

Electronic Supplementary Information

Effect of a π -Linker of Push–Pull D– π –A Donor Molecules on the Performance of Organic Photodetectors

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Syntheses and characterizations:

Reagents and materials

All the chemical reagents were used without further purification. Tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄), tris(dibenzylideneacetone)dipalladium(0) (Pd(dba)₃), 2,5-dibromothiophene, 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile were purchased from Toyko Chemical Industry (TCI). N-bromosuccinimide (NBS), tetrabutylammonium hexafluorophosphate (TBAPF₆), phosphorus(V) oxychloride (POCl₃), 4-bromo-N,N-diphenylaniline, potassium carbonate (K₂CO₃), sodium bicarbonate (NaHCO₃), and N,N'-dimethylformamide (DMF) were purchased from Sigma-Aldrich and SAMCHUN. Fullerene-C₆₀ (C₆₀, 99.95%) was purchased from SES Research.

Synthesis of Donor Molecules

Dithieno[3,2-b:2',3'-d]thiophene (compound 4) was prepared according to the literature procedure.¹

2-bromodithieno[3,2-b:2',3'-d]thiophene (5)

To a solution of compound 4 (0.8 g, 4.1 mmol) in CHCl₃ (20 ml) cooled in an ice bath was slowly added acetic acid (20 ml). The reaction mixture was treated with NBS (0.881 g, 4.9 mmol) and stirred for 10 h. The reaction mixture was treated with aqueous solution of NaOH (25 ml, 1 M), stirred in an ice bath for 2 h, then concentrated under vacuum, and extracted with dichloromethane. The organic phase was washed with water and brine, and dried over anhydrous MgSO₄. All volatiles were evaporated and the crude product was purified by column chromatography on silica gel using dichloromethane to give a yellow solid product (yield: 0.95 g, 85%). ¹H NMR (300 MHz, acetone-*d*₆, ppm) δ: 7.67 (s, 1H), 7.65 (d, 1H, 4.3 Hz), 7.50 (d, 1H, 5.2 Hz).

6-bromodithieno[3,2-b:2',3'-d]thiophene-2-carbaldehyde (6)

DMF (0.85 ml, 11.6 mmol) and POCl₃ (0.55 ml, 5.8 mmol) were added to a solution of compound 5 (0.8g, 2.9 mmol) in distilled dichloromethane (25 ml) cooled in an ice bath. The reaction mixture was stirred at room temperature for 2 h and then heated at 70 °C for 12 h. The reaction mixture was cooled to room temperature, treated with aqueous sodium acetate (20 ml, 2 M), and stirred for 2 h. Volatiles were evaporated under vacuum and the resulting residue was extracted with dichloromethane. The organic phase was washed with water and brine, and dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography on silica gel using dichloromethane and hexane (1:4 v/v) to give a yellow-red solid product (yield: 0.66 g, 75 %). ¹H NMR (300 MHz, acetone-*d*₆, ppm) δ: 10.06 (s, 1H), 8.40 (s, 1H), 7.75 (s, 1H).

***N,N*-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (7)**

n-Butyllithium (8.5 ml, 1.6 M in hexane) was slowly added to a solution of 4-bromo-*N,N*-diphenylaniline (2g, 6.17 mmol) in distilled THF (40 ml) under a nitrogen atmosphere cooled at -70 °C (dry ice/isopropanol). After 90 min, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.53 g, 13.57 mmol) was added dropwise via syringe. The reaction mixture was stirred overnight and then treated with water (20 ml). The resulting mixture was extracted with dichloromethane. The organic phase was washed with water and brine, and dried over anhydrous MgSO₄. Volatiles were evaporated and the resulting residue was purified by column chromatography on silica gel using dichloromethane and hexane (1:5 v/v) to give a white solid product (yield: 1.57 g, 79 %). ¹H NMR (300 MHz, acetone-*d*₆, ppm) δ: 7.63 (d, 2H, 8.4 Hz), 7.34 (t, 4H, 15.6 Hz), 7.11 (m, 6H), 6.98 (d, 2H, 8.4 Hz), 1.33 (s, 12H).

6-(4-(diphenylamino)phenyl)dithieno[3,2-*b*:2',3'-*d*]thiophene-2-carbaldehyde (8)

A mixture of compound **7** (0.66 g, 2.2 mmol), compound **6** (0.89 g, 2.4 mmol), Pd(PPh₃)₄ (0.083 g, 0.07 mmol) and NaHCO₃ (2.74 g, 32.7 mmol) in THF and H₂O (30 ml/10 ml, 3:1 v/v) was refluxed for 48 h. The reaction mixture was concentrated under vacuum and was extracted with dichloromethane. The organic phase was washed with water and brine, and dried over anhydrous MgSO₄. Volatiles were evaporated and the residue was purified by column chromatography on silica gel using dichloromethane and hexane (2:1 v/v) to give yellow solid product (yield: 0.68 g, 67 %). ¹H NMR (300 MHz, acetone-*d*₆, ppm) δ: 10.04 (s, 1H), 8.38 (s, 1H), 7.84 (s, 1H), 7.69 (d, 2H, 8.7 Hz), 7.37 (t, 4H, 7.8 Hz), 7.16 (d, 6H, 8.3 Hz), 7.10 (t, 3H, 7.0 Hz).

2-((6-(4-(diphenylamino)phenyl)dithieno[3,2-*b*:2',3'-*d*]thiophen-2-yl)methylene)-1H-indene-1,3(2H)-dione (H1)

To a solution of compound **8** (0.60 g, 1.28 mmol) in THF (20 ml) at 65 °C was added dropwise 1,3-indandione (0.215 g, 1.47 mmol) in THF (7 ml). The reaction mixture was stirred at the same temperature for 60 h, cooled to room temperature and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using dichloromethane to give dark pink solid product, which was treated with dichloromethane and ethanol to isolate the product as precipitates. The precipitate was purified further by temperature gradient sublimation under reduced pressure (10⁻³ torr) to give dark green solid product (yield: 0.27 g, 35%). ¹H NMR (300 MHz, DMSO-*d*₆, ppm) δ: 8.63 (s, 1H), 8.13 (s, 1H), 7.93 (m, 5H), 7.66 (d, 2H), 7.37 (t, 4H, 7.7 Hz), 7.16 (s, 1H), 7.11 (d, 5H, 7.9 Hz), 7.01 (d, 2H, 8.5 Hz). HRMS (FAB) *m/z*: calcd C₃₆H₂₁NO₂S₃ 595.07, [M+H]⁺: observed 595.07. Elemental analysis calc.: C, 72.58; H, 3.55; N, 2.35; O, 5.37; S, 16.14; found: C, 72.68; H, 3.47; N, 2.32; O, 5.37; S, 16.23

2,2':5',2''-terthiophene (9)

A mixture of 2,5-dibromothiophene (1 g, 4.13 mmol), thiophen-2-ylboronic acid (1.59 g, 12.4 mmol), Pd(PPh₃)₄ (0.29 mg, 0.25 mmol), and K₂CO₃ (5 ml, 2M) in THF and methanol (20:4 ml v/v) was heated at 100 °C for 36 h. Then the reaction mixture was cooled to room temperature, then concentrated under vacuum, and the resulting mixture was extracted with dichloromethane. The organic phase was washed with water and brine, and dried over anhydrous MgSO₄. Volatiles were evaporated and the crude product was purified by column chromatography on silica gel using hexane to give yellow solid product (yield: 0.70 g, 70%). ¹H NMR (300 MHz, acetone-*d*₆, ppm) δ: 7.46 (dd, 2H, 0.9, 5.1 Hz), 7.32 (dd, 2H, 0.9, 3.5 Hz), 7.23 (s, 2H), 7.11 (dd, 2H, 3.7, 5.0 Hz).

5-bromo-2,2':5',2''-terthiophene (10)

To a solution of compound **9** (0.7 g, 2.82 mmol) in CHCl₃ (20 ml) cooled in an ice bath was slowly added acetic acid (20 ml). The reaction mixture was treated with NBS (0.553 g, 3.1 mmol) and stirred overnight. The reaction mixture was treated with saturated aqueous NaHCO₃ (20 ml), stirred at room temperature for 2 h, then concentrated under vacuum, and extracted with dichloromethane. The organic phase was washed with water and brine, and dried over anhydrous MgSO₄. All volatiles were evaporated and the crude product was purified by column chromatography on silica gel using hexane to give yellow solid product (yield: 0.70 g, 76%). ¹H NMR (300 MHz, acetone-*d*₆, ppm) δ: 7.47 (t, 1H, 5.3 Hz), 7.33 (t, 1H, 3.5 Hz), 7.24 (s, 2H), 7.17 (m, 2H), 7.11 (m, 1H).

5''-bromo-[2,2':5',2''-terthiophene]-5-carbaldehyde (11)

DMF (0.66 ml, 8.59 mmol) and POCl₃ (0.41 ml, 4.30 mmol) were added to a solution of compound **10** (0.7 g, 2.15 mmol) in distilled dichloromethane (20 ml) cooled in an ice bath. The reaction mixture was stirred at room temperature for 2 h and then heated at 70 °C for 12 h. The reaction mixture was cooled to room temperature, treated with sodium acetate (20 ml, 2 M), and stirred for 2 h. Volatiles were evaporated under vacuum and the resulting residue was extracted with dichloromethane. The organic phase was washed with water and brine, and dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography on silica gel using dichloromethane and hexane (2:1 v/v) to give orange solid product (yield: 0.58 g, 76 %). ¹H NMR (300 MHz, acetone-*d*₆, ppm) δ: 9.95 (s, 1H), 7.96 (d, 1H, 4.0 Hz), 7.52 (d, 2H, 3.1 Hz), 7.33 (d, 1H, 3.9 Hz), 7.22 (dd, 2H, 3.9, 7.3 Hz).

5''-(4-(diphenylamino)phenyl)-[2,2':5',2''-terthiophene]-5-carbaldehyde (12)

A mixture of compound **7** (0.71 g, 2.46 mmol), compound **11** (0.58 g, 1.64 mmol), Pd(PPh₃)₄ (0.057 g, 0.049 mmol) and NaHCO₃ (2.07 g, 24.6 mmol) in THF and H₂O (30 ml/10 ml, 3:1 v/v) was refluxed for 48 h. The reaction mixture was concentrated under vacuum and was extracted with dichloromethane. The organic phase was washed with water and brine, and dried over

anhydrous MgSO₄. Volatiles were evaporated and the residue was purified by column chromatography on silica gel using dichloromethane and hexane (2:1 v/v) to give orange-red solid product (yield: 0.72 g, 84 %). ¹H NMR (300 MHz, acetone-*d*₆, ppm) δ: 9.95 (s, 1H), 7.96 (d, 1H, 3.9 Hz), 7.63 (d, 2H, 8.6 Hz), 7.52 (dd, 2H, 3.9, 6.7 Hz), 7.39 (d, 3H, 3.7 Hz), 7.34 (t, 4H, 3.9 Hz), 7.13 (d, 6H, 7.8 Hz), 7.07 (d, 2H, 8.7 Hz).

2-((5''-(4-(diphenylamino)phenyl)-[2,2':5',2''-terthiophen]-5-yl)methylene)-1H-indene-1,3(2H)-dione (H2)

To a solution of compound **12** (0.72 g, 1.4 mmol) in THF (25 ml) at 65 °C was added dropwise 1,3-indandione (0.235 g, 1.61 mmol) in THF (7 ml). The reaction mixture was stirred at the same temperature for 60 h, cooled to RT and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using dichloromethane to give dark pink solid product, which was treated with dichloromethane and ethanol to isolate the product as precipitates. The precipitate was purified further by temperature gradient sublimation under reduced pressure (10⁻³ torr) to give dark green solid product (yield: 0.25 g, 28%). ¹H NMR (300 MHz, DMSO-*d*₆, ppm) δ: 8.23 (d, 1H, 4.1 Hz), 8.08 (s, 1H), 7.95 (s, 4H), 7.70 (d, 1H, 3.9 Hz), 7.67 (d, 1H, 4.0 Hz), 7.61 (d, 2H, 8.6 Hz) 7.47 (dd, 3H, 3.8, 11.1 Hz), 7.36 (t, 4H, 7.7 Hz), 7.10 (t, 6H, 9.2 Hz), 7.00 (d, 2H, 8.5 Hz). HRMS (FAB) m/z: calcd C₄₀H₂₅NO₂S₃ 647.83, [M+H]⁺: observed 647.10. Elemental analysis calc.: C, 74.16; H, 3.89; N, 2.16; O, 4.94; S, 14.85; found: C, 74.18; H, 3.78; N, 2.09; O, 4.98; S, 14.93

N,N-diphenyl-4-(thiophen-2-yl)aniline (13)

A mixture of (4-(diphenylamino)phenyl)boronic acid (2.13 g, 7.4 mmol), 2-bromothiophene (1.0 g, 6.1 mmol), Pd(PPh₃)₄ (0.35 g, 0.31 mmol) and K₂CO₃ (15 ml, 2M) in THF (45 ml) was refluxed for 24 h. The reaction mixture was concentrated under vacuum and was extracted with dichloromethane. The organic phase was washed with water and brine, and dried over anhydrous MgSO₄. Volatiles were evaporated and the residue was purified by column chromatography on silica gel using hexane to give white solid product (yield: 1.43 g, 71 %). ¹H NMR (300 MHz, acetone-*d*₆, ppm) δ: 7.59 (d, 2H, 8.6 Hz), 7.39 (t, 2H, 4.6 Hz), 7.34 (t, 4H, 7.9 Hz), 7.07 (m, 9H)

5-(4-(diphenylamino)phenyl)thiophene-2-carbaldehyde (14)

DMF (1.35 ml, 17.5 mmol) and POCl₃ (0.83 ml, 8.74 mmol) were added to a solution of compound **13** (1.43 g, 4.37 mmol) in distilled dichloromethane (25 ml) cooled in an ice bath. The reaction mixture was stirred at RT for 2 h and then heated at 70 °C for 12 h. The reaction mixture was cooled to room temperature, treated with sodium acetate (25 ml, 2 M), and stirred for 2 h. Volatiles were evaporated under vacuum and the resulting residue was extracted with dichloromethane. The organic phase was washed with water and brine, and dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography on silica gel using dichloromethane and hexane

(2:1 v/v) to give yellow-green solid product (yield: 0.58 g, 76 %). ^1H NMR (300 MHz, acetone- d_6 , ppm) δ : 9.92 (s, 1H), 7.95 (d, 1H, 3.9 Hz), 7.70 (dd, 2H, 1.9, 6.8 Hz), 7.57 (d, 1H, 4.0 Hz), 7.37 (dd, 4H, 5.4, 10.3 Hz), 7.14 (dd, 6H, 6.3, 7.6 Hz), 7.05 (d, 2H, 6.9 Hz)

2-((5-(4-(diphenylamino)phenyl)thiophen-2-yl)methylene)-1H-indene-1,3(2H)-dione (H3)

To a solution of compound **14** (0.51 g, 1.4 mmol) in THF (25 ml) at 65 °C was added dropwise 1,3-indandione (0.252 g, 1.72 mmol) in THF (7 ml). The reaction mixture was stirred at the same temperature for 60 h, cooled to RT and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using dichloromethane to give pink-red solid product, which was treated with dichloromethane and ethanol to isolate the product as precipitates. The precipitate was purified further by temperature gradient sublimation under reduced pressure (10^{-3} torr) to give dark pink solid product (yield: 0.29 g, 37%). ^1H NMR (300 MHz, DMSO- d_6 , ppm) δ : 8.25 (d, 1H, 4.1 Hz), 8.04 (s, 1H), 7.93 (m, 4H), 7.76 (d, 2H, 8.7 Hz), 7.69 (d, 1H, 4.1 Hz), 7.39 (t, 4H, 7.8 Hz), 7.15 (m, 6H), 7.00 (d, 2H, 8.7 Hz). HRMS (FAB) m/z : calcd $\text{C}_{32}\text{H}_{21}\text{NO}_2\text{S}$ 483.13, $[\text{M}+\text{H}]^+$: observed 483.13. Elemental analysis calc.: C, 79.48; H, 4.38; N, 2.90; O, 6.62; S, 6.63; found: C, 79.59; H, 4.25; N, 2.78; O, 6.96; S, 6.42

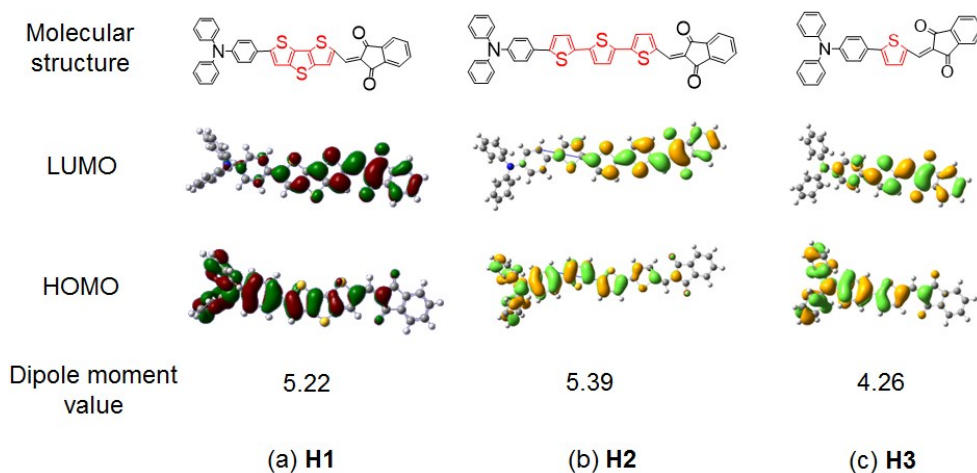


Fig. S1. Calculated geometries, orbital density maps, and dipole moment values of (a) **H1**, (b) **H2**, and (c) **H3**.

Table S1. Gibbs free energy changes (ΔG^0) for the driving force of electron transfer from donor to C_{60} .

Molecules	Reorganization energy (λ) ^a	$\lambda_{abs,max}$ (eV) ^b	PES value ^c	EA(C_{60})	ΔG^0 (PES – EA(C_{60}))
	$(\lambda_{abs,max} (eV) - \lambda_{flu,max} (eV))$	transition			
H1	0.58	2.96	3.54		– 0.96
H2	0.66	2.90	3.56	4.5	– 0.94
H3	0.54	2.99	3.53		– 0.97

^a Reorganization energy is the Stokes shift in the optical spectra of thin films. ^b $\lambda_{abs,max}$ transition is the absorption peak from thin films. ^c PES is $\lambda_{abs,max}(eV) + Reorganization\ energy (eV)$.

$$\Delta G^0 = PES_{donor} - EA_{C60} = \lambda_{abs,max}(eV) + reorganization\ energy (\lambda_{abs,max} - \lambda_{flu,max}) (eV) - EA_{C60}$$

Where PES_{donor} is the lowest potential energy surface of the excited donor and EA_{C60} is the electron affinity of C_{60} as an acceptor molecule. The PES_{donor} values were estimated by the Stokes shift in optical spectra of thin films.²

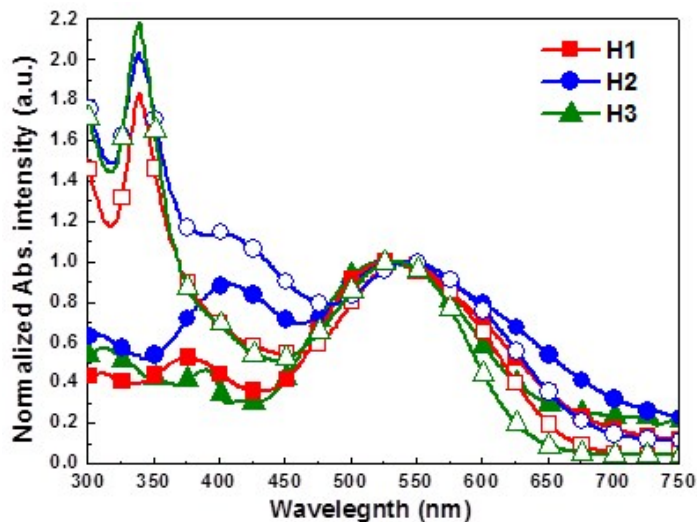


Fig. S2. (a) Normalized UV-vis absorption spectra of **H1**, **H2**, and **H3** (filled symbol lines: neat thin films, open symbol lines: donor: C_{60} (1:1) blend thin films) (rectangle: **H1**, circle: **H2**, and triangle: **H3**).

Table S2. Crystallographic data of donor molecules (**H1**, **H2**, and **H3**)

Molecule	H1	H2	H3
Empirical formula	C ₃₆ H ₂₁ NO ₂ S ₃	C ₄₀ H ₂₅ NO ₂ S ₃	C ₃₂ H ₂₁ NO ₂ S ₁
Formula weight	595.72	647.79	483.56
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
a (Å)	8.4093(5)	8.2841(5)	10.3229(9)
b (Å)	12.8870(9)	8.8440(6)	13.2772(10)
c (Å)	16.3827(11)	47.831(2)	18.3232(16)
α (°)	112.326(7)	86.851(4)	83.967(7)
β (°)	95.792(5)	88.026(4)	74.029(8)
γ (°)	99.968(5)	62.183(7)	87.616(6)
Volume (Å ³)	1590.2(2)	3094.5(4)	2400.8(4)
Density (calc) (g/cm ³)	1.244	1.390	1.338
μ (mm ⁻¹)	2.382	0.279	1.440
F (000)	616.0	1344.0	1008.0
Radiation	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)

Temperature (K)	293.2(2)	292.4(4)	293.15
Reflections collected	10998	51956	17054
Independent reflections	6230	15355	9408
	(R_{int} : 0.0567, R_{sigma} : 0.0707)	(R_{int} : 0.1362, R_{sigma} : 0.2456)	(R_{int} : 0.0738, R_{sigma} : 0.1171)
GOF	1.014	0.902	1.049
Final R indexes ($I \geq 2\sigma(I)$)	$R_1 = 0.0545$, $wR_2 = 0.1391$	$R_1 = 0.0846$, $wR_2 = 0.1780$	$R_1 = 0.0690$, $wR_2 = 0.1473$
Largest diff. peak and hole ($e \text{ \AA}^{-3}$)	0.28 / -0.27	0.20 / -0.28	0.41 / -0.33

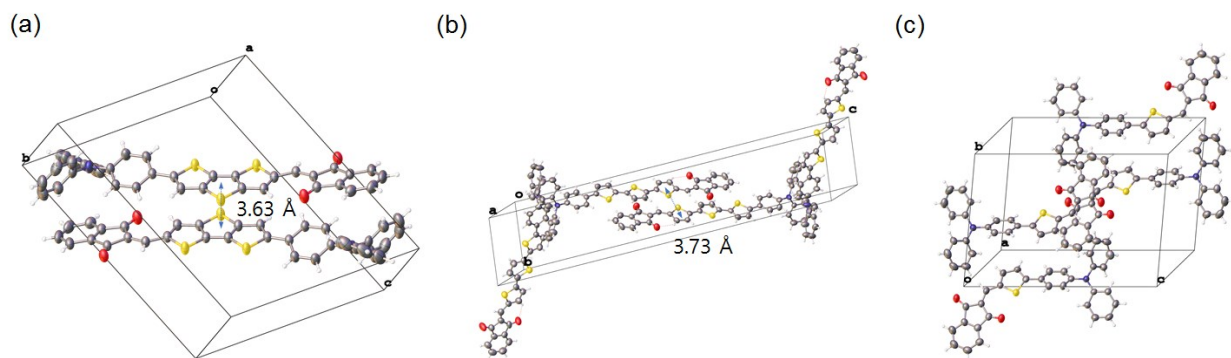


Fig. S3. Molecular packing structures of (a) **H1**, (b) **H2**, and (c) **H3**.

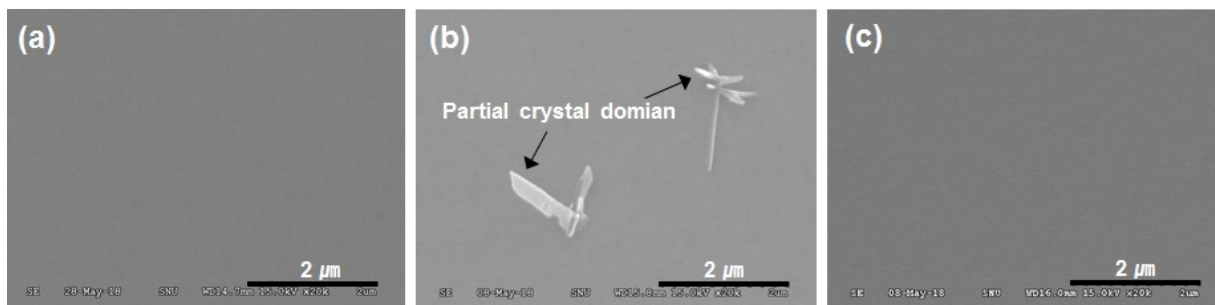


Fig. S4. SEM images of (a) H1, (b) H2, and (c) H3.

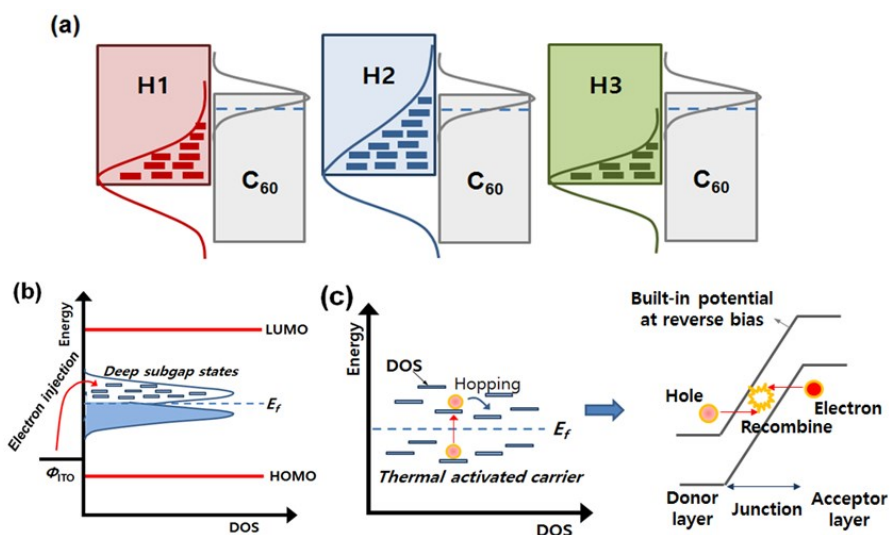


Fig. S5. (a) Schematic views of density-of-states of donor molecules, (b) and (c) plausible dark current mechanism of OPD devices at reverse bias.^{3,4}

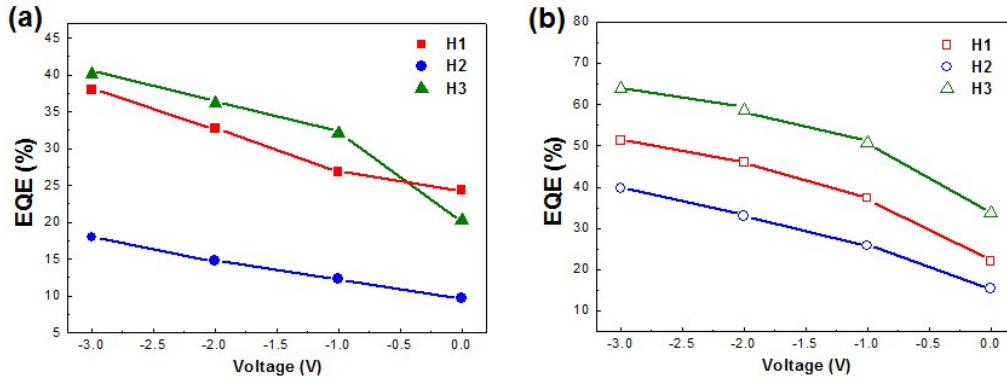


Fig. S6. EQE_{max} values (a) PJH and (b) BHJ devices under reverse bias

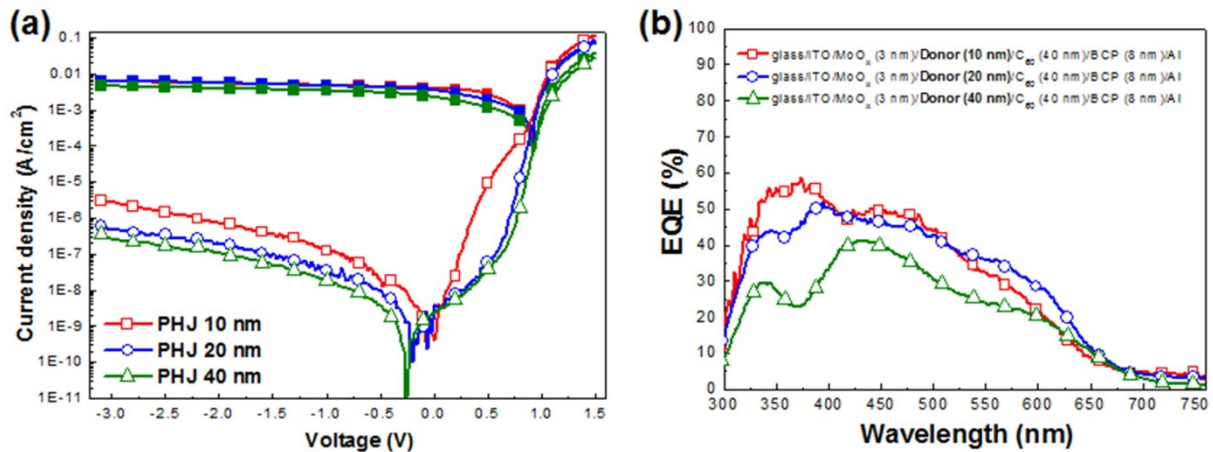


Fig. S7. (a) J - V characteristics of H1-based PHJ devices under dark conditions (filled symbol lines) and under white light (open symbol lines) conditions and (b) EQE spectra at -3 V. (rectangle: 10 nm of donor layer thickness, circle: 20 nm of donor layer thickness, triangle: 40 nm of donor layer thickness)

Table S3. Performance of the OPD devices based on **H1** according to the active layer thickness

@ -3 V	Thickness	$J_{d, best}$	J_d	J_{ph}	D^*	EQE (%)
	(nm)	(A/cm ²)	(A/cm ²)	(A/cm ²)	(cmHz ^{1/2} /W)	(@530 nm)
	10 nm	1.4×10^{-6}	2.6×10^{-6}	6.1×10^{-3}	0.7×10^{11}	36.7
PHJ	20 nm	6.7×10^{-8}	5.1×10^{-7}	6.4×10^{-3}	2.2×10^{11}	38.0
	40 nm	2.5×10^{-8}	1.5×10^{-7}	4.5×10^{-3}	2.1×10^{11}	26.5

All PHJ devices were deposited by vacuum thermal evaporation. All devices consist of glass/ITO/MoO₃(3 nm)/**H1** (X nm)/C₆₀ (40 nm)/BCP (8 nm)/Al.

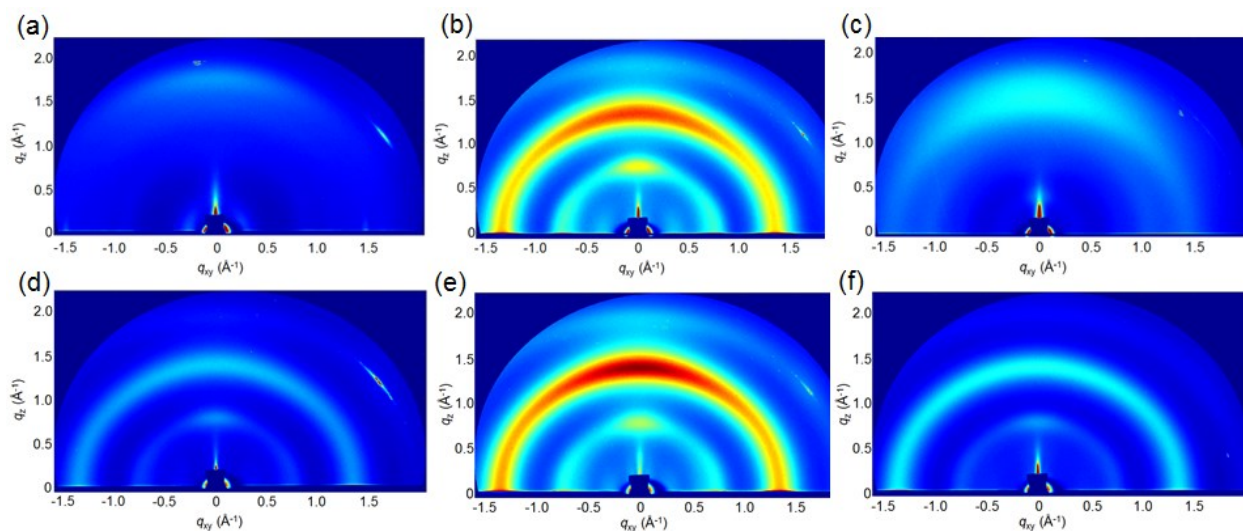


Fig. S8. 2D GIWAXS patterns of neat thin films of (a) **H1**, (b) **H2**, and (c) **H3**, and blend thin films of (d) **H1**:C₆₀ (1:1), (e) **H2**:C₆₀ (1:1), and (f) **H3**:C₆₀ (1:1).

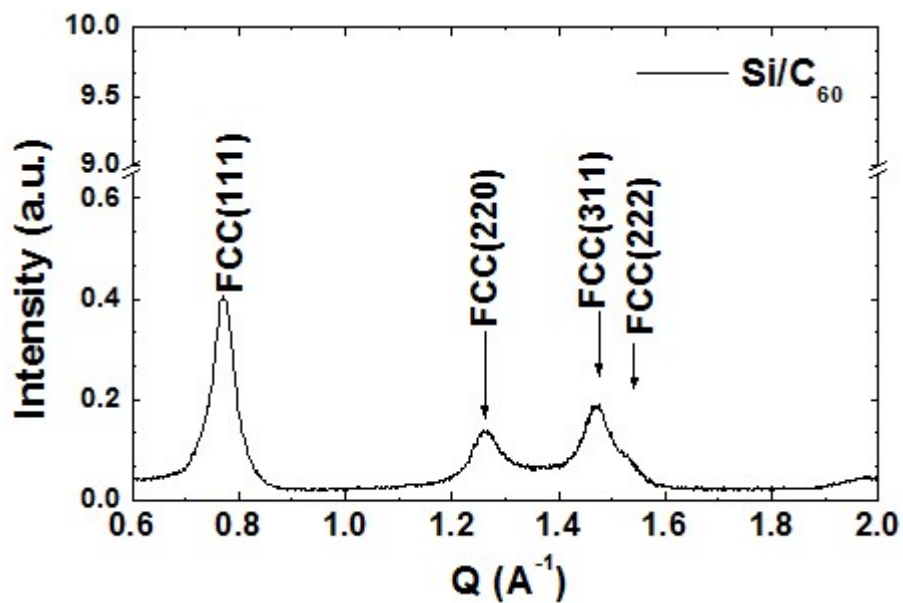


Fig. S9. Grazing incidence wide-angle X-ray scattering (GIWAXS) pattern of the C₆₀ thin film (40 nm) on Si substrate. The incident angle is 0.15°.

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