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Supporting Information

An All-Small-Molecule Organic Solar Cell derived from Naphthalimide for Solution Processed High Efficiency Nonfullerene Acceptors

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Contents

1. Experimental section	S3
2. Materials and methods	S3
3. Computational details	S3
4. Energy level diagram of BYG-1	S5
5. Energy level diagram of BYG-2	S8
(Samthaging	C10
o. Synthesis	
7 Device fabrication and characterization	S16
8. ¹ H-NMR and ¹³ C-NMR Spectra	S17
A	
9. References	S30

1. Experimental Section:

2. Materials and methods

All precursor materials were purchased directly from commercial sources and used as such without any further purification and solvents were dried under vacuum by following standard procedure. UV-vis spectrophotometer used to record absorption spectra in dichloromethane (DCM) solution and for TiO₂ film. NMR (¹H and ¹³C) spectra were measured with advance spectrometers at 300, 400 and 500 MHZ, using tetramethylsilane (TMS) as an internal standard. High resolution mass spectra were measured on a Shimadzu LCMS-2010 EV model with ESI probe and the final compounds are also characterized by using MALDI-TOF. Cyclic voltammetry was performed on CH-Instruments with a three electrode system consisting of Ag/AgCl reference electrode, a working electrode and a platinum wire counter-electrode. The redox Electronic potentials of the dyes were measured in chloroform (CHCl₃) containing 0.1 M Bu₄NHClO₄ at a scan rate of 100 mV s⁻¹.

3. Computational details

Density Functional Theory (DFT) and Time Dependent DFT (TDDFT) calculations were performed using *Gaussian09* software program package¹. The corresponding structures are shown (Figure S1 and S2). Long alkyl groups are replaced with methyl groups so as to decrease the computational complexity.

TDDFT calculations were performed at B3LYP² /6-311g (d,p) level of theory in ethanol solvent by means of the Polarizable Continuum Model^{3,4}(PCM), as implemented in *Gaussian* 09.50 singlet-singlet excitations at S₀ optimized geometry are calculated. The software *GaussSum* 2.2.⁵ was used to simulate the major portion of the absorption spectrum and to interpret the nature of transitions. The molecular orbital surfaces are visualized with *Gaussview*,⁶ and the molecular orbital were calculated using *GaussSum*.



TableS1: Molecular orbital of BYG-1 calculated at B3LYP/6-311g (d,p) level of theory in DCM solvent.

4. Energy level diagram of BYG-1



Figure S1. Schematic representation of the energy levels of the **BYG-1** complexes based on computational studies.

Table S2. Major allowed transitions in the range of 290-450 nm of **BYG-1** calculated atB3LYP/6-311g (d,p)level of theory in DCM solvent.

S1 443.9869 3.0706 HOMO->LUMO (63%), HOMO->L+2 (3%) S1 443.9869 3.0706 H-1->L+1 (25%) HOMO->L+1 (50%), H-3- >L+2 (2%), H-2->L+1 (4%), HOMO->L+3 (3%) HOMO->L+3 (3%)
S1 443.9869 3.0706 (63%), HOMO->L+2 (3%) H-1->L+1 (25%) HOMO->L+1 (50%), H-3- L+2 (2%), H-2->L+1 (4%), HOMO->L+3 (3%)
S1 443.9869 3.0706 HOMO->L+2 (3%) H-1->L+1 (25%) H-1->L+1 (25%) HOMO->L+1 (50%), H-3- >L+2 (2%), H-2->L+1 (4%), S2 419.3585 0.0521 H-1->LUMO (36%) HOMO->L+3 (3%)
S1 443.9869 3.0706 H-1->L+1 (25%) HOMO->L+1 (50%), H-3- HOMO->L+1 (50%), H-3- >L+2 (2%), H-2->L+1 (4%), S2 419.3585 0.0521 H-1->LUMO (36%) HOMO->L+3 (3%)
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419.3585 0.0521 H-1->LUMO (36%) >L+2 (2%), H-2->L+1 (4%), S2 HOMO->L+3 (3%)
419.3585 0.0521 H-1->LUMO (36%) HOMO->L+3 (3%)
32
H-1->L+1 (16%), H-1-
S3 349 1013 0 2329 H_{-2} UIMO (29%) (23%) H_{-3} $L+1 (7%)$
55 547.1015 0.2527 11-2->LONO (2570) (2570),11-5->L+1 (770)
H-1->L+2 (19%), HOMO-
S4 344.6088 0.0051 H-2->L+1 (22%) (9%), H-2->L+3 (3%)
H-1->L+1 (10%), H-1->L+3 (24%)
HOMO->LUMO (10%),
S5 318.0691 0.1969 H-2->LUMO (12%) HOMO->L+2 (11%)
H-1->LUMO (18%), H-1-
S6 314 1602 0 0007 H 2 >L +1 (12%) $>L+2 (19\%), HOMO->L+1 (28\%) H 2 >L +3 (0\%)$
30 314.1002 0.0007 11-2->L+1 (12/0) (20/0),11-2->L+3 (9/0)
H-7->L+1 (26%), H-7->L+2
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
37 300.3472 0.0440 H-7->LUMO (24%) (5%)
H-8->L+1 (26%), H-8->L+2 (14%)
H = 2 (120%) H =
S8 300.2745 0.05 H-8->LUMO (24%) (13%), n-3->L+7
HOMO->L+2 (10%),H-10- >L UMO (5%) H-10->L+1
S9 292.5446 0.0908 H-3->L+1 (15%) (4%), H-10->L+2 (4%)
HOMO->L+3 (11%),H-9- >LUMO (6%), H-9->L+1
S10 291.3964 0.0914 H-3->LUMO (17%) (4%), H-9->L+2 (4%)



Table S3: Molecular orbital of BYG-2 calculated at B3LYP/6-311g (d,p) level of theory in DCM solvent.

5. Energy level diagram of BYG-2



Figure S2. Schematic representation of the energy levels of the BYG-2 complexes based on computational studies.

Table S4. Major allowed transitions in the range of 290-450 nm of **BYG-1** calculated atB3LYP/6-311g (d,p)level of theory in DCM solvent.

Excited State	Wavelength (nm)	Osc. Strength	Major contributions	Minor contributions
				HOMO->LUMO (64%)
S 1	449.6059	3.1307	H-1->L+1 (24%)	HOMO->L+2 (3%)
				HOMO->L+1 (49%)
S2	422.1572	0.0513	H-1->LUMO (37%)	H-2->L+1 (3%)
				H-1->L+1 (14%)
\$3	352.1054	0.258	H-2->LUMO (23%)	H-1->L+3 (16%)
				H-1->L+2 (24%)
S4	347.6818	0.0044	H-2->L+1 (17%)	HOMO->L+3 (37%)
				H-1->L+1 (13%)
S5	319.9818	0.1801	H-2->LUMO (18%)	H-1->L+3 (22%)
				H-1->LUMO (22%)
S6	315.1104	0.0002	H-2->L+1 (16%)	H-1->L+2 (15%)
				H-7->L+1 (26%)
S 7	299.4984	0.0378	H-7->LUMO (22%)	H-7->L+2 (16%)
				H-8->L+1 (25%)
S8	299.4477	0.051	H-8->LUMO (23%)	H-8->L+2 (16%)
				H-3->L+1 (11%)
S9	291.7186	0.0217	H-3->LUMO (14%)	H-10->LUMO (3%)
				H-3->L+1 (13%)
S10	290.5632	0.0752	H-3->LUMO (11%)	H-9->LUMO (3%)

6. Synthesis



Scheme-S1: Synthetic procedure for compound BYG-1 and BYG-2.

6-bromo-2-(2-ethylhexyl)-1H-benzo[d]isoquinoline-1,3(2H)-dione (1).

A dry flask (250 mL) was charged with 4-bromo-1,8-naphthalic anhydride (8 g, 28.80mmol) and ethanol (100ml) in the presence of inert nitrogen atmosphere. After stirring the reaction for 30minutes, the 2-ethylhexyl amine (4.48 g, 34.50mmol) was added dropwise. Then reflex the reaction mixture up to 24 hours at 78 °C. After completion of the reaction, the corresponding reaction solvent was removed by rotary evaporation and exacted by using EtOAc as a solvent. The combined organic layer was washed with brine and dried over anhydrous sodium sulphate and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using EtOAc and hexane (2:3), to afford the product-1as white solid to yield (9g, 81%).¹H NMR (300 MHz, CDCl₃) δ =8.66(d, *J*=7.3 Hz, 1H), 8.58(d, *J*=8.5 Hz, 1H), 8.42(d, *J*=8.0 Hz, 1H), 8.05(d, *J*=7.8 Hz, 1H), 7.85(t, *J*=8.0 Hz, 1H), 4.17-4.06(m, 2H), 1.98-1.89(m, 1H), 1.41-1.24(m, 8H), 0.93(t, 3H), 0.87(t, 3H). ¹³C NMR (400 MHz, CDCl₃):163.97, 163.94, 133.11, 132.04, 131.24, 131.05, 130.56, 130.12, 129.01, 128.01, 123.15, 122.26, 44.25, 37.88, 30.73, 28.65, 24.05, 23.05, 14.07, 10.62. MS(ESI): Calculated for C₂₀H₂₂BrNO₂(M+H): 388.30 Found: 390.40

2-(2-ethylhexyl)-6-(3-hydroxy-3-methylbut-1-ynyl)-1H-benzo[d]isoquinoline-1,3(2H) dione (2).

A dry flask (100 ml) was charged with compound-1 (8g, 20.65mmol), 2-methyl-3-butyne-2ol (2.25g, 26.76mmol), triethyl amine (6 ml), triphenyl phosphine (50 mg) and dry 1,4dioxane (50 ml) in the presence of inert nitrogen atmosphere. De gassed the reaction mixture up to 20 minutes in nitrogen atmosphere, then added the Pd(II) (10%) catalyst and copper iodide (50 mg). Then reflex the reaction mixture up to 12 hours at 100 °C, after completion of the reaction the corresponding solvent was removed by rotary evaporation and extracted by using EtOAc as a solvent. The combined organic layer was washed with brine and dried over anhydrous sodium sulphate and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using EtOAc and hexane (4:1), to afford the product-2 yield (6g, 82%) ¹H NMR (400 MHz, CDCl₃): δ =8.62(d, *J*=7.3 Hz, 1H), 8.56(d, *J*=7.2 Hz, 1H), 8.50(d, *J*=7.5 Hz, 1H), 7.83(d, *J*=7.7 Hz, 1H), 7.80(t, *J*=8.0 Hz, 1H), 4.15-4.06(m, 2H), 1.98-1.89(m, 1H), 1.75(s, 6H), 1.59(s,1H), 1.41-1.24(m, 8H), 0.93(t, 3H), 0.87(t, 3H).¹³C NMR (300 MHz, CDCl₃):164.36, 164.06, 131.95, 131.61, 131.36, 130.64, 130.28, 127.75, 127.35, 126.85, 122.75, 122.05, 103.70, 103.62, 78.82, 65.78, 44.24, 38.01, 31.38, 30.71, 28.64, 24.01, 23.02, 14.07, 10.62. MS(ESI): Calculated for C₂₅H₂₂NO₃(M⁺): 391.21 Found: 392.00

2-(2-ethylhexyl)-6-ethynyl-1H-benzo[d]isoquinoline-1,3(2H)-dione (3)

A dry flask (100 ml) was charged with compound-2 (4.4g, 11.27 mmol), sodium hydroxide (1.24g, 33.62mmol) and toluene (60 ml) in the presence of nitrogen atmosphere. Then the reflex the reaction up to 4 hours at 110 °C, after completion of the reaction the corresponding solvent was removed by rotary evaporation and extracted by using EtOAc as a solvent. The combined organic layer was washed with brine and dried over anhydrous sodium sulphate and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using EtOAc and hexane (3:2), to afford the product-3 yield (2.8g, 75%).¹H NMR (400 MHz, CDCl₃): δ =8.66(d, *J*=8.3 Hz, 1H), 8.63(d, *J*=7.3 Hz, 1H), 8.53(d, *J*=7.5 Hz, 1H), 7.94(d, *J*=7.5 Hz, 1H), 7.83(t, *J*=7.3 Hz, 1H), 4.15-4.06(m, 2H), 3.73(s, 1H), 1.98-1.89(m, 1H), 1.41-1.24(m, 8H), 0.93(t, 3H), 0.87(t, 3H).¹³C NMR (300 MHz, CDCl₃):164.20, 164.92, 131.95, 131.99, 131.85, 131.63, 131.57, 130.10, 127.85, 127.61, 126.04, 122.94, 122.78, 86.38, 80.29, 44.20, 37.89, 30.71, 28.67, 24.03, 23.04, 14.07, 10.62. MS(ESI): Calculated for C₂₂H₂₃NO₂(M⁺): 333.17 Found: 334.

6-((7-bromobenzo[c][1,2,5]thiadiazol-4-yl)ethynyl)-2-(2-ethylhexyl)-1Hbenzo[d]isoquinoline-1,3(2H)-dione (4)

A dry flask (50 ml) was charged with compound-3 (624 mg, 1.87mmol), 4,7dibromobenzo[c]-1,2,5-thiadiazole (500 mg, 1.70mmol), triethylamine (2.5 ml), triphenyl phosphine (25 mg) and dry 1,4-dioxane (35 ml) in the presence of inert nitrogen atmosphere. De gassed the reaction mixture up to 20 minutes in nitrogen atmosphere, then added the Pd(II) (10%) catalyst and copper iodide (25 mg). Reflex the reaction mixture up to 12 hours at 100 °C, after completion of the reaction the corresponding solvent was removed by rotary evaporation and extracted by using EtOAc as a solvent. The combined organic layer was washed with brine and dried over anhydrous sodium sulphate and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using EtOAc and hexane (4:1), to afford the product-4 yield (270mg, 60%).¹H NMR (400 MHz, CDCl₃): δ =9.0(d, *J*=8.3 Hz, 1H), 8.68(d, *J*=8.3 Hz, 1H), 8.60(d, *J*=7.5 Hz, 1H), 8.08(d, *J*=7.5 Hz, 1H), 7.94(t, *J*=3.9 Hz, 1H), 7.91(d, *J*=4.2 Hz 1H), 7.81(d, *J*=7.5 Hz 1H), 4.20-4.06(m, 2H), 2.0-1.92(m, 1H), 1.41-1.24(m, 8H), 0.93(t, 3H), 0.87(t, 3H).¹³C NMR (300 MHz, CDCl₃) 164.13, 164.28, 133.17, 132.44, 131.95, 131.80, 131.09, 130.28, 128.09, 127.90, 127.67, 126.46, 123.70, 123.03, 122.90, 116.14, 115.69, 93.62, 93.44, 37.93, 30.74, 29.70, 28.70, 24.06, 23.07, 14.09, 10.64.MS(ESI): Calculated for C₂₈H₂₄N₃BrO₂S(M⁺): 546.48 Found: 557

6-((7-bromo-6-fluorobenzo[c][1,2,5]thiadiazol-4-yl)ethynyl)-2-(2-ethylhexyl)-1Hbenzo[d]isoquinoline-1,3(2H)-dione (5)

A dry flask (50 ml) was charged with compound-3 (294.0 mg, 1.06mmol), 4,7-dibromo-5fluoro-2,1,3-benzothiadiazole (300 mg, 0.961mmol), triethyl amine (1.5 ml), triphenyl phosphine (15 mg) and dry 1,4-dioxane (35 ml) in the presence of inert nitrogen atmosphere. De gassed the reaction mixture up to 20 minutes in nitrogen atmosphere, then added the Pd(II) (10%) catalyst and copper iodide (25 mg). Reflex the reaction mixture up to 12 hours at 100 °C, after completion of the reaction the corresponding solvent was removed by rotary evaporation and extracted by using EtOAc as a solvent. The combined organic layer was washed with brine and dried over anhydrous sodium sulphate and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using EtOAc and hexane (4:1), to afford the product-5 yield (230 mg, 60%).¹H NMR (500 MHz, CDCl³):δ=8.97(d, J=8.4 Hz, 1H), 8.68(d, J=8.2 Hz, 1H), 8.60(d, J=7.5 Hz, 1H), 8.09(d, J=7.5 Hz, 1H), 7.94(t, J=7.4 Hz, 1H), 7.82(d, J=9.0 Hz 1H), 4.20-4.06(m, 2H), 2.0-1.92(m, 1H), 1.41-1.27(m, 8H), 0.93(t, 3H), 0.87(t, 3H).¹³C NMR (400 MHz, CDCl₃)164.13, 163.90, 161.10, 159.10, 151.34, 132.33, 131.88, 131.71, 131.35, 130.17, 128.02, 125.77, 123.77, 123.49, 123.23, 123.04, 115.89, 115.79, 94.64, 92.77, 44.30, 37.91. 30.71. 28.69, 24.06, 23.07, 14.07, 10.62. MS(ESI):Calculated for C₂₈H₂₃BrFN₃O₂S(M⁺): 564.47 Found: 566.46

2,7-dibromo-9,9-didecyl-9H-fluorene (6)

A dry flask (250 mL) was charged with 2,7-Dibromofluorene (5.0 g, 30.54mmol), KOH (6.74 g, 120.0mmol) and DMSO (50ml) under nitrogen gas atmosphere. After the system had been stirred for 20 min, 1-Bromodecane (19.26 g, 91.62mmol) was slowly added by string the solution was stirred for 24 h. After completion of the reaction, the reaction mixture was diluted with ice-water/ water (more than two times) and extracted with EtOAc by separatory funnel. The combined organic layer was washed with brine and dried over anhydrous sodium sulphate and then the organic solvents were completely removed by rotary evaporation. The

residue was purified by column chromatography using petroleum as eluent, to afford product-6 yield (8g, 83%).¹H NMR (500 MHz, CDCl₃): δ =7.52(S, 1H), 7.51(S, 1H), 7.45(d, 1H), 7.44-7.43(m, 3H), 1.93-1.89(m, 4H), 1.28-1.22(m, 6H), 1.22-1.12(m, 13H), 1.11-1.02(m, 13H), 0.85(t, 6H).¹³C NMR (400 MHz, CDCl₃): 152.54, 139.05, 130.09, 126.14, 121.44, 121.12, 55.66, 40.09, 31.85, 29.85, 29.48, 29.25, 29.17, 23.61, 22.64, 14.10. MS(ESI): Calculated for C₃₃H₄₈Br₂(M⁺): 604.54 Found: 601

2,2'-(9,9-didecyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (7)

А dry flask (100 ml) was charged with compound-6 (1.46g, 4.96mmol), Bis(pinacolato)diborane(2.89g, 12.40mmol) and potassium acetate(0.852g, 29.76mmol) in inert nitrogen condition. De gassed the reaction mixture up to 20 minutes in nitrogen atmosphere, then added the Pd(II) (10%) catalyst. Then reflex the reaction mixture up to 24 h at 100°C. After completion of the reaction, the reaction mixture was workup by using EtOAc as an eluent. The combined organic layer was washed with brine and dried over anhydrous sodium sulphate and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using petroleum and EtOAc (1:4) are elutes, to afford product-7 yield (2.5g, 73%).¹H NMR (500 MHz, CDCl₃): $\delta = 7.81(S, 1H), 7.79(S, 1H), 7.74(d, 2H), 7.72(S, 1H), 7.71(S, 1H), 2.02-1.897(m, 4H),$ 1.39(S, 24H), 1.26-1.19(m, 6H), 1.22-1.08(m, 13H), 1.10-1.00(m, 13H), 0.85(t, 6H).¹³C NMR (400 MHz, CDCl₃): 150.44, 143.89, 133.62, 128.87, 119.35, 83.69, 55.17, 40.11, 31.83, 30.00, 29.55, 29.51, 29.24, 24.91, 23.64, 22.61, 14.09. MS(ESI): Calculated for C₄₅H₇₂B₂O₄(M⁺): 698.67 Found 699.8

6-((7-(9,9-didecyl-7-(7-((2-(2-ethylhexyl)-1,3-dioxo-2,3-dihydro-1Hbenzo[de]isoquinolin-6-yl)ethynyl)-5-fluorobenzo[c][1,2,5]thiadiazol-4-yl)-9H-fluoren-2-yl)-6fluorobenzo[c][1,2,5]thiadiazol-4-yl)ethynyl)-2-(3-ethylheptyl)-1Hbenzo[de]isoquinoline-1,3(2H)-dione (8)

A dry flask (50 mL) was charged with compound 7 (120mg, 0.171mmol), compound 6 (223mg, 0.395mmol), DME (30 ml) and 2M sodium carbonate (1.06 g) in inert nitrogen condition. De gassed the reaction mixture up to 20 minutes in nitrogen atmosphere then added the Pd(II) (10%) catalyst, reflex the reaction mixture up to 12 h at 70 $^{\circ}$ C. After completion of the reaction, the reaction mixture was workup by using EtOAc as a solvent. The combined organic layer was washed with brine and dried over anhydrous sodium

sulphate and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using petroleum and EtOAc (1:4) are elutes, to afford product 8 as orange yellow solid. Yield (200 mg 65%). ¹H NMR (400 MHz, CDCl₃): δ =9.06(d, *J*=8.4 Hz, 2H), 8.70(d, *J*=6.409 Hz, 2H), 8.63(d, *J*=7.6 Hz, 2H), 8.13(d, *J*=7.5 Hz, 2H), 7.96(t, *J*=7.32 Hz, 5H), 7.94(s, 1H), 7.91(d, *J*=5.5 Hz 3H), 4.20-4.10(m, 4H), 2.20-2.11(m, 4H), 2.02-1.93(m, 2H), 1.57(s, 12H), 1.48-1.38(m, 6H), 1.38-1.24(m, 12H), 1.24-1.07(m, 18H), 0.95(t, 6H), 0.89(t, 8H), 0.82(t, 6H).¹³C NMR (400 MHz, CDCl₃)164.28, 164.00, 160.00, 159.98, 157.46, 157.33, 154.32, 154.23, 152.51, 151.41, 141.30, 132.46, 131.84, 131.26, 130.26, 129.61, 128.07, 127.95, 126.28, 125.65, 124.85, 124.51, 123.03, 121.22, 121.08, 120.02, 115.02, 114.88, 93.77, 93.35, 55.52, 44.30, 40.01, 37.94, 31.87, 30.74, 30.06, 29.66, 29.56, 29.25, 28.70, 24.04, 23.08, 22.63, 14.08, 10.63. MS(ESI):Calculated for C₉₀H₉₆F₂N₆O₄S₂(M⁺): 1413.89 Found1413.92.

6-((7-(9,9-didecyl-7-(7-((2-(2-ethylhexyl)-1,3-dioxo-2,3-dihydro-1Hbenzo[de]isoquinolin6- yl)ethynyl)benzo[c][1,2,5]thiadiazol-4-yl)-9H-fluoren-2-yl)benzo[c][1,2,5]thiadiazol4-yl)ethynyl)-2-(3-ethylheptyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (9)

A dry flask (50 mL) was charged with compound-7 (140mg, 0.200 mmol), compound-4 (252mg, 0.461 mmol), DME (30ml) and 2M sodium carbonate (1.06 g) in inert nitrogen condition. De gassed the reaction mixture up to 20 minutes in nitrogen atmosphere then added the Pd(II) (10%) catalyst, reflex the reaction mixture up to 12 h at 70 °C. After completion of the reaction, the reaction mixture was workup by using EtOAc as an eluent. The combined organic layer was washed with brine and dried over anhydrous sodium sulphate and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using petroleum and EtOAc (1:4) are elutes, to afford product-8 yield (210mg 65%).¹H NMR (400 MHz, CDCl₃): δ =9.11(d, J=8.4 Hz, 2H), 8.70(d, J=7.3 Hz, 2H), 8.62(d, J=7.5 Hz, 2H), 8.12(d, J=7.5 Hz, 2H), 8.07(t, J=4.4 Hz, 6H), 7.97(d, J=8.4 Hz 3H), 7.94(s, J=9.0 Hz 1H), 7.89(d, J=7.3 Hz 2H), 4.20-4.10(m, 4H), 2.20-2.11(m, 4H), 2.02-1.93(m, 2H), 1.57(s, 12H), 1.48-1.38(m, 6H), 1.38-1.24(m, 12H), 1.24-1.07(m, 18H), 0.95(t, 6H), 0.89(t, 8H), 0.82(t, 6H).¹³C NMR (400 MHz, CDCl₃)164.28, 163.98, 160.00, 157.51, 157.37, 154.33, 154.23, 152.54, 151.43, 141.30, 13246, 131.84, 131.26, 130.26, 129.61, 128.07, 127.95, 126.28, 125.65, 124.85, 124.51, 123.03, 121.22, 121.08, 120.02, 115.02, 114.88, 93.77, 93.35, 55.52, 44.30, 40.01, 37.94, 31.87, 30.74, 30.06, 29.66, 29.56, 29.25, 28.70, 24.04, 23.08, 22.63, 14.08, 10.63. MS(ESI):Calculated for $C_{90}H_{98}N_6O_4S_2(M^+)$: 1377.88 Found1378.07

7. Device fabrication and characterization

Indium tin oxide(ITO) coated glass substrates were used to fabricate the devices. At first, the glass substrates were initially cleaned with detergent followed by ultrasonication in deionized water, acetone, and isopropyl alcohol. The cleaned substrates were dried in an oven overnight. Aqueous PEDOT:PSS (Baytron) was spin-casted at 4000rpm for 50 s to make a film of 50 nm thickness. The PEDOT:PSS coated ITO glass substrate was dried at 100 °C for 10 min in air atmosphere. SMD and non-fullerene acceptors (BYG-1 or BYG-2) were dissolved in different weight ratios in the chloroform at a concentration of 14 mg/mL. Then the solutions of SMD and non-fullerenes were spin-coated on the top of PEDOT:PSS layer at 2500 rpm for 2 min and dried at 40 °C for 4 h. For solvent vapour annealing the active layer was placed in the petri-disc containing THF solvent for different times. A thin film of PFN in methanol solution was deposited on the top of active layer. Finally the aluminium (Al) electrode with thickness of 40 nm was thermally deposited on the active layer through a mask with an area of 20 mm2. The current-voltage (J-V) measurements were conducted with a computer-controlled Keithley source meter. The device was illuminated using a solar simulator. The IPCE spectra of the devices were recorded on Bentem IPCE system. The electron and hole only devices were fabricated to measure the electron and hole only devices

8. ¹H-NMR and ¹³C-NMR Spectra

¹H-NMR of 1



¹³C-NMR of 1



ESI spectra of 1



¹H-NMR of 2



¹³C-NMR of 2



ESI spectra of 2



¹H-NMR of 3



¹³C-NMR of 3



ESI spectra of 3



¹H-NMR of 4



¹³C-NMR of 4



ESI spectra of 4



¹H-NMR of 5



¹³C-NMR of 5



ESI spectra of 5



¹H-NMR of 6



¹³C-NMR of 6



ESI spectra of 6



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¹H-NMR of 7



¹³C-NMR of 7



ESI spectra of 7



¹H-NMR of 8



¹³C-NMR of 8



MALDI-TOF spectra of 8



¹H-NMR of 9



¹³C-NMR of 9



MALDI-TOF spectra of 9





Figure S3 Normalized absorption spectra of blend active layers



BYG1:SMD

BYG2:SMD

Figure S4. TEM images of as cast **BYG-1**:SMD and **BYG-2**:SMD in active layers. Scale bar is 200 nm.

9. References

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