Electronic supplementary information (ESI)

Influence of the Intermolecular Interactions of Electron Donating Small Molecules on the Molecular Packing and the Performance of Organic Electronic Devices

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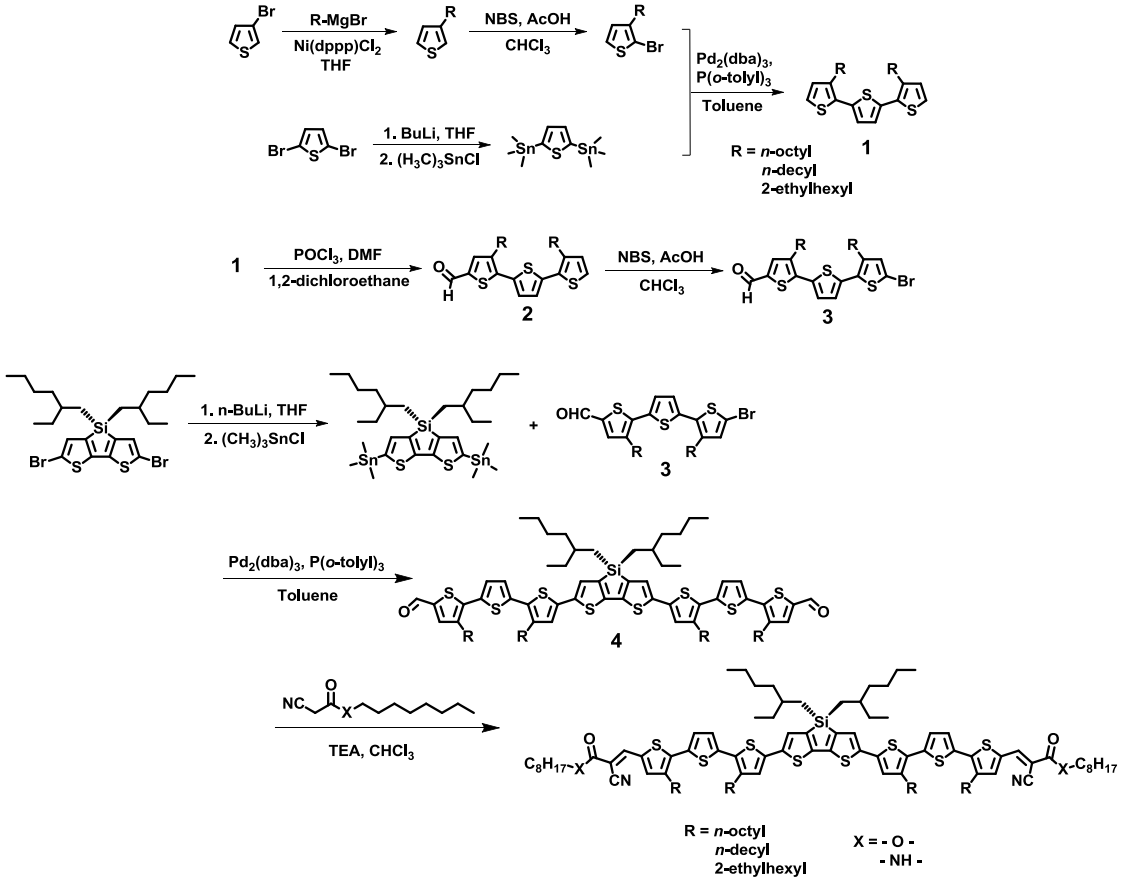
1 Synthesis of Materials

All commercially available reagents were used without further purification unless otherwise indicated. The organic solvents were used as anhydrous solvents. The progress of reaction was checked by thin-layer chromatography (TLC) analysis using Merck silica gel 60 F254 pre-coated plates (0.25 mm) with a fluorescent indicator and visualized with UV light or by iodine vapor staining. Column chromatography was carried out on Merck silica gel 60 (230-400 mesh).

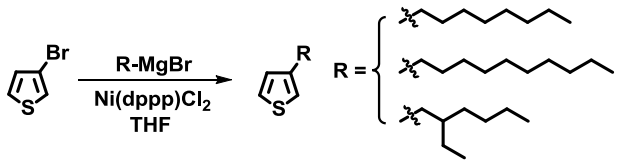
^{1}H-Nuclear Magnetic Resonance (^{1}H-NMR): All ^{1}H-NMR spectra were recorded at 400 MHz using $CDCl_3$ as a solvent at room temperature. The chemical shifts of all ^{1}H-NMR spectra are referenced to the residual signal of $CDCl_3$ (δ 7.26 ppm) by Agilent 400 MHz 54mm NMR DD2 instrument.

Matrix Assisted Laser Desorption Ionization Mass Spectra (MALDI-TOF MS): All MALDI-TOF MS were recorded by Bruker 500 MHz NMR instrument with RP_PepMix method.

Detail Synthetic Scheme



General procedure for the preparation of 3-alkylthiophene



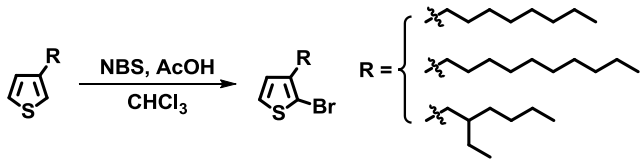
To a solution of 3-bromothiophenes (1 equiv.) and Ni(dppp)Cl_2 (1 mol%) in dry THF (0.1 M conc.) cooled to -78 °C was slowly added 1.1 equiv of appropriate alkylmagnesium bromide (1.1 equiv., *n*-octyl-MgBr or *n*-decyl-MgBr or 2-ethylhexyl-MgBr), and stirred for 1 h under N_2. The solution was gradually heated to reflux and stirred overnight. The reaction mixture was cool to R.T. and quenched by diluted HCl, then extracted with CH_2Cl_2. The organic layer was washed with water and brine; dried over $MgSO_4$; and concentrated in vacuo. The crude compound was purified by gravity column chromatography using hexane as the eluent to afford the corresponding product (70~80% yield) as a colorless liquid.

3-Octylthiophene ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 7.23 (dd, 1H), 6.94-6.91 (m, 2H), 2.62 (t, 2H), 1.61 (q, 2H), 1.30 (m, 10H), 0.88 (t, 3H).

3-Decylthiophene ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 7.23 (dd, 1H), 6.94-6.91 (m, 2H), 2.62 (t, 2H), 1.61 (q, 2H), 1.30 (m, 14H), 0.88 (t, 3H).

3-(2-Ethylhexyl)thiophene ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 7.23 (dd, 1H), 6.94-6.91 (m, 2H), 2.57 (d, 2H), 1.60 (m, 1H), 1.28 (m, 8H), 0.88 (t, 6H).

General procedure for the preparation of 2-bromo-3-alkylthiophene



To a stirred solution of appropriate 3-alkylthiophene (1 equiv.) in chloroform and acetic acid (1:1 v/v), NBS (1 equiv.) was added in dark at room temperature for 2 h. The reaction was monitored by TLC to establish completion. The organic layer was extracted with hexane, washed with $NaHCO_3$ (aq), water

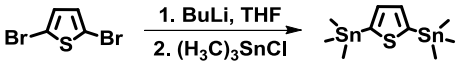
and brine; dried over $MgSO_4$; and concentrated in vacuo. The crude compound was purified by gravity column chromatography using hexane as the eluent to afford the corresponding product (90~95% yield) as colorless oil.

2-Bromo-3-octylthiophene ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 7.18 (d, 1H), 6.80 (d, 1H), 2.56 (t, 2H), 1.58 (q, 2H), 1.31 (m, 10H), 0.89 (t, 3H).

2-Bromo-3-decylthiophene ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 7.18 (d, 1H), 6.79 (d, 1H), 2.55 (t, 2H), 1.57 (q, 2H), 1.30 (m, 14H), 0.88 (t, 3H).

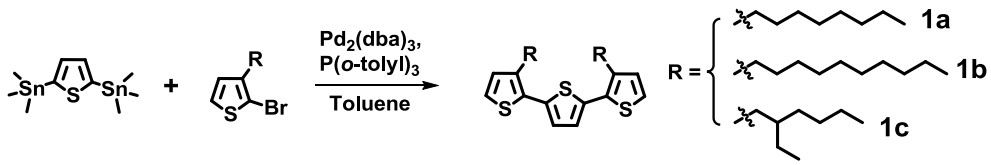
2-Bromo-3-(2-ethylhexyl)thiophene ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 7.18 (d, 1H), 6.76 (d, 1H), 2.49 (d, 2H), 1.59 (m, 1H), 1.28 (m, 8H), 0.88 (t, 6H).

2,5-Bis(trimethylstannyl)thiophene



To a solution of 2,5-dibromothiophene (2 g, 8.27 mmol) in dry THF (20 mL) cooled to -78 °C was slowly added 2.2 equiv. of n-butyllithium (11.4 mL, 1.6 M in THF), and stirred for 1 h under N_3. Then, 2.2 equiv. of trimethyltin chloride (18.2 mL, 1.0 M in THF) was added and the reaction was allowed to warm to R.T. The mixture was stirred overnight. The reaction mixture was quenched with NH_4Cl (aq) and extracted with Et_2O. The organic layer was washed with water and brine; dried over $MgSO_4$; and concentrated in vacuo. The crude compound was purified by recrystallization using EtOH to afford the corresponding product (2.55 g, 75.3% yield) as a needle-like white powder: ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 7.37 (s, 2H), 0.36 (s, 18H).

General procedure for the preparation of 3,3-dialkyl-2,2':5',2"-terthiophene (1)



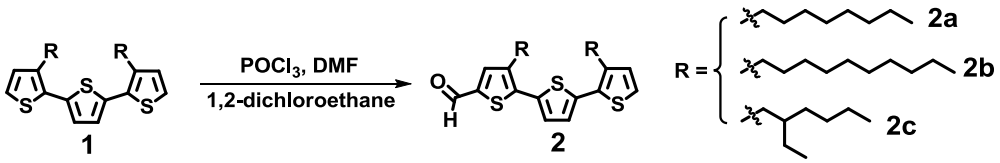
A solution of 2,5-bis(trimethylstannyl)thiophene (1 equiv.), appropriate 2-bromo-3-alkylthiophene (2.1 equiv.), $Pd_2(dba)_3$ (3 mol%) and P(*o*-tolyl)$_3$ (4 equiv. to Pd catalyst) in dry toluene (0.1 M conc.) was refluxed and stirred overnight. The reaction mixture was cool to R.T. and diluted with CH_2Cl_2. The organic layer was washed with water and brine; dried over $MgSO_4$; and concentrated in vacuo. The crude compound was purified by flash column chromatography using hexane as the eluent to afford the corresponding product (80~90% yield) as a yellow oil.

3,3-Dioctyl-2,2':5',2"-terthiophene (1a) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 7.18 (d, 2H), 7.07 (s, 2H), 6.95 (d, 2H) 2.80 (t, 4H), 1.67 (q, 4H), 1.31 (m, 20H), 0.89 (t, 6H).

3,3-Didecyl-2,2':5',2"-terthiophene (1b) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 7.17 (d, 2H), 7.05 (s, 2H), 6.94 (d, 2H), 2.77 (t, 4H), 1.64 (q, 4H), 1.30 (m, 28H), 0.87 (t, 6H).

3,3-Di(2-ethylhexyl)-2,2':5',2"-terthiophene (1c) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 7.17 (d, 2H), 7.04 (s, 2H), 6.91 (d, 2H), 2.72 (d, 4H), 1.64 (m, 2H), 1.30 (m, 16H), 0.83 (m, 12H).

General procedure for the preparation of 3,3"-dialkyl-[2,2':5',2"-terthiophene]-5-carbaldehyde (2)



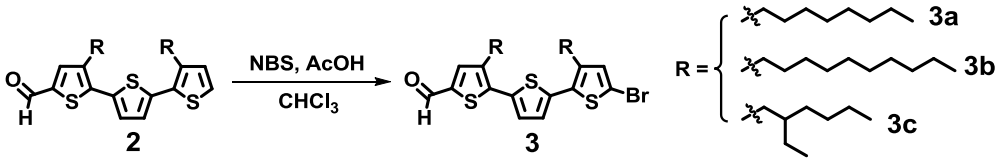
To a solution of appropriate 3,3-dialkyl-2,2':5',2"-terthiophene (**1**) (1 equiv.) and N,N-dimethylformamide (1 equiv.) in 1,2-dichloroethane (0.15 M conc.) was slowly added 1 equiv. of $POCl_3$ at 0 °C, and stirred for 1 h under N_3. Then, the reaction mixture was allowed to heat to 60 °C and stirred overnight. The mixture was cool to °C and neutralized using $NaHCO_3$ (aq). The organic layer was extracted using CH_2Cl_2 and dried over $MgSO_4$; and concentrated in vacuo. The crude compound was purified by flash column chromatography using the mixture of hexane and CH_2Cl_2 (1:2 v/v) as the eluent to afford the corresponding product (75~80% yield) as a orange oil.

3,3"-Dioctyl-[2,2':5',2"-terthiophene]-5-carbaldehyde (2a) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 9.84 (s, 1H), 7.60 (s, 1H), 7.25 (d, 1H), 7.23 (d, 1H), 7.11 (d, 1H), 6.97 (d, 1H), 2.84 (t, 2H), 2.82 (t, 2H), 1.67 (m, 4H), 1.43-1.24 (m, 20H), 0.89 (m, 6H).

3,3"-Didecyl-[2,2':5',2"-terthiophene]-5-carbaldehyde (2b) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 9.83 (s, 1H), 7.60 (s, 1H), 7.24 (d, 1H), 7.21 (d, 1H), 7.10 (d, 1H), 6.95 (d, 1H), 2.82 (t, 2H), 2.78 (t, 2H), 1.66 (m, 4H), 1.43-1.25 (m, 28H), 0.87 (m, 6H).

3,3"-Di(2-ethylhexyl)-[2,2':5',2"-terthiophene]-5-carbaldehyde (2c) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 9.84 (s, 1H), 7.56 (s, 1H), 7.23 (d, 1H), 7.21 (d, 1H), 7.10 (d, 1H), 6.92 (d, 1H), 2.77 (d, 2H), 2.72 (d, 2H), 1.67 (m, 2H), 1.38-1.23 (m, 16H), 0.88-0.82 (m, 12H).

General procedure for the preparation of 5"-bromo-3,3"-dialkyl-[2,2':5',2"-terthiophene]-5-carbaldehyde (3)



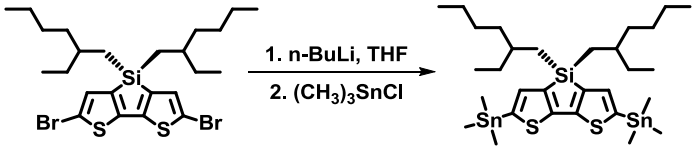
To a stirred solution of appropriate 3,3"-dialkyl-[2,2':5',2"-terthiophene]-5-carbaldehyde (**2**) (1 equiv.) in chloroform and acetic acid (1:1 v/v), NBS (1 equiv.) was added in dark at room temperature for 2 h. The reaction was monitored by TLC to establish completion. The organic layer was extracted with hexane, washed with $NaHCO_3$ (aq), water and brine; dried over $MgSO_4$; and concentrated in vacuo. The crude compound was purified by gravity column chromatography using hexane as the eluent to afford the corresponding product (90~95% yield) as orange oil.

5"-Bromo-3,3"-dioctyl-[2,2':5',2"-terthiophene]-5-carbaldehyde (3a) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 9.81 (s, 1H), 7.58 (s, 1H), 7.20 (d, 1H), 7.01 (d, 1H), 6.89 (s, 1H), 2.79 (t, 2H), 2.70 (t, 2H), 1.64 (m, 4H), 1.43-1.26 (m, 20H), 0.87 (m, 6H).

5"-Bromo-3,3"-didecyl-[2,2':5',2"-terthiophene]-5-carbaldehyde (3b) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 9.83 (s, 1H), 7.59 (s, 1H), 7.22 (d, 1H), 7.04 (d, 1H), 6.91 (s, 1H), 2.81 (t, 2H), 2.71 (t, 2H), 1.65 (m, 4H), 1.43-1.25 (m, 28H), 0.87 (m, 6H).

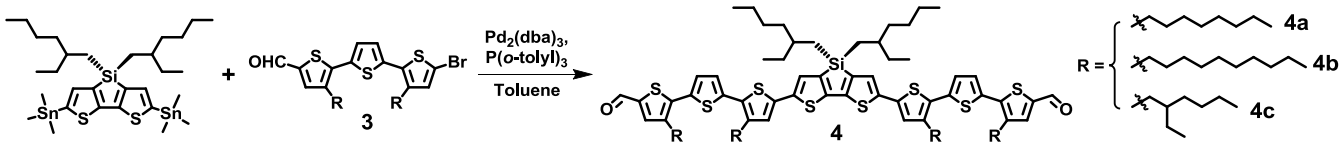
5"-Bromo-3,3"-di(2-ethylhexyl)-[2,2':5',2"-terthiophene]-5-carbaldehyde (3c) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 9.84 (s, 1H), 7.56 (s, 1H), 7.20 (d, 1H), 7.04 (d, 1H), 6.88 (s, 1H), 2.75 (d, 2H), 2.65 (d, 2H), 1.63 (m, 2H), 1.37-1.22 (m, 16H), 0.90-0.81 (m, 12H).

4,4-Bis(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4*H*-silolo[3,2-b:4,5-b']dithiophene



To a solution of 2,6-dibromo-4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-b:4,5-b']dithiophene (1 equiv., purchased from Solarmer Materials Inc.) in dry THF (0.05 M conc.) cooled to -78 °C was slowly added 2.2 equiv. of n-butyllithium (1.6 M in THF), and stirred for 1 h under N_3. Then, 2.2 equiv. of trimethyltin chloride (1.0 M in THF) was added and the reaction was allowed to warm to R.T. The mixture was stirred overnight. The reaction mixture was quenched with NH_4Cl (aq) and extracted with Et_2O. The organic layer was washed with water and brine; dried over $MgSO_4$; and concentrated in vacuo. The crude compound was used without further purification as a greenish oil, which contain a small amount of mono-stannyl product. Although we tried to purification *via* silica or alumina column chromatography pre-treated with triethylamine, the Sn-C chemical bonds were decomposed.

General procedure for the preparation of 5'',5'''''-(4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3''-dialkyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (4)



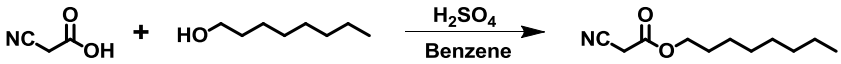
A solution of 2,6-dibromo-4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-b:4,5-b']dithiophene (1 equiv.), appropriate 5"-bromo-3,3"-dialkyl-[2,2':5',2"-terthiophene]-5-carbaldehyde (**3**) (2.1 equiv.), $Pd_2(dba)_3$ (3 mol%) and P(*o*-tolyl)$_3$ (4 equiv. to Pd catalyst) in dry toluene (0.05 M conc.) was refluxed and stirred overnight. The reaction mixture was cool to R.T. and diluted with CH_2Cl_2. The organic layer was washed with water and brine; dried over $MgSO_4$; and concentrated in vacuo. The crude compound was purified by flash column chromatography using the mixture of hexane and CH_2Cl_2 (1:1.5 v/v) as the eluent to afford the corresponding product (40~50% yield) as a dark red solid. The moderate yield is due to using the reactant as the mixture of mono-stannyl and bis-stannyl compounds.

5'',5'''''-(4,4-Bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3''-dioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (4a) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 9.83 (s, 2H), 7.60 (s, 2H), 7.25 (d, 2H), 7.16 (s, 2H), 7.13 (d, 2H), 7.00 (s, 2H), 2.83 (t, 4H), 2.77 (t, 4H), 1.70 (m, 8H), 1.42-1.18 (m, 62H), 0.88 (m, 24H).; MALDI-TOF MS: calculated for $C_{82}H_{114}O_2S_8Si$ 1416.39; found: 1416.49 (M+).

5'',5'''''-(4,4-Bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3''-didecyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (4b) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 9.83 (s, 2H), 7.61 (s, 2H), 7.24 (d, 2H), 7.17 (s, 2H), 7.13 (d, 2H), 7.01 (s, 2H), 2.85 (t, 4H), 2.78 (t, 4H), 1.71 (m, 8H), 1.43-1.20 (m, 78H), 0.88 (m, 24H).; MALDI-TOF MS: calculated for $C_{90}H_{130}O_2S_8Si$ 1528.60; found: 1528.29 (M+).

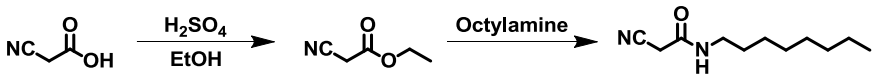
5'',5'''''-(4,4-Bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3''-di(2- ethylhexyl)-[2,2':5',2''-terthiophene]-5-carbaldehyde) (4c) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 9.82 (s, 2H), 7.59 (s, 2H), 7.22 (d, 2H), 7.14 (s, 2H), 7.11 (d, 2H), 6.98 (s, 2H), 2.80 (d, 4H), 2.74 (d, 4H), 1.69 (m, 4H), 1.42-1.21 (m, 54H), 0.89-0.80 (m, 36H).; MALDI-TOF MS: calculated for $C_{82}H_{114}O_2S_8Si$ 1416.39; found: 1416.17 (M+).

Octyl 2-cyanoacetate



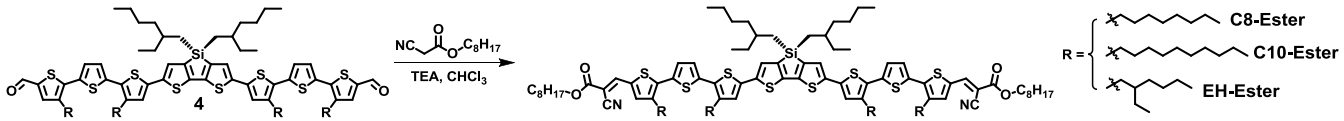
A solution of cyanoacetic acid (5 g, 58.8 mmol, 1 equiv.) and 1-octanol (10.2 mL, 64.7 mmol, 1.1 equiv.) in benzene (60 mL) was refluxed for 4 hours with catalytic amounts of H_2SO_4. The reaction mixture was cool to R.T. and quenched with $NaHCO_3$ (aq) and extracted with Et_2O. The organic layer was washed with water and brine; dried over $MgSO_4$; and concentrated in vacuo. The crude compound was purified by flash column chromatography using the mixture of hexane and ethyl acetate (8:1 v/v) to afford the corresponding product (11.2 g, 96.6% yield) as a light yellow liquid.: ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 4.14 (t, 2H), 3.43 (s, 2H), 1.62 (q, 2H), 1.22 (m, 10H), 0.82 (t, 3H).

2-Cyano-*N*-octylacetamide



A solution of cyanoacetic acid (5 g, 58.8 mmol) in EtOH (50 mL) was refluxed for 4 hours with catalytic amounts of H_2SO_4. The reaction mixture was cool to R.T. and quenched with $NaHCO_3$ (aq) and extracted with Et_2O. The organic layer was washed with water and brine; dried over $MgSO_4$; and concentrated in vacuo. The crude compound was purified by flash column chromatography using the mixture of hexane and ethyl acetate (4:1 v/v) to afford the ethyl 2-cyanoacetate (2.79 g, 42% yield) as a light yellow liquid. This compound (24.7 mmol, 1 equiv.) was stirred with octylamine (4.1 mL, 1 equiv.) overnight. The precipitate was recrystallized with EtOH to afford the corresponding product (2.34 g, 48.4% yield) as a needle-like white solid.: ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 6.16 (br, 1H), 3.36 (s, 2H), 3.29 (qr, 2H), 1.53 (q, 2H), 1.28 (m, 10H), 0.87 (t, 3H).

General procedure for the preparation of ester-terminated small molecule donors



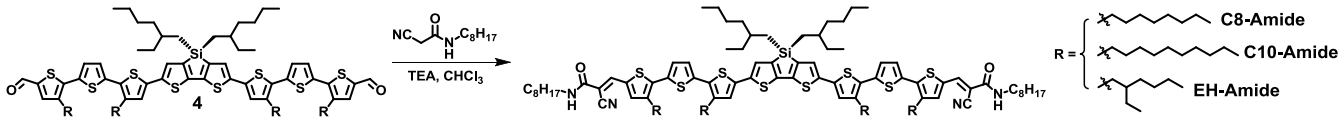
A solution of appropriate 5",5""-(4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3"-dialkyl-[2,2':5',2"-terthiophene]-5-carbaldehyde) (**4**) (1 equiv.) and octyl 2-cyanoacetate (10 equiv.) in $CHCl_3$ (0.01 M conc.) was refluxed overnight with catalytic amounts of triethylamine. The reaction mixture was cool to R.T. diluted with CH_2Cl_2. The organic layer was washed with water and brine; dried over $MgSO_4$; and concentrated in vacuo. The crude compound was purified by flash column chromatography using the mixture of hexane and CH_2Cl_2 (1:1 v/v) as the eluent to afford the corresponding product (80~90% yield) as a dark red solid.

(2,2')-Dioctyl 3,3'-(5'',5''''''-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3''-dioctyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(2-cyanoacrylate) (C8-Ester) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 8.20 (s, 2H), 7.60 (s, 2H), 7.30 (d, 2H), 7.13 (m, 4H), 7.01 (s, 2H), 4.29 (t, 4H), 2.84 (t, 4H), 2.78 (t, 4H), 1.72 (m, 12H), 1.42-1.18 (m, 82H), 0.89-0.78 (m, 30H).; MALDI-TOF MS: calculated for $C_{104}H_{148}N_2O_4S_8Si$ 1774.90; found: 1774.55 (M+).

(2,2')-Dioctyl 3,3'-(5'',5''''''-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3''-didecyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(2-cyanoacrylate) (C10-Ester) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 8.21 (s, 2H), 7.61 (s, 2H), 7.30 (d, 2H), 7.14 (m, 4H), 7.01 (s, 2H), 4.29 (t, 4H), 2.86 (t, 4H), 2.79 (t, 4H), 1.73 (m, 12H), 1.43-1.19 (m, 98H), 0.89-0.79 (m, 30H).; MALDI-TOF MS: calculated for $C_{112}H_{164}N_2O_4S_8Si$ 1887.12; found: 1887.36 (M+).

(2,2')-Dioctyl 3,3'-(5'',5''''''-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3''-di(2-ethylhexyl)-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(2-cyanoacrylate) (EH-Ester) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 8.21 (s, 2H), 7.59 (s, 2H), 7.29 (d, 2H), 7.13 (m, 4H), 7.00 (s, 2H), 4.28 (t, 4H), 2.83 (d, 4H), 2.75 (d, 4H), 1.71 (m, 8H), 1.42-1.20 (m, 74H), 0.88-0.79 (m, 42H).; MALDI-TOF MS: calculated for $C_{104}H_{148}N_2O_4S_8Si$ 1774.90; found: 1775.12 (M+).

General procedure for the preparation of amide-terminated small molecule donors



A solution of appropriate 5",5""-(4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3"-dialkyl-[2,2':5',2"-terthiophene]-5-carbaldehyde) (**4**) (1 equiv.) and 2-cyano-*N*-octylacetamide (20 equiv.) in $CHCl_3$ (0.01 M conc.) was refluxed overnight with catalytic amounts of triethylamine. The reaction mixture was cool to R.T. diluted with CH_2Cl_2. The organic layer was washed with water and brine; dried over $MgSO_4$; and concentrated in vacuo. The crude compound was purified by flash column chromatography using the mixture of hexane and CH_2Cl_2 (1:2 v/v) as the eluent to afford the corresponding product (75~80% yield) as a dark red solid.

(2,2')-Dioctyl 3,3'-(5'',5''''-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3''-dioctyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(2-cyano-N-octylacrylamide) (C8-Amide) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 8.28 (s, 2H), 7.52 (s, 2H), 7.27 (d, 2H), 7.12 (m, 4H), 7.00 (s, 2H), 6.23 (t, 2H), 3.41 (qr, 4H), 2.83 (t, 4H), 2.78 (t, 4H), 1.68 (m, 8H), 1.59 (m, 4H), 1.44-1.17 (m, 82H), 0.90-0.78 (m, 30H).; MALDI-TOF MS: calculated for $C_{104}H_{150}N_4O_2S_8Si$ 1772.93; found: 1772.99 (M+).

(2,2')-Dioctyl 3,3'-(5'',5''''-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3''-didecyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(2-cyano-N-octylacrylamide) (C10-Amide) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 8.27 (s, 2H), 7.53 (s, 2H), 7.28 (d, 2H), 7.12 (m, 4H), 7.00 (s, 2H), 6.23 (t, 2H), 3.41 (qr, 4H), 2.84 (t, 4H), 2.78 (t, 4H), 1.69 (m, 8H), 1.59 (m, 4H), 1.44-1.18 (m, 98H), 0.89-0.78 (m, 30H).; MALDI-TOF MS: calculated for $C_{112}H_{166}N_4O_2S_8Si$ 1885.15; found: 1885.31 (M+).

(2,2')-Dioctyl 3,3'-(5'',5''''-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3''-di(2-ethylhexyl)-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(2-cyano-N-octylacrylamide) (EH-Amide) ^{1}H-NMR (400 MHz, $CDCl_3$, δ) 8.27 (s, 2H), 7.51 (s, 2H), 7.27 (d, 2H), 7.11 (m, 4H), 6.98 (s, 2H), 6.22 (t, 2H), 3.40 (qr, 4H), 2.82 (d, 4H), 2.77 (d, 4H), 1.68 (m, 4H), 1.58 (m, 4H), 1.43-1.19 (m, 74H), 0.88-0.77 (m, 42H).; MALDI-TOF MS: calculated for $C_{104}H_{150}N_4O_2S_8Si$ 1772.93; found: 1773.14 (M+).

2 Supporting Data

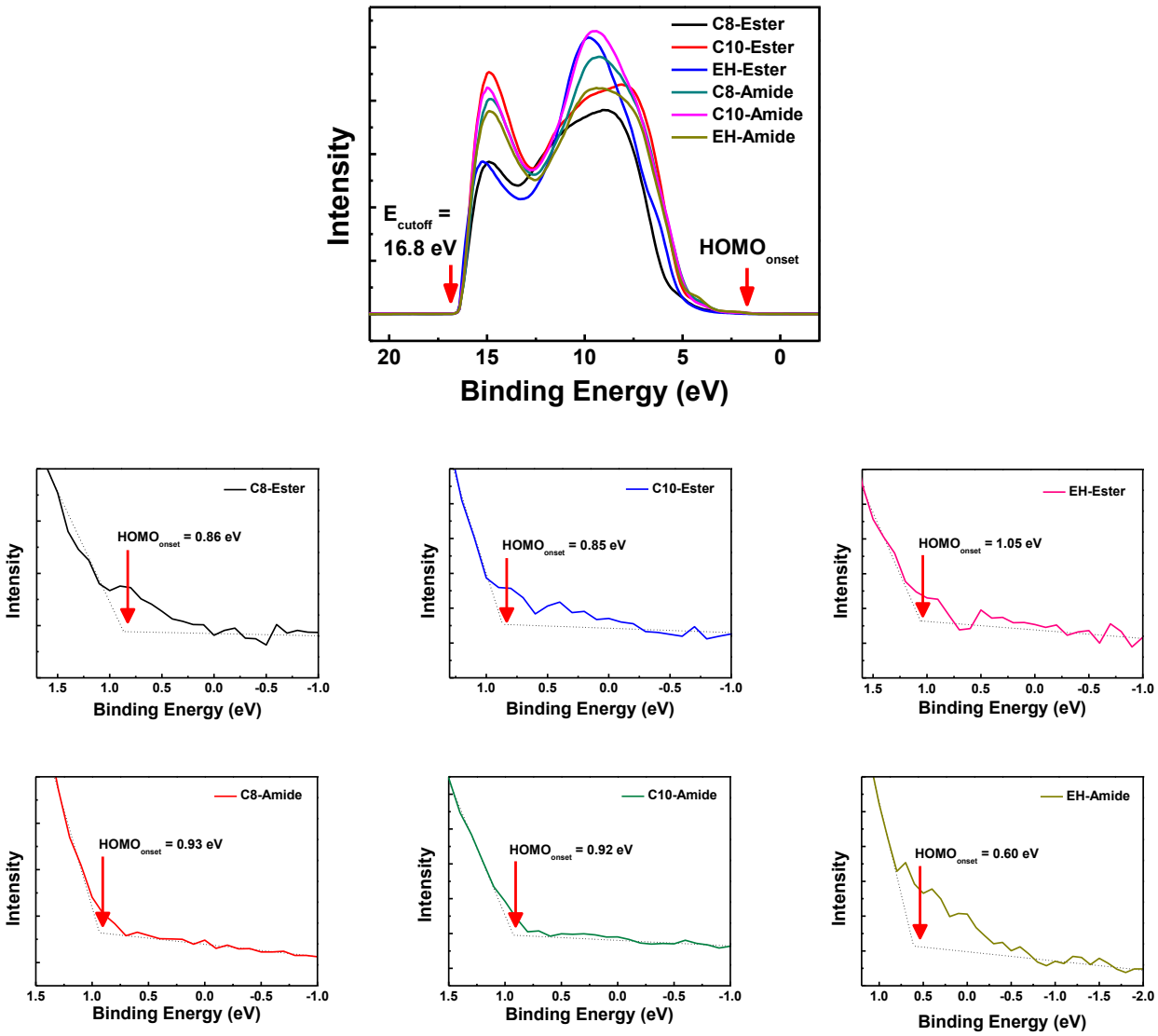


Fig. S1 Detail UPS data of small molecule donors to calculate their HOMO levels.

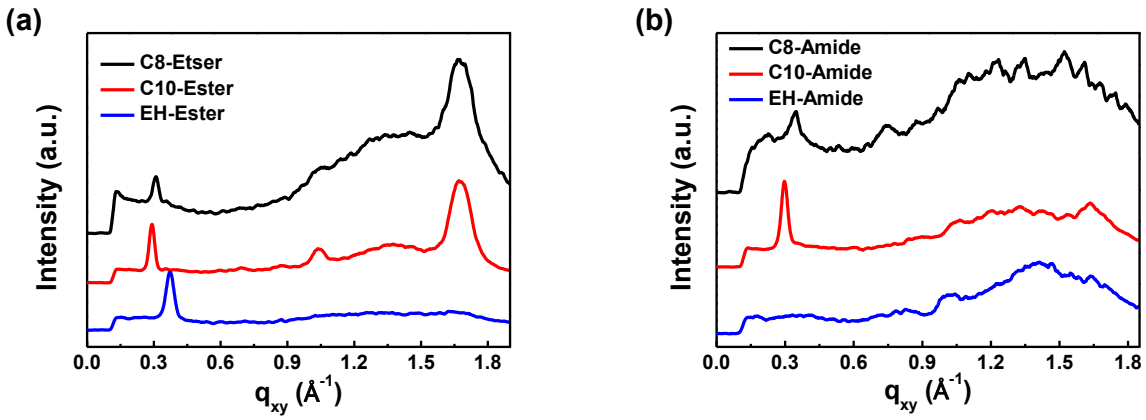


Fig. S2 GIXS line profiles for pristine thin film of six small molecule donors; in-plane line profiles of (a) ester terminated materials and (b) amide terminated materials.

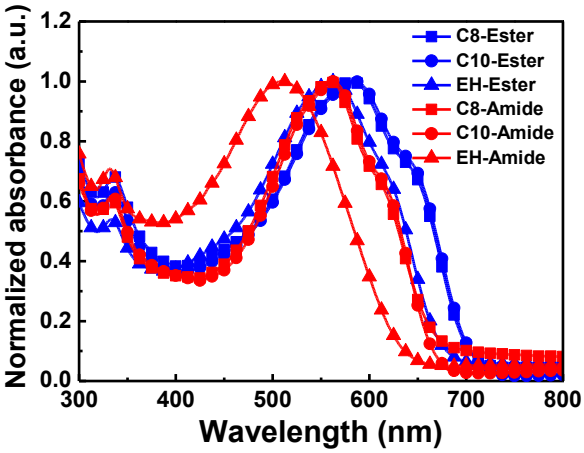


Fig. S3 UV-vis absorption spectra of six small molecule donors in optimized blend thin film with PCBM as cast from $CHCl_3$; ester terminated (blue line), amide terminated (red line), *n*-octyl side chain (squre), *n*-decyl side chain (circle) and 2-ethylhexyl side chain (triangle) derivatives.

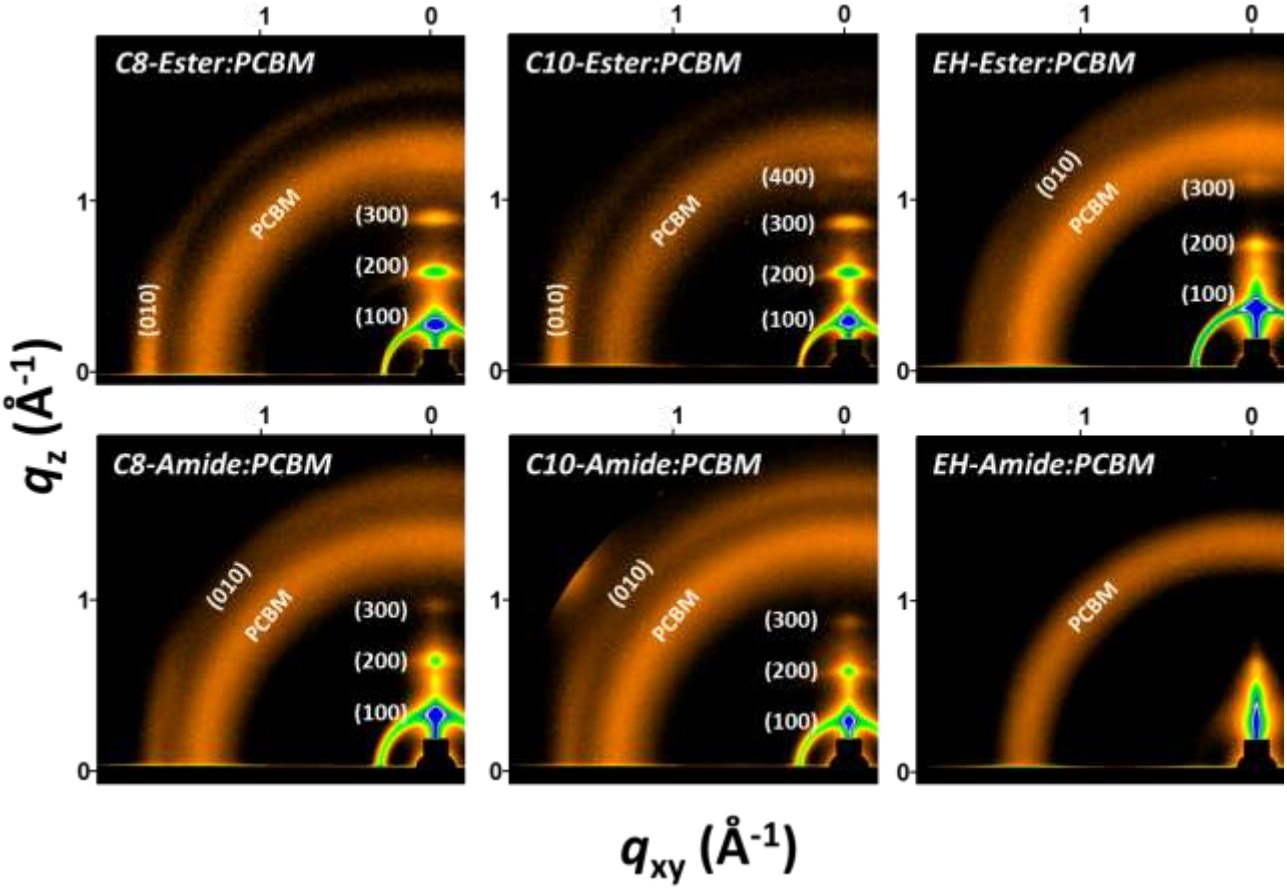


Fig. S4 GIXS images of optimized active layers consisting of small molecule donors and PCBM prepared by spin casting from $CHCl_3$ solution.

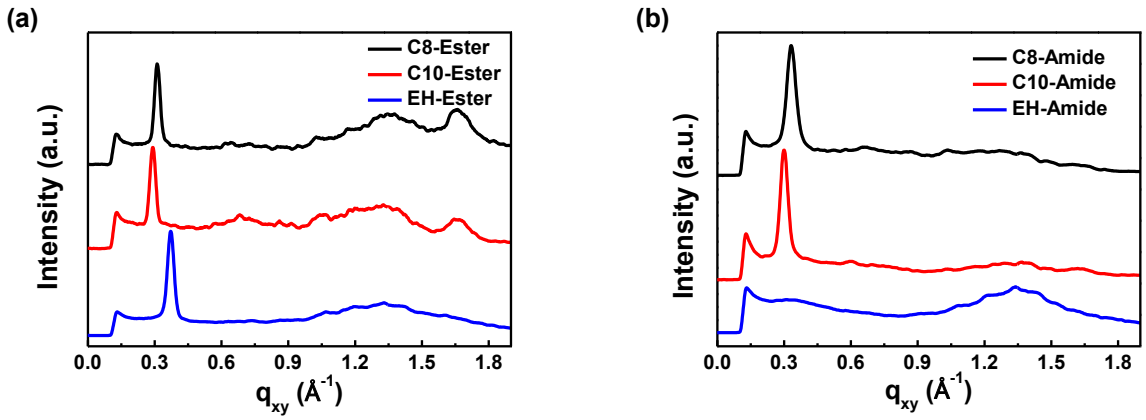


Fig. S5 GIXS line profiles for optimized active layers consisting of small molecule donors and PCBM; in-plane line profiles of (a) ester terminated and (b) amide terminated materials.