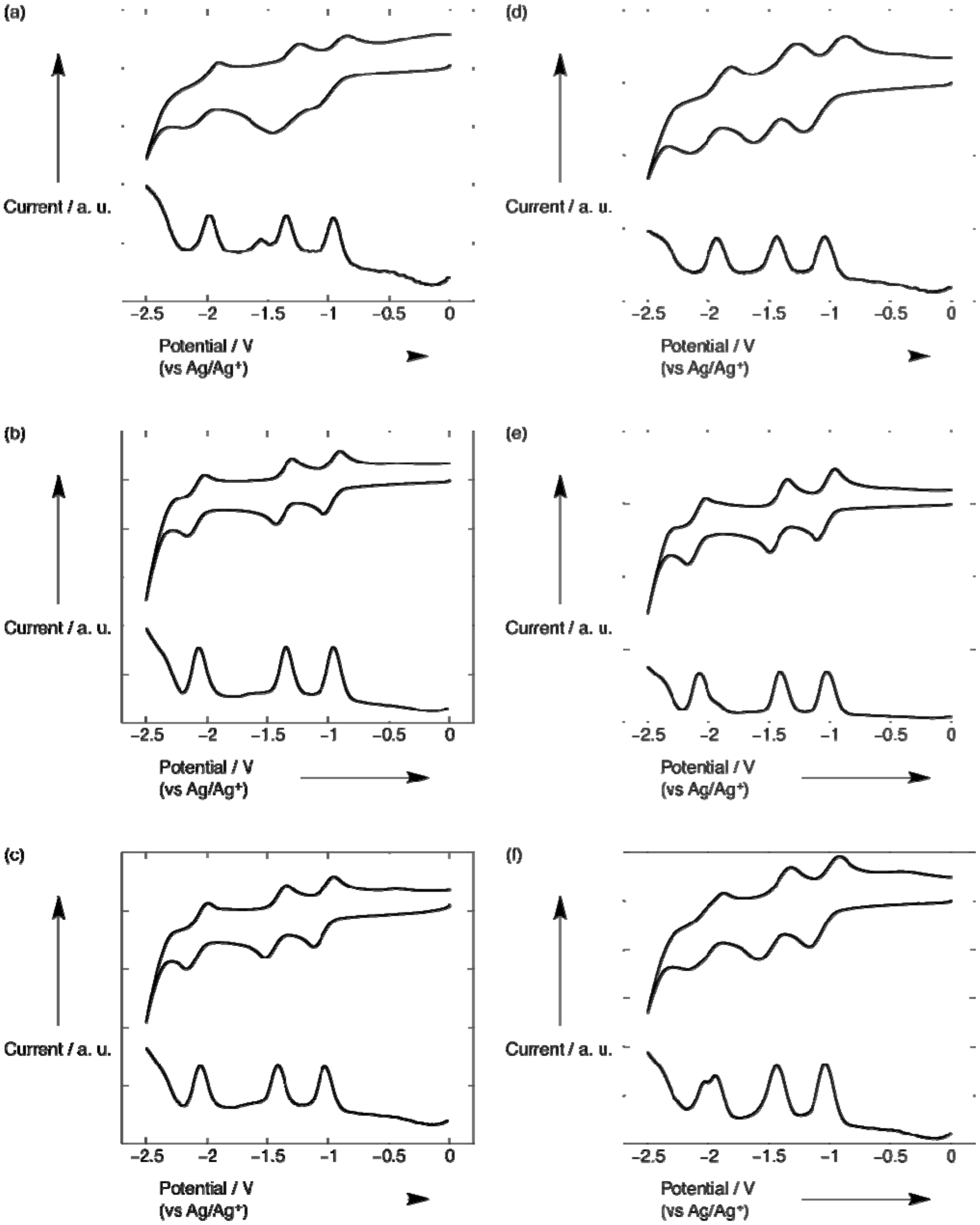

Fig. S3. Cyclic voltammograms (upper) and differential pulse voltammograms (lower) of (a) *trans*-1, (b) *trans*-2, (c) *trans*-3, (d) *trans*-4, (e) *e* and (f) *cis*-2+*cis*-3 (mixture) isomers measured in ODCB/acetonitrile mixture (v:v=5:1) containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6). Sweep rate: 0.1 V s^{-1}; reference electrode, Ag/Ag^+ (0.01 M $AgNO_3$, 0.09 M Bu_4NPF_6 in acetonitrile).

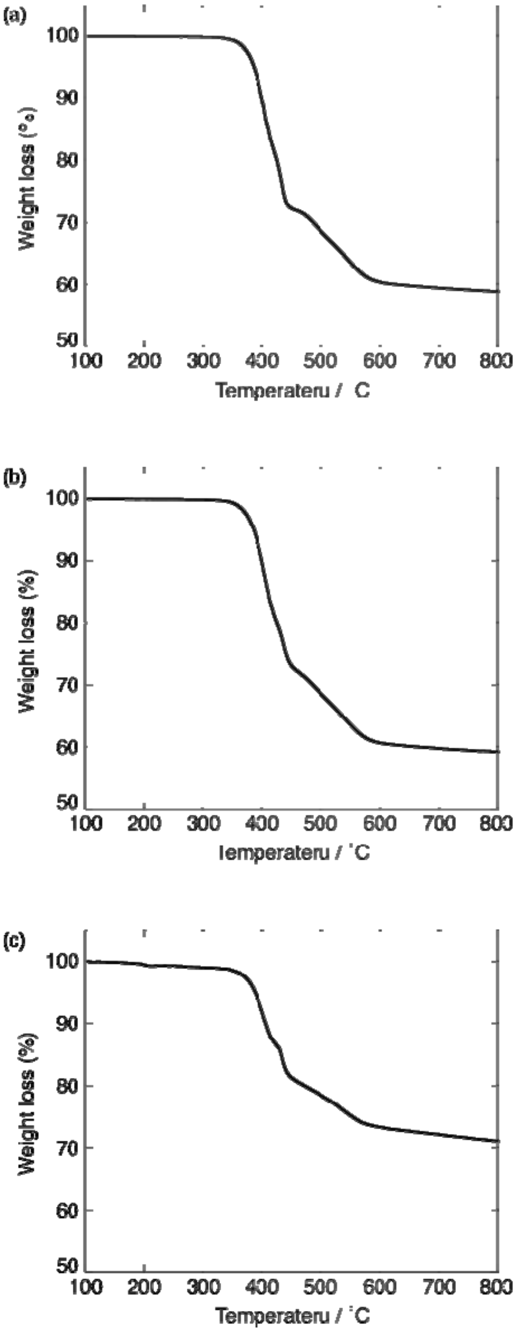

Fig. S4. TGA data of (a) *trans*-2 and (b) *trans*-3 isomers and (c) $NC_{60}MA$.

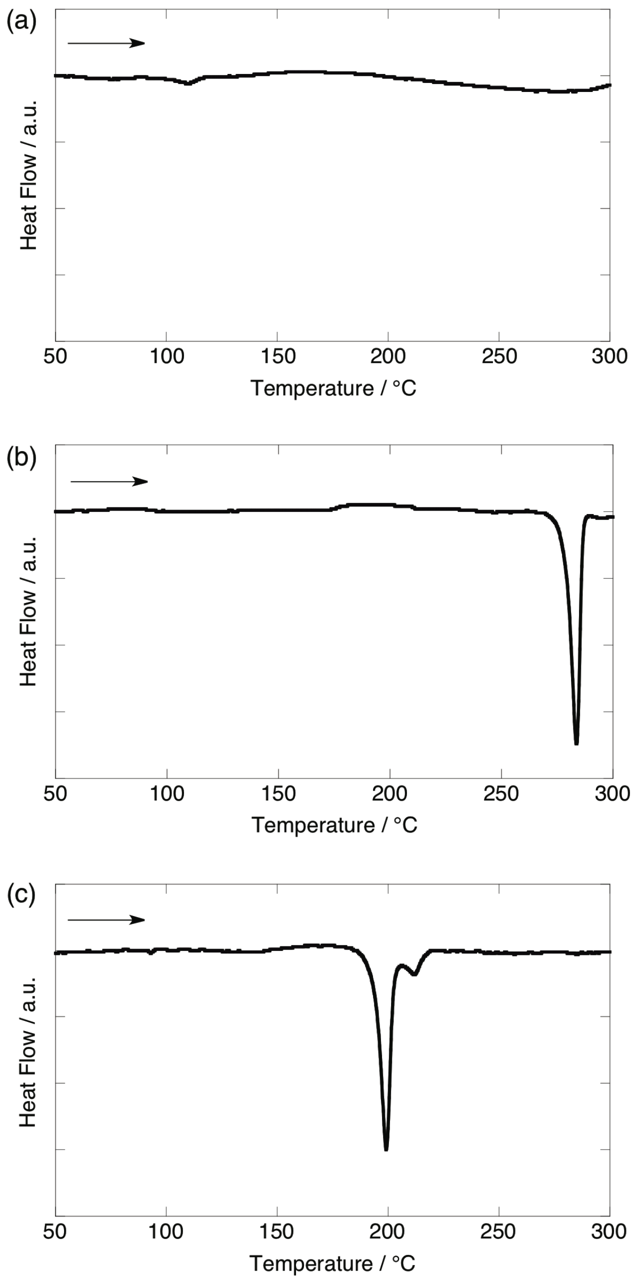

Fig. S5. DSC data of (a) *trans*-2 and (b) *trans*-3 isomers and (c) $NC_{60}MA$.

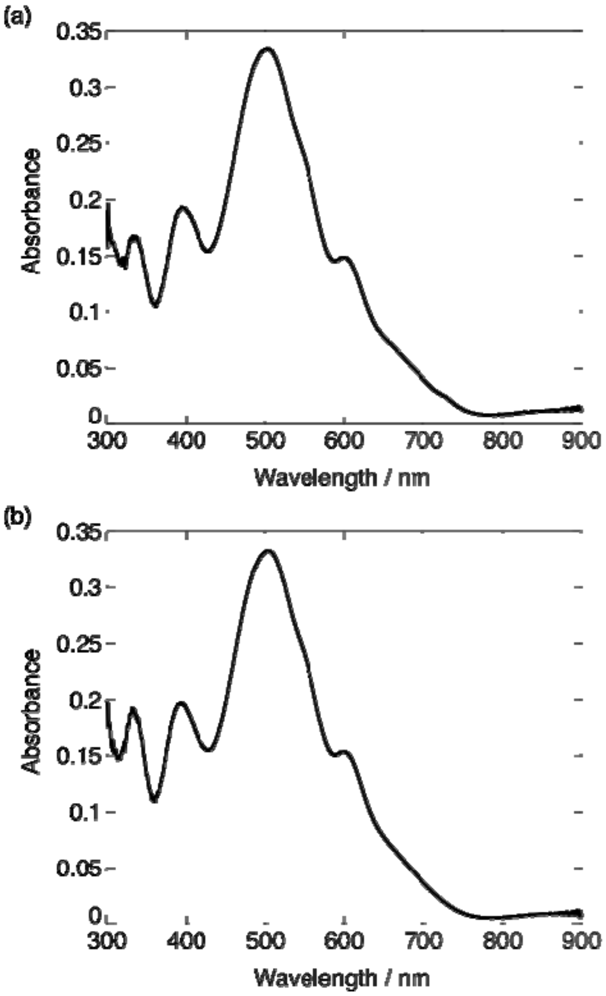

Fig. S6. Absorption spectra of (a) ITO/PEDOT:PSS/P3HT:*trans*-2 and (b) ITO/PEDOT:PSS/P3HT:*trans*-3 isomer films. The absorption arising from the ITO and PEDOT/PSS was subtracted.

Table S1. UV-Vis Spectral data of $NC_{60}BA$ isomers, $NC_{60}MA$ and [60]PCBM.

compound	wavelength / nm	ε / M^{-1} cm^{-1}
trans-1	318	30000
	497	3700
trans-2	474	4200
trans-3	464	3600
trans-4	305	50000
	641	830
	705	670
e	316	43000
	423	5600
cis-2+*cis*-3 (mixture)	472	3800
	530	1500
	658	520
$NC_{60}MA$	307	41000
	432	5700
[60]PCBM	327	52000
	430	3000

Table S2. HOMO and LUMO energy levels calculated using B3LYP/6-31G*.

compound	$NC_{60}MA$	*trans*-1	*trans*-2	*trans*-3	*trans*-4	*e*	*cis*-3	*cis*-2
LUMO /eV	–3.15	–3.11	–3.09	–3.00	–3.00	–2.99	–2.95	–3.04
HOMO /eV	–5.69	–5.56	–5.56	–5.53	–5.50	–5.56	–5.39	–5.65

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