

Supporting Information

Dihydropyreno[1,2-b:6,7-b']dithiophene Based Electron Acceptors for High Efficiency As-Cast Organic Solar Cells

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1.1 Materials and Instruments

Unless otherwise noted, all chemicals were purchased from Aldrich or Acros and used without further purification. The catalyst precursor $\text{Pd}(\text{PPh}_3)_4$ was prepared according to the literature and stored in a Schlenk tube under nitrogen atmosphere. Unless otherwise noted, all reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC) on silica gel. Column chromatography was carried out on silica gel (200-300 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 and 600 spectrometer. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 750. MS (MALDI-TOF) results were performed with an AutoflexIII instrument Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on TA2100 and Perkin-Elmer Diamond DSC instrument, respectively, under an nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ to record TGA and DSC curves. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode. Transmission electron microscopy (TEM) was performed on Talos-f 200s operated at 200kV. The thickness of the blend films was determined by a Dektak 6 M surface profile meter. The powder X-ray diffraction (XRD) patterns were collected using a PAN alytical X'Pert PRO MPD diffractometer with Cu KR radiation. The electrochemical behavior of the polymers was investigated using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a standard three-electrode electrochemical cell in a 0.1 M Bu_4NPF_6 solution in

CH₃CN at room temperature under an atmosphere of nitrogen with a scanning rate of 0.1 V/S. A Pt plate working electrode, a Pt wire counter electrode, and an Ag/AgNO₃ (0.01M in CH₃CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (Fc) redox system and assumption that the energy level of Fc is 4.8 eV below vacuum.

1.2 Solar Cells Fabrication and Characterization

OSCs were fabricated with the device configuration of ITO/ZnO/active layer (100 nm)/MoO₃ (85 Å)/Ag (100 nm). The conductivity of ITO is 20 Ω. A mixture of PBDB-T and small-molecule acceptor in 1,2-dichlorobenzene (DCB) was stirred at 90 °C at least two hours to ensure sufficient dissolution and then the blend solution was spin-coated (1500 rpm unless otherwise noted) onto ZnO layer to form active layer. On one substrate six cells with an effective area of 0.04 cm² for each were fabricated. Current-voltage characteristics were recorded using an Enli Technology Ltd., Taiwan (SS-F53A) under an AM 1.5G AAA class solar simulator with an intensity of 100 mW cm⁻² as the white light source and the intensity was calibrated with a standard single crystal Si photovoltaic cell. The temperature while measuring the J-V curves was approximately 25 °C. The EQE measurements of OSCs were performed by the solar cell spectral response measurement system QE-R3011 (Enli Technology Ltd., Taiwan), which was calibrated by monocrystalline silicon solar cell in advance.

1.3 Space-Charge Limited Current Measurement

Hole/electron devices with a structure of ITO/PEDOT:PSS (30 nm)/active layer/Au and ITO/ZnO/active layer/Al were fabricated. A solution of PBDB-T and **PDT** or **PDT-T** in 1,2-dichlorobenzene (DCB) was spin-coated onto PEDOT:PSS or ZnO to form active layer like OSC devices, and Au (Al) was thermally evaporated at a pressure of 10^{-4} Pa through a shadow mask. Dark $J-V$ curves of the hole/electron devices were measured by the space-charge limited current (SCLC) method. Hole and electron mobilities of devices were measured by SCLC model and calculated according to equations reported in previous literature.^{S1} Dark $J-V$ curves were fitted by using the Mott-Gurney equation: $J = 9\epsilon_0\epsilon_r\mu V^2/8d^3$, where J is the space charge limited current, ϵ_0 is the vacuum permittivity ($\epsilon_0=8.85\times 10^{-12}$ F/m), ϵ_r is the permittivity of the active layer ($\epsilon_r = 3$), μ is mobility, and d is the thickness of the active layer.

Table S1. Photovoltaic performance of devices fabricated with PBDB-T and **PDT**.

D:A	Add. (%)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
1.5:1		0.95	10.38	48.26	4.75
1.2:1		0.96	11.09	48.34	5.13
1:1		0.96	12.53	51.78	6.21
1:1.2		0.97	13.48	54.03	7.07
1:1.5		0.96	11.89	56.00	6.40

Table S2. Photovoltaic performance of devices fabricated with PBDB-T and **PDT-T**.

D:A	Add. (%)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
1.2:1	-	0.88	15.79	60.27	8.45
1:1	-	0.88	16.94	64.30	9.61
1:1.2	-	0.88	17.50	67.09	10.34

1:1.5	-	0.88	17.13	67.00	10.12
1:2	-	0.88	15.70	61.88	8.50
1:2	DIO ^c (0.25)	0.88	17.76	65.96	9.83
1:2	DIO (0.5)	0.83	14.79	59.97	7.40
1:2	DIO (1)	0.83	9.87	48.61	3.99
1:2	CN ^d (0.25)	0.87	16.61	53.37	7.66
1:2	CN (0.5)	0.87	16.93	63.50	9.31
1:2	CN (0.75)	0.87	18.90	49.13	8.07
1:1.2 ^a	-	0.88	18.16	66.76	10.71
1:1.2 ^b	-	0.88	18.88	66.31	11.02

^a 1200 rpm. ^b 1800 rpm. ^c DIO = 1,8-diiodooctane. ^d CN = 1-chloronaphthalene.

XRD analysis was carried out to investigate the molecular stacking in films of small molecules, polymers and the blends (Figure S2). The pure **PDT** film displayed no obvious peak, whereas **PDT-T** exhibited a sharp diffraction peak located at the angle of $2\theta = 25.31^\circ$, corresponding to a π - π stacking distance of 3.52 Å, indicating it can form ordered molecular packing in films

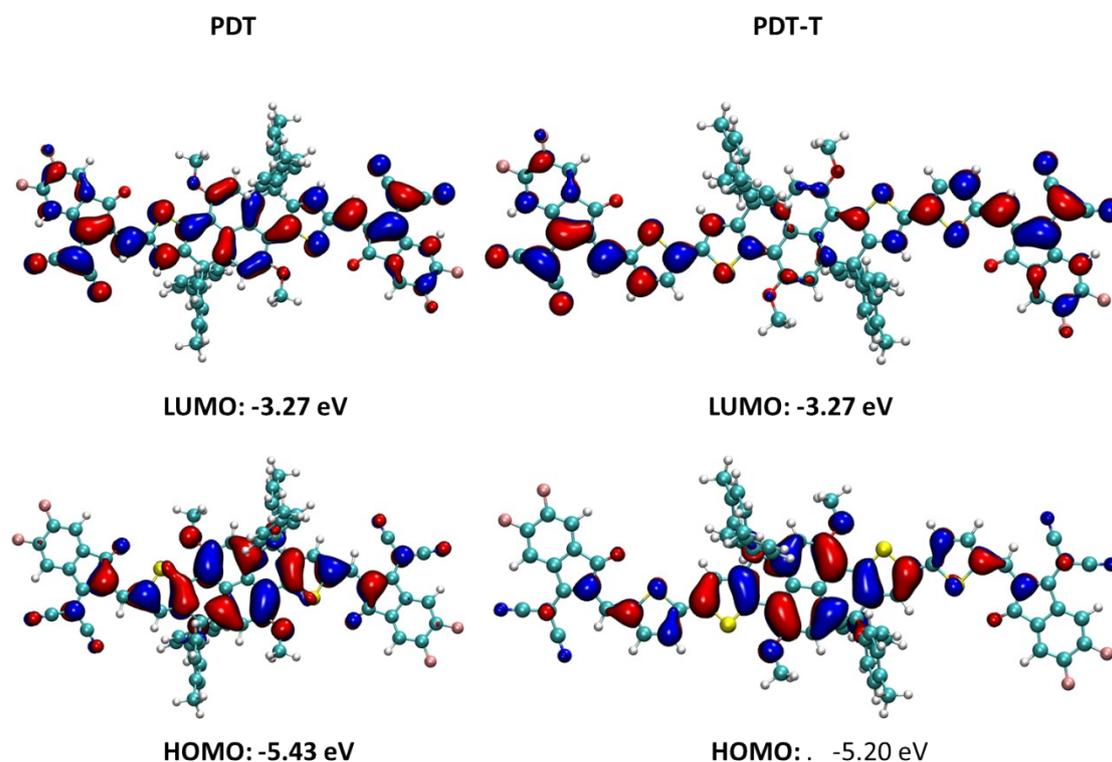


Figure S1. Frontier molecular orbitals calculated by density functional theory.

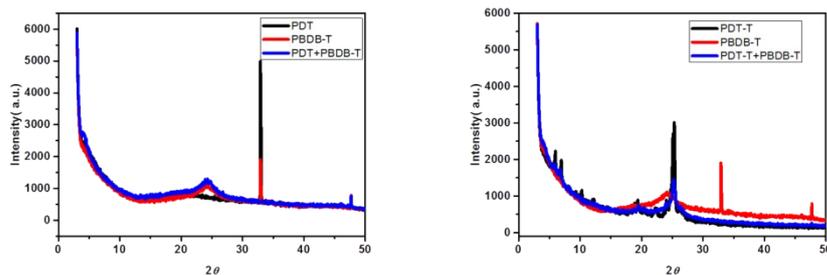
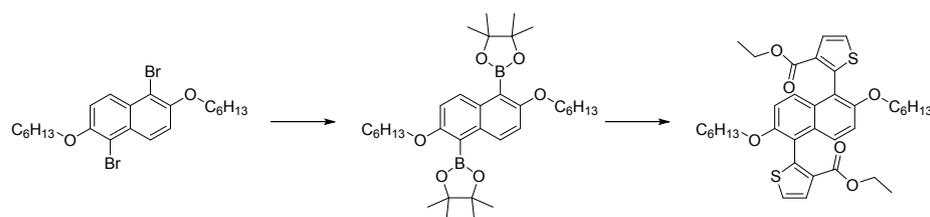


Figure S2. XRD curves of **PDT**, **PDT-T**, **PBDB-T** and the blend films.

1.4 Synthesis

1,5-dibromo-2,6-bis(hexyloxy)naphthalene was synthesized from start material naphthalene-2,6-diol according literatures reported before^[S2,S3].

Diethyl 2,2'-(2,6-bis(hexyloxy)naphthalene-1,5-diyl)bis(thiophene-3-carboxylate) (**4**)

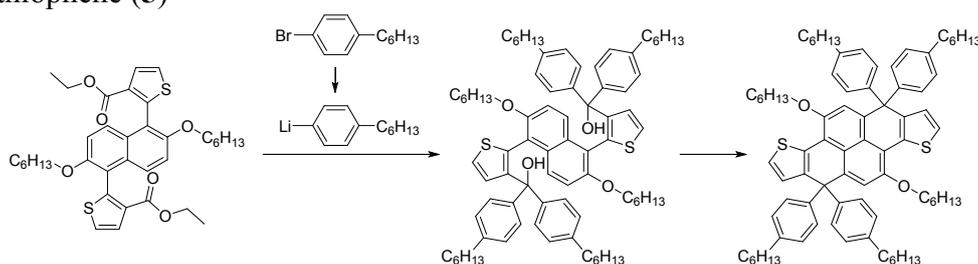


In a 100-mL Schlenk flask, was placed a 2.43 g (5.0 mmol) sample of **2** in 50 mL of dry THF. A solution (12.5 mL, 30.0 mmol) of 2.4 M n-butyllithium was added dropwise into the reactant solution at $-78\text{ }^{\circ}\text{C}$ under nitrogen. After the solution was stirred for 1 h at the same temperature, it was allowed to warm to $0\text{ }^{\circ}\text{C}$ and stirred for 4 h. Then the solution was colded to $-78\text{ }^{\circ}\text{C}$ again and 5.58 g (30 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added to the solution. The reaction was quenched and washed with H_2O ($3 \times 50\text{ mL}$), then brine ($2 \times 50\text{ mL}$), and dried over MgSO_4 after the solution was stirred overnight. After the solvent was evaporated, the residue was dried in a vacuum overnight. The compound was used

without further purification.

A mixture of ethyl 2-bromothiophene-3-carboxylate (3.5 g, 15 mmol) and crude product of borate ester in mixed solution of THF and 2 M K_2CO_3 was degassed before $Pd(PPh_3)_4$ (138 mg, 0.12 mmol) was added. And the mixture was refluxed under N_2 for 3 days. After the reaction was finished, the organic layer was separated, washed with water, dried with $MgSO_4$, filtered and moved out with rotary evaporator. The residue was chromatographically purified on silica gel column with ethyl acetate/petroleum ether (1:20, v/v) to give diethyl 2,2'-(2,6-bis(hexyloxy)naphthalene-1,5-diyl)bis(thiophene-3-carboxylate) as a pale yellow solid in a yield of 53% based on 1,5-dibromo-2,6-bis(hexyloxy)naphthalene (1.69 g). 1H NMR (400 MHz, $CDCl_3$) δ : 7.65-7.66 (m, 2H), 7.47-7.50 (m, 2H), 7.41-7.42 (m, 2H), 7.16-7.19 (m, 2H), 3.88-3.98 (m, 8H), 1.55-1.60 (m, 4H), 1.17-1.26 (m, 12 H) 0.86 -0.79 (m, 12H). HRMS (ESI) calcd. for: $C_{36}H_{45}O_6S_2$ $[M+H]^+$ 637.2652, found 637.2658.

4,10-bis(hexyloxy)-6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydropyreno[1,2-b:6,7-b']dithiophene (**5**)

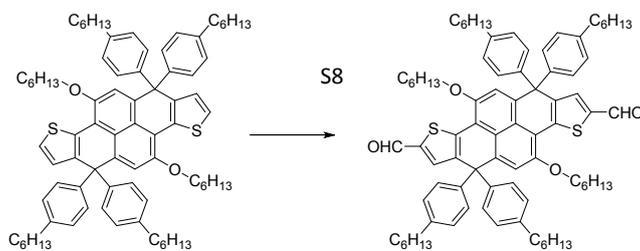


$n-BuLi$ (12.5 mL, 2.4 M in hexane) was added dropwise to a solution of 1-bromo-4-hexylbenzene (7.23 g, 30 mmol) in anhydrous THF (50 mL) at 78 °C and under inert atmosphere. The stirred mixture was kept the same temperature for 1 h and then added into a degassed solution of **4** (3.18 g, 5.0 mmol) in THF (50 mL) via

cannula. When the addition was completed and another 10 min continued, the resulting mixture was slowly warmed to room temperature and stirred overnight, followed by quenching with a saturated NH_4Cl solution (30 mL). The organic layer was separated, and the aqueous phase was extracted with ethyl acetate for three times. The combined organic layer was washed with brine, dried over MgSO_4 , filtered, and concentrated via a rotary evaporator to obtain a crude diol as a viscous oil, which could be directly used for the next step without further purification .

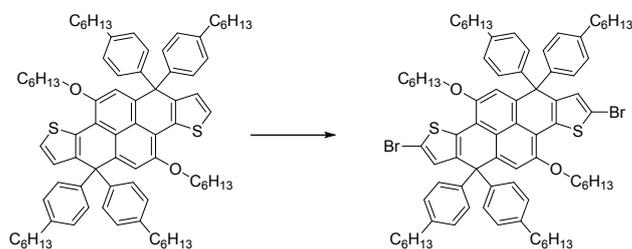
The crude diol obtained above was dissolved in degassed dichloromethane (DCM, 100 mL) and then a $\text{BF}_3\text{-Et}_2\text{O}$ solution (1 mL) was added. After being stirred overnight, 50 mL of MeOH was added into the mixture to quench the reaction. The mixture was concentrated to give a viscous oil which was loaded onto a silica gel column and eluted with DCM/petroleum ether (1:3, v/v) to yield 4,10-bis(hexyloxy)-6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydropyreno[1,2-b:6,7-b']dithiophene as a yellow solid (4.57 g, 79%) ^1H NMR (600 MHz, CDCl_3) δ : 7.17 (d, $J = 5.2$ Hz, 2H), 7.02-7.06 (m, 18H), 6.79 (d, $J = 5.2$ Hz, 2H), 3.96 (t, $J = 6.6$ Hz, 4H), 2.55 (t, $J = 7.8$ Hz, 8H), 1.80-1.85 (m, 4H), 1.55-1.60 (m, 8H), 1.46-1.51 (m, 4H), 1.29-1.36 (m, 32H), 0.87-0.91 (m, 18H). ^{13}C NMR (150 MHz, CDCl_3) δ : 149.28, 146.29, 142.31, 141.54, 140.59, 130.28, 129.59, 128.37, 127.70, 124.42, 122.91, 118.24, 113.14, 69.49, 58.22, 35.43, 31.71, 31.64, 31.27, 29.42, 29.08, 25.88, 22.60, 22.55, 14.07, 14.03.

4,10-bis(hexyloxy)-6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydropyreno[1,2-b:6,7-b']dithiophene-2,8-dicarbaldehyde (**6**)



In a 100-mL Schlenk flask, was placed a 200 mg (0.17 mmol) sample of **5** in 50 mL of dry THF. A solution (0.5 mL, 12.0 mmol) of 2.4 M *n*-butyllithium was added dropwise into the reactant solution at -78 °C under nitrogen. After the solution was stirred for 1 h at the same temperature, 1 mg (13.7 mmol) of *N,N*-dimethylformamide was added to the solution. The reaction was quenched and washed with H₂O (3 × 50 mL), then brine (2 × 50 mL), and dried over MgSO₄ after the solution was stirred overnight. After the solvent was evaporated, the residue was chromatographically purified on silica gel column with DCM/petroleum ether (1:2, v/v) to give 4,10-bis(hexyloxy)-6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydropyreno[1,2-b:6,7-b']dithiophene-2,8-dicarbaldehyde as a yellow solid (117 mg, 56%). ¹H NMR (400 MHz, CDCl₃) δ: 9.81 (s, 2H), 7.44 (s, 2H), 7.08 (s, 2H), 6.99-7.07 (m, 16H) 4.00-4.04 (m, 4H), 2.56 (t, *J* = 7.6 Hz, 8H), 1.79-1.86 (m, 4H), 1.53-1.62 (m, 8H), 1.40-1.47 (m, 4H), 1.26-1.33 (m, 32H), 0.85-0.90 (m, 18H).

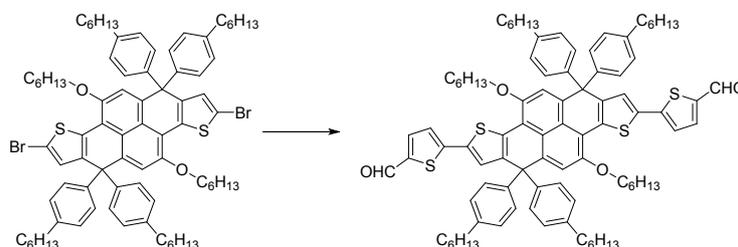
2,8-dibromo-4,10-bis(hexyloxy)-6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydropyreno[1,2-b:6,7-b']dithiophene (**7**)



1-bromopyrrolidine-2,5-dione (70 mg, 0.39 mmol) was added into a solution of **5** (200 mg, 0.17 mmol) in DCM and stirred overnight under dark condition. The mixture was washed with H₂O (3 × 2 mL), and dried over MgSO₄. After the solvent

was evaporated, the residue was chromatographically purified on silica gel column with DCM/petroleum ether (1:2, v/v) to give 2,8-dibromo-4,10-bis(hexyloxy)-6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydropyreno[1,2-b:6,7-b']dithiophene as a yellow solid (216 mg, 95%) ¹H NMR (600 MHz, CDCl₃) δ: 7.02-7.06 (m, 16H), 6.98 (s, 2H), 6.74 (s, 2H), 3.94 (m, 4H), 2.56 (t, *J* = 7.8 Hz, 8H), 1.77-1.82 (m, 4H), 1.56-1.61 (m, 8H), 1.42-1.47 (m, 4H), 1.28-1.34 (m, 32H), 0.87-0.90 (m, 18H).

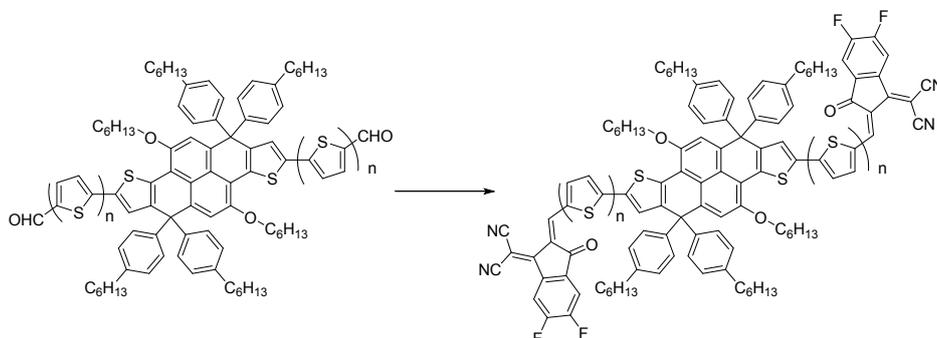
5,5'-(4,10-bis(hexyloxy)-6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydropyreno[1,2-b:6,7-b']dithiophene-2,8-diyl)bis(thiophene-2-carbaldehyde) (**8**)



A mixture of (5-formylthiophen-2-yl)boronic acid (94 mg, 0.6 mmol) and **7** (200 mg, 0.15 mmol) in mixed solution of THF and 2 M K₂CO₃ was degassed before Pd(PPh₃)₄ (173 mg, 0.15mmol) was added. And the mixture was refluxed under N₂ for 3 days. After the reaction was finished, the organic layer was separated, washed with water, dried with MgSO₄, filtered and moved out with rotary evaporator. The residue was chromatographically purified on silica gel column with DCM/petroleum ether (1:1, v/v) to give 5,5'-(4,10-bis(hexyloxy)-6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydropyreno[1,2-b:6,7-b']dithiophene-2,8-diyl)bis(thiophene-2-carbaldehyde) as an orange solid (172 mg, 83%). ¹H NMR (600 MHz, CDCl₃) δ: 9.81 (s, 2H), 7.62 (d, *J* = 3.9 Hz, 2H), 7.19 (d, *J* = 3.9 Hz, 2H), 7.06 (m, 16H) 7.053 (s, 2H), 7.045 (s, 2H), 4.00 (t, *J* = 6.4 Hz, 4H), 2.56 (t, *J* = 7.6 Hz, 8H), 1.82-1.87 (m, 4H), 1.56-1.61 (m, 8H),

1.40-1.47 (m, 4H), 1.27-1.37 (m, 32H), 0.86-0.92 (m, 18H).

Small molecular acceptors.



A mixture of dialdehydes (1.0 eq.) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (5.0 eq.) in chloroform was carefully degassed before and after pyridine was added. The reaction was kept at room temperature under N₂ overnight. Then, the solvent was evaporated out, and the residue was purified on silica gel column with DCM/petroleum ether to give target molecules (**n** = **0**, yield 49%, **n** = **1**, yield 76%). **n** = **0**, ¹H NMR (600MHz, CDCl₃) δ: 8.73 (s, 2H), 8.50-8.53 (m, 2H), 7.60-7.63 (m, 4H), 7.11 (s, 2H), 6.99-7.09 (m, 16H), 4.10 (t, *J* = 6.3 Hz, 4H), 2.56-2.59 (m, 8H), 2.03-2.08 (m, 4H), 1.57-1.64 (m, 8H), 1.26-1.38 (m, 32H), 0.86-0.91 (m, 18H). ¹³C NMR (100 MHz, CDCl₃) δ: 185.25, 158.89, 153.16, 148.54, 146.08, 145.51, 145.24, 144.49, 141.76, 138.49, 136.44, 129.40, 128.31, 128.19, 128.13, 122.82, 121.15, 118.61, 118.11, 114.90, 114.73, 114.59, 114.37, 112.57, 112.41, 112.27, 70.12, 57.95, 35.40, 31.77, 31.68, 31.19, 29.30, 29.05, 26.23, 22.59, 22.53, 14.13, 14.08. **Mass (MALDI-TOF):** *m/z*, calcd for C₁₀₆H₁₀₅F₄N₄O₄S₂ [M+H]⁺: 1636.74; found: 1637.48. **n** = **1**, ¹H NMR (600MHz, CDCl₃) δ: 8.82 (s, 2H), 8.52-8.55 (m, 2H), 7.78 (m, 2H), 7.64-7.67 (m, 2H), 7.35 (m, 2H), 7.06-7.10 (m, 18H), 7.03 (m, 2H), 4.05 (m, 4H), 2.58 (t, *J* = 7.7 Hz, 8H), 1.82-1.87 (m, 4H), 1.58-1.63 (m, 8H), 1.28-1.37 (m,

36H), 0.86-0.93 (m, 18H).¹³C NMR (100 MHz, CDCl₃)δ: 186.45, 158.24, 158.22, 155.52, 155.49, 155.41, 153.45, 153.39, 153.34, 153.28, 141.40, 136.70, 136.65, 134.45, 134.40, 129.52, 128.20, 115.05, 114.88, 114.28, 112.53, 112.38, 69.53, 35.47, 31.72, 31.26, 29.71, 29.31, 29.13, 25.99, 22.67, 22.62, 14.14, 14.11. **Mass (MALDI-TOF):** *m/z*, calcd for C₁₁₄H₁₀₉F₄N₄O₄S₄ [M+H]⁺: 1801.72; found: 1801.80.

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