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Supporting Information

Asymmetric A-DA'D-π-A Type Nonfullerene Acceptor for High-performance Organic Solar Cells

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1.1 Methods and measurements

Unless otherwise noted, all chemicals were purchased from Aldrich or Acros and used without further purification. The catalyst precursor $Pd(PPh_3)_4$ 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 spectrometer. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 750. Elemental analyses were performed on a Flash EA 1112 analyzer. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Bruker Dimension Icon™ operating in the tapping mode. Transmission electron microscopy (TEM) images were obtained with a FEI Tecna·G2 F20 transmission electron microscopy. The thickness of the blend films was determined by a Dektak 6 M surface profilometer. 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_4NPF6 solution in CH_3CN 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 $Ag/AgNO_3$ (0.01 M in CH_3CN) 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.

Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) Characterization: GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source. Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.12°-0.16°, selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector.

1.2 Solar Cells Fabrication and Characterization

PSCs were fabricated with the device configuration of ITO/ZnO/active layer (150 nm)/MoO_3 (85 Å)/Ag (100 nm). The conductivity of ITO is 20 Ω. A mixture of PBDB-T and acceptor molecule (**L1**, **L2** and **L3**) in 1,2-dichlorobenzene (*o*-DCB) was stirred at 110 ^{o}C at least two hours to ensure sufficient dissolution and then the blend solution was spin-coated onto ZnO layer to form active layer. On one substrate five cells with an effective area of 0.04 cm^2 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 ^{o}C. The EQE measurements of PSCs 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 Fabrication and characterization of the hole/electron-only devices

Devices with an architecture of ITO/PEDOT:PSS (30 nm)/active layer/Au was applied to measure the hole mobility. The electron-only devices had a structure of ITO/ZnO/active layer/Al to obtain the electron mobility. The active layers were prepared under the same conditions as the optimal OSCs. According to the Mott-Gurney equation: $J = 9\varepsilon\varepsilon_0\mu/(8L^3)V^2$, the mobility can be described as $\mu = 8JL^3/9\varepsilon\varepsilon_0V^2$. Herein, ε denotes the dielectric constant of the blend film based on organic materials, and it is assumed to be constant (3.0); $\varepsilon_0 = 8.85419\times10^{-12}$ F m^{-1}, which means the permittivity of the vacuum; μ represents the zero-field mobility; J is the current density; L is the thickness of the film; $V = V_{\text{appl}} - V_{\text{bi}}$, here, V_{appl} and V_{bi} are the applied voltage to the device and the build-in voltage, respectively.

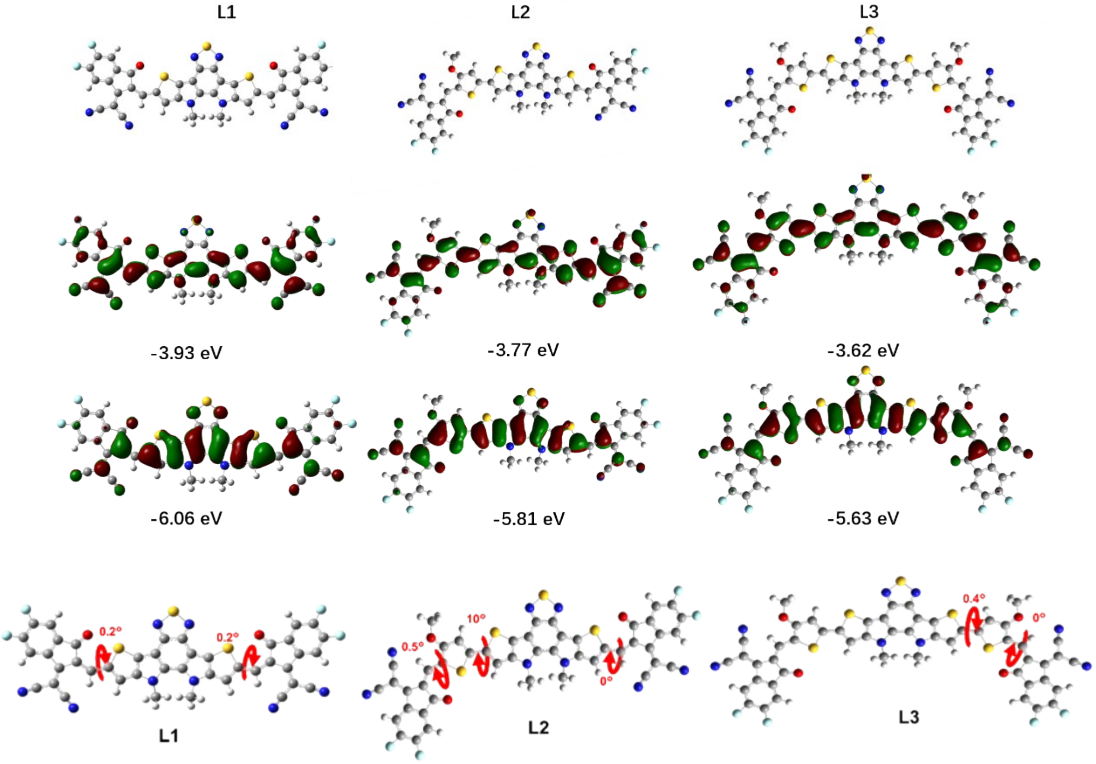


Figure S1. Simulated HOMO and LUMO energy levels and of simplified **L1**, **L2** and **L3**.

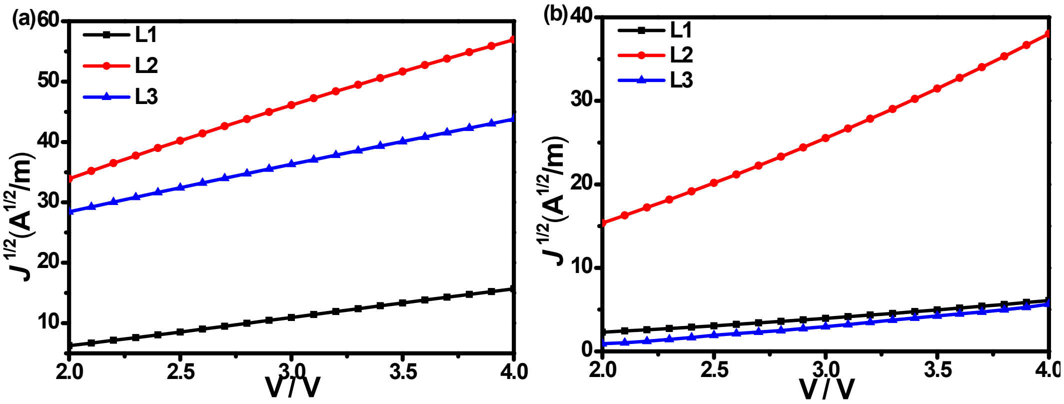


Figure S2. $J^{1/2}$-V curves of **L1**, **L2** and **L3** based hole-only (a) and electron-only (b) devices

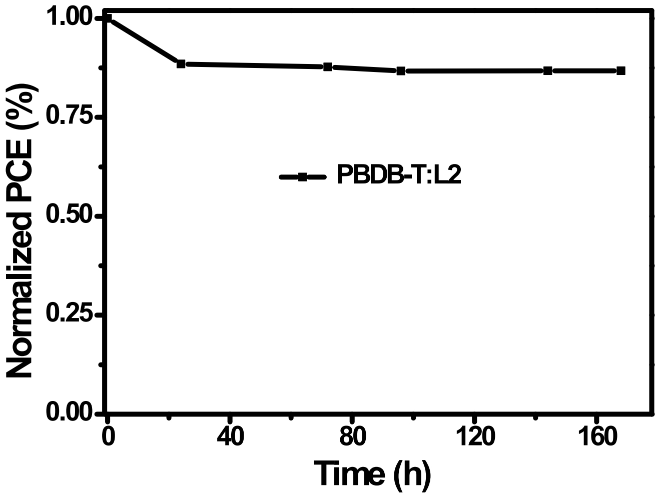


Figure S3. The placement stability of **L2** based device.

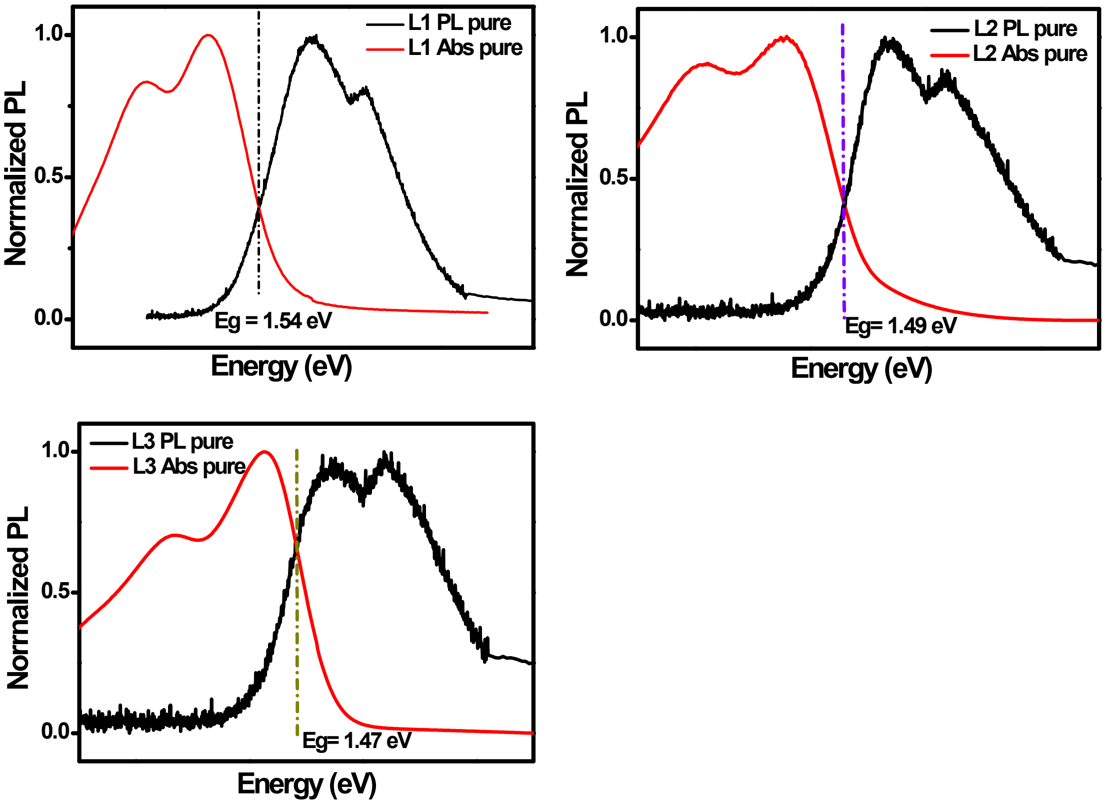
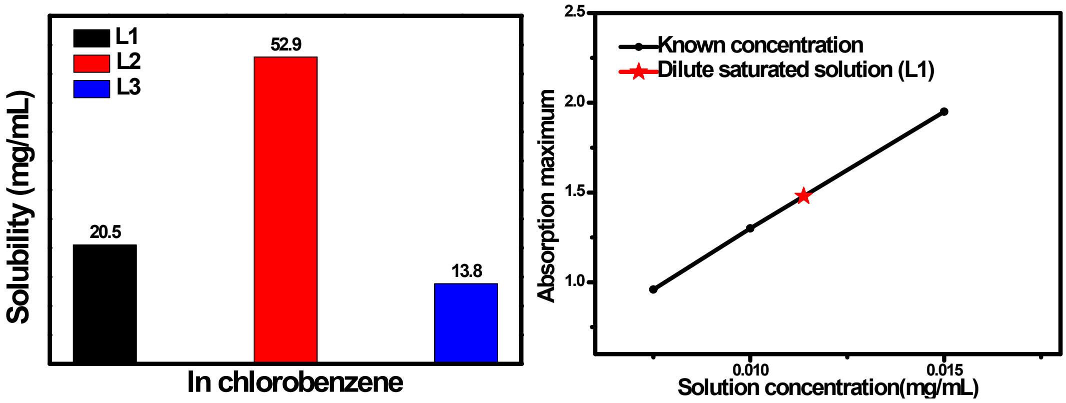


Figure S4. Normalized absorption and PL spectra of neat **L1**, **L2** and **L3** films.



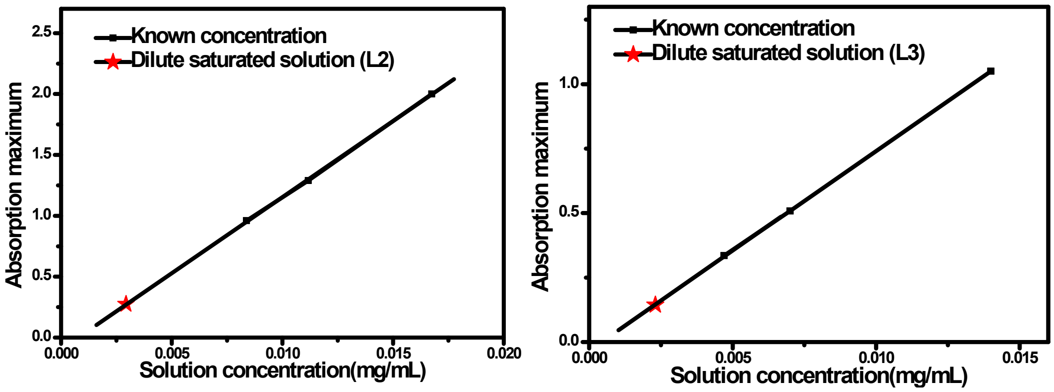


Figure S5. The solubility of **L1**, **L2** and **L3** in chlorobenzene.

Table S1. Photovoltaic parameter of **L1** based devices with different weight ratios.

PBDB-T:**L1**	V_{oc}(V)	J_{sc} (mA/cm^2)	FF(%)	PCE (%)
1:1.25	0.69	7.44	40.27	2.07
1:1	0.67	7.18	28.48	1.37
1:0.75	0.67	7.74	25.08	1.30

Table S2. Photovoltaic parameter of **L2** based devices with different weight ratios.

PBDB-T:**L2**	V_{oc}(V)	J_{sc} (mA/cm^2)	FF(%)	PCE (%)
1:1.25	0.86	19.84	63.08	10.72
1:1	0.86	19.69	63.62	10.74
1:0.75	0.86	18.70	59.91	9.63

Table S3. Photovoltaic parameter of **L3** based devices with different weight ratios.

PBDB-T:**L3**	V_{oc}(V)	J_{sc} (mA/cm^2)	FF(%)	PCE (%)
1:1	0.91	2.35	34.00	0.73
1:0.75	0.91	3.60	36.33	1.19
1:0.5	0.92	7.70	40.86	1.78

Table S4. Photovoltaic parameter of **L2** based devices with different additives.

PBDB-T:**L2**	additives	V_{oc}(V)	J_{sc} (mA/cm^2)	FF(%)	PCE (%)
1:1	0.5%1-CN	0.86	18.93	66.72	10.83
1:1	0.7%1-CN	0.86	19.46	67.60	11.36
1:1	1% 1-CN	0.86	19.19	66.35	10.90

Table S5. Photovoltaic parameter of **L2** based devices with 1% 1-CN at different annealing temperature.

PBDB-T:L2	Temperature	V_{oc}(V)	J_{sc} (mA/cm^2)	FF(%)	PCE (%)
1:1	100 ^{o}C	0.82	24.01	71.73	13.79

1:1	110 °C	0.81	24.00	70.46	14.06
1:1	120 °C	0.81	24.23	68.71	13.50

Table S6. Hole and electron transport mobility values of **L1**, **L2** and **L3** based device.

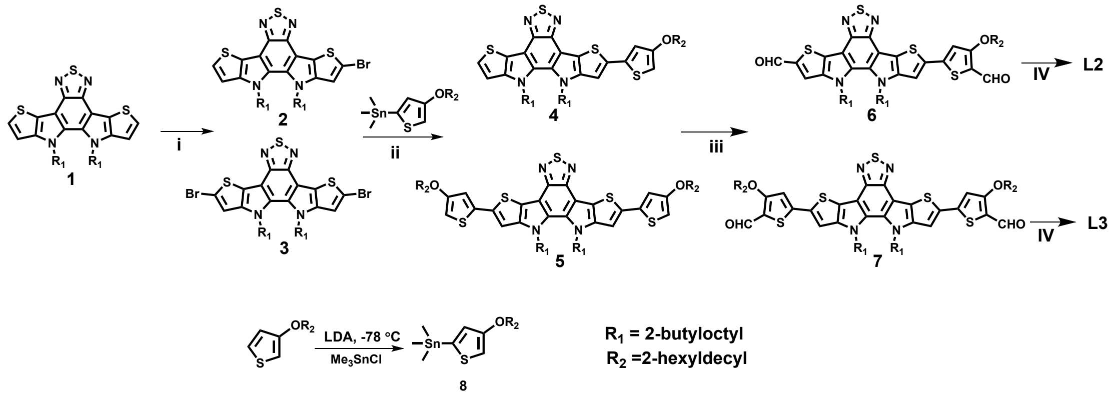
Active layer	μ_h(cm^2 V^{-1}s^{-1})	μ_e(cm^2 V^{-1}s^{-1})	μ_h/μ_e	Thickness (nm)
PBDB-T:**L1=1:1**	7.57×10^{-6}	1.47×10^{-6}	5.14	110
PBDB-T:**L2=1:1**	1.52×10^{-4}	1.48×10^{-4}	1.03	125
PBDB-T:**L3=1:1**	3.49×10^{-5}	3.28×10^{-6}	10.64	120

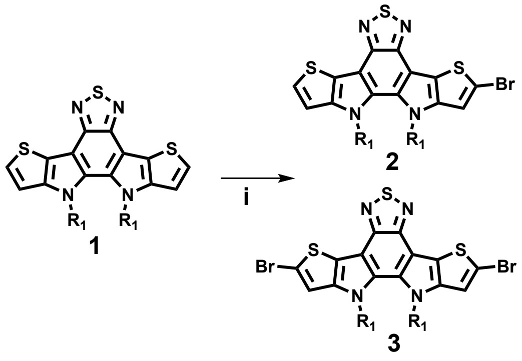
Table S7. Relative data of pure and blend films obtained from GIWAXS measurement.

		out of plane(010)		
item	location(Å^{-1})	*d*-spacing(Å)	FWHM	CL(Å)
L1	1.80	3.48	0.23	24.30
L2	1.78	3.52	0.24	23.28
L3	0.33	19.62	0.05	111.78
PBDB-T:**L1**	1.74	3.60	0.256	21.83
PBDB-T:**L2**	1.75	3.58	0.253	22.09
PBDB-T:**L3**	1.67	3.76	0.34	16.43

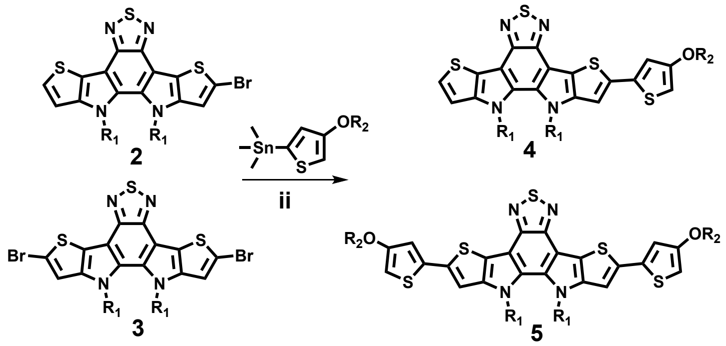
1.4 Synthesis Section

All of the reagents involved were purchased from commercial suppliers and used as received. Tetrahydrofuran (THF) and toluene were distilled following standard procedures. 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (IC-2F) was purchased from SunaTech and used without further purification. Compound **1** and **8** was synthesized and purified according to the relevant references.[S1, S2]

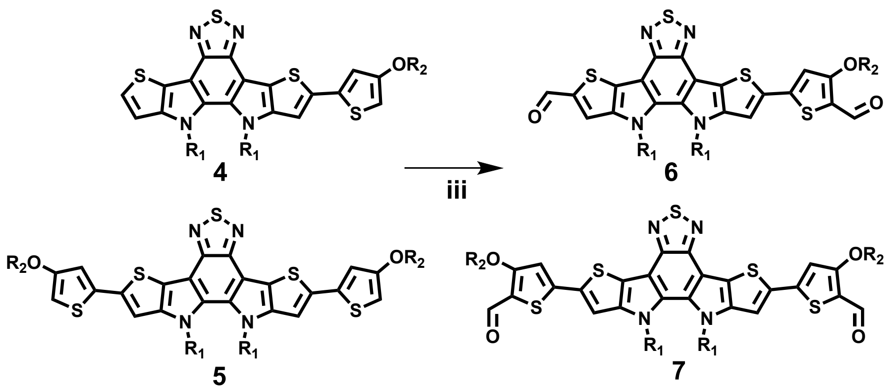




Compound 1 (600 mg, 0.90 mmol) was dissolved in 20 mL tetrahydrofuran solution at 0 °C , then N-bromosuccinimide (241.3 mg, 1.35 mmol) was added to reaction system. After being stirred for 20 min at 0 °C, the mixture was then quenched with water, extracted with dichloromethane, and the solvent is removed to obtain a mixture of red solid (**2** and **3)** 650 mg.



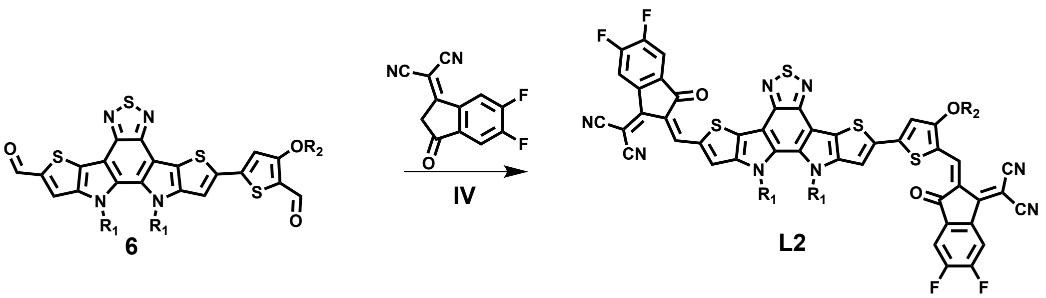
To a bottom flask were added the mixture of compound **2** and **3** (650 mg), (4-((2-hexyldecyl)oxy)thiophen-2-yl)trimethylstannane (excess, 1.5 g), and toluene (20 mL). The mixture was deoxygenated with N_2 for 10 min. $Pd(PPh_3)_4$ (30 mg) was added quickly. The mixture was refluxed at 120 °C for 12 h and then cooled down to room temperature. Water (50 mL) was added and the mixture was extracted with dichloromethane for three times. The organic phase was dried over anhydrous $MgSO_4$ and filtered. After removing the solvent, the residue was purified by silica gel column chromatography using dichloromethane as the eluent to obtain an orange viscous oil 800 mg (mixed compounds **4** and **5**).



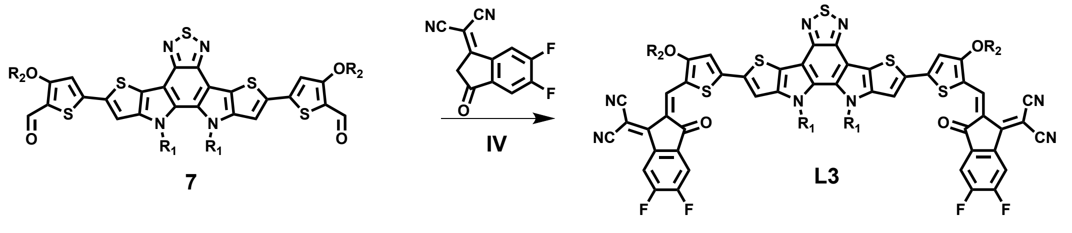
To a Schlenk tube under N_2 atmosphere at 0 °C, 2 mL DMF and 1 mL $POCl_3$ were successively injected. After being stirred for 0.5 h at 0 °C, the mixture of compounds **4** and **5** (800 mg) was added into the reaction system through 1,2-dichloroethane (20 mL) as the solvent. The mixture was refluxed at 80 °C for 8 h. After cooling to r.t., the mixture was extracted with a syringe and injected into a $NaHCO_3$ aqueous solution dropwise, then stirred for 3 h. Using water to wash the crude product and dichloromethane to obtain the organic phase. After removing the solvent, pure compound **6** (240 mg) and **7** (260 mg) can be separated as orange viscous oils by silica gel column chromatography eluting with petroleum ether:dichloromethane (1:3, v/v).

Compound **6**: ^{1}H NMR (600 MHz, Chloroform-d) δ 10.00 (s, 1H), 9.99 (s, 1H), 7.80 (s, 1H), 7.41 (s, 1H), 7.02 (s, 1H), 4.50 (dt, *J* = 14.1, 6.8 Hz, 4H), 4.11 (d, *J* = 5.6 Hz, 2H), 1.99 (dt, *J* = 12.5, 6.3 Hz, 2H), 1.85 (p, *J* = 6.0 Hz, 1H), 1.37 - 1.24 (m, 24H), 1.03 – 0.86 (m, 32H), 0.76 - 0.61 (m, 18H). ^{13}C NMR (150 MHz, Chloroform-d) δ 183.03, 180.47, 164.93, 147.60, 147.43, 146.70, 145.85, 144.43, 143.91, 138.31, 135.57, 122.42, 119.92, 112.66, 111.98, 111.03, 110.28, 54.71, 38.37, 38.34, 38.19, 32.00, 31.97, 31.90, 31.60, 31.35, 30.47, 30.43, 30.39, 30.36, 30.05, 29.77, 29.74, 29.71, 29.65, 29.44, 29.40, 29.35, 28.07, 27.95, 26.93, 26.89, 25.37, 22.80, 22.76, 22.53, 14.18, 14.02, 13.81.

Compound **7**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.98 (s, 2H), 7.40 (s, 2H), 7.00 (s, 1H), 4.48 (d, *J* = 8.8 Hz, 4H), 4.10 (d, *J* = 5.6 Hz, 4H), 1.92 (dt, *J* = 59.7, 6.1 Hz, 4H), 1.54 - 1.17 (m, 48H), 1.16 - 0.71 (m, 42H), 0.72 - 0.57 (m, 12H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 180.43, 164.97, 147.46, 132.85, 119.51, 111.68, 110.33, 54.64, 38.24, 38.19, 31.97, 31.91, 31.62, 31.35, 30.43, 30.34, 30.06, 29.72, 29.65, 29.40, 29.37, 28.08, 27.94, 26.93, 26.90, 22.76, 22.56, 14.19, 14.04, 13.82.



To a Schlenk tube were added compound **6** (0.16 g, 0.14 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (0.11 g, 0.46 mmol) and dried $CHCl_3$ (30mL). Add 0.3 mL pyridine. The mixture was stirred overnight at room temperature. After the reaction was completed, the solvent was removed, and methanol was added for suction filtration. The obtained filter cake was purified by silica gel column chromatography using dichloromethane and petroleum ether (1:1 v/v) as the eluent to obtain an orange viscous solid compound **L2** (140 mg, 70%).^{1}H NMR (600 MHz, Chloroform-d) δ 9.17 (s, 1H), 8.93 (s, 1H), 8.56 - 8.46 (m, 2H), 8.03 (s, 1H), 7.70 - 7.61 (m, 3H), 7.06 (s, 1H), 4.54 (s, 4H), 4.19 (d, *J* = 5.7 Hz, 2H), 2.09 (s, 2H), 2.01 - 1.95 (m, 1H), 1.30 (d, *J* = 19.9 Hz, 14H), 1.09 - 0.78 (m, 44H), 0.74 - 0.64 (m, 16H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ: 186.62, 185.44, 158.39, 155.41, 153.42, 153.31, 153.02, 147.27, 136.64, 134.58, 134.24, 124.31, 114.97, 114.80, 114.46, 114.15, 112.64, 112.49, 112.14, 111.99, 54.99, 38.46, 38.34, 38.06, 31.97, 31.93, 31.58, 30.87, 30.50, 30.45, 30.38, 30.30, 30.02, 29.70, 29.67, 29.42, 29.38, 28.10, 28.03, 27.94, 26.73, 25.61, 25.54, 25.46, 22.87, 22.82, 22.72, 22.51, 14.16, 13.99, 13.85. MALDI-TOF-MS m/s:[M] calcd. For $C_{84}H_{92}F_4N_8O_3S_4$, 1465.95, found 1465.86



To a Schlenk tube were added compound **7** (0.16 g, 0.12 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (0.08 g, 0.35 mmol) and dried $CHCl_3$ (30mL). Add 0.3 mL pyridine. The mixture was stirred overnight at room temperature. After the reaction was completed, the solvent was removed, and methanol was added for suction filtration. The obtained filter cake was purified by silica gel column chromatography using dichloromethane as the eluent to obtain an orange viscous solid compound **L3** (130 mg, 62%).^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.18 (s, 1H), 8.51 (s, 1H), 7.71 (s, 1H), 7.63 (s, 1H), 7.07 (s, 1H), 4.52 (s, 2H), 4.19 (d, *J* = 5.7 Hz, 2H), 2.01 (d, *J* = 54.3 Hz, 2H), 1.61 - 1.23 (m, 30H), 1.13 - 0.97 (m, 10H), 0.89 (s, 6H), 0.70 (q, *J* = 7.1 Hz, 6H).^{13}C NMR (150 MHz, Chloroform-*d*) δ 186.56, 170.01, 158.40, 155.09, 155.00, 153.05, 152.93, 147.30, 136.66, 134.20, 133.26, 124.66, 115.15, 114.74, 114.55, 112.04, 111.90, 109.45, 54.94, 38.33, 38.03, 31.97, 31.93, 31.60, 30.88, 30.85, 30.39, 30.32, 30.03, 29.70, 29.67, 29.43, 29.38, 28.06, 27.98, 26.73, 26.71, 25.52, 22.87, 22.72, 22.53, 14.17, 14.15, 14.01, 13.85. MALDI-TOF-MS m/s:[M] calcd. For $C_{104}H_{126}F_4N_8O_4S_5$, 1786.84, found 1786.64.

References

[S1] R. Ming, J. Gao, W. Gao, W. Ning, Z. Luo, F. Zhang and C. Yang, *Dyes and Pigments*, 2021, **185**, 108970.

[S2] X. Ji, T. Zhou, X. Ke, W. Wang, S. Wu, M. Zhang, D.Lu, X. Zhang and Y Liu, *Journal of Materials Chemistry A*, 2020, **8**, 5163.