Side-chain Engineering of bifunctional linkage units-linked giant molecular acceptors in organic solar cells

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1. Experimental Section

Materials and Synthesis

All reagents and chemicals were purchased from Energy Chemical. Titan, etc. All reagents and chemicals were used as received without further purification unless otherwise specified. The *s*-Indacene-1,3,5,7(2H,6H)-tetrone was purchased from Bidepharm. The 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile(2F-IC) was purchased from HWRK Chem Co., Ltd. Both DY-C11 and DY-BO were synthesized according to previously reported literature methods.[1] The detailed synthetic procedures of these compounds and polymers are shown as followings.

The synthetic path of DY-C11 and DY-BO

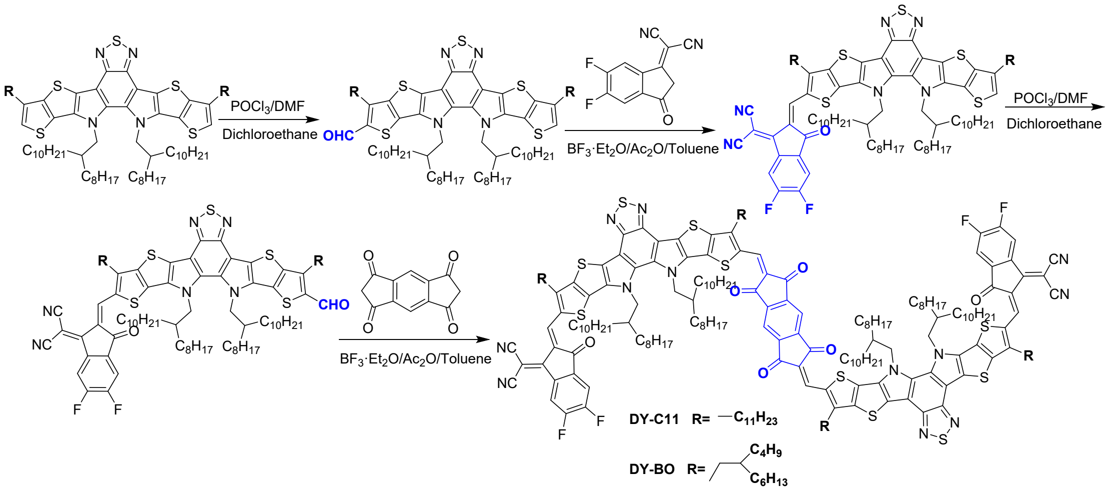

Figure S1. The synthetic path of DY-C11 and DY-BO.

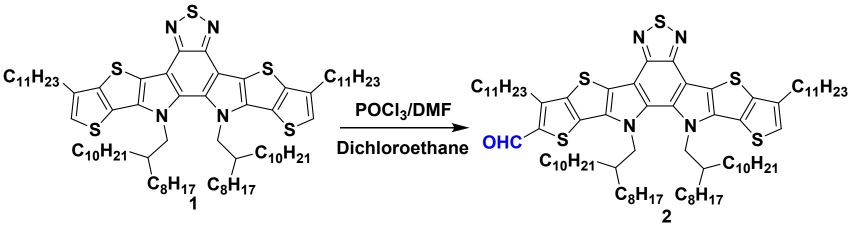

Figure S2. Synthesis of compound **2**.

Under argon protection, the flask was added with raw material **1**(0.420 g 0.322 mmol), DMF(0.045 mL), dichloroethane(20 mL) and add POCl$_3$(0.052 mL) under ice bath. After stirring for 1 hour, the reaction was carried out under the ice bath for 6 hours. Extraction of reaction solution with dichloromethane/water, and concentrate the organic phase. The compound **2** was obtained by column chromatography(PE:DCM=5:1). Yellow oil(0.355 mg, yield 83%). ^{1}H NMR (400 MHz, Chloroform-d) δ 10.13 (s, 1H), 7.05 (s, 1H), 4.60 (t, J = 7.1 Hz, 4H), 3.19 (t, J = 7.8 Hz, 2H), 2.82 (t, J = 7.8 Hz, 2H), 2.04 (dd, J = 14.1, 7.5 Hz, 3H), 1.89 (dt, J = 27.8, 7.5 Hz, 4H), 1.57 (s, 5H), 1.47 (qd, J = 8.3, 5.3, 4.2 Hz, 4H), 1.43 – 1.36 (m, 5H), 1.28 (q, J = 6.9, 6.3 Hz, 38H), 1.15 (dq, J = 13.9, 6.5 Hz, 15H), 1.09 – 0.67

(m, 72H).

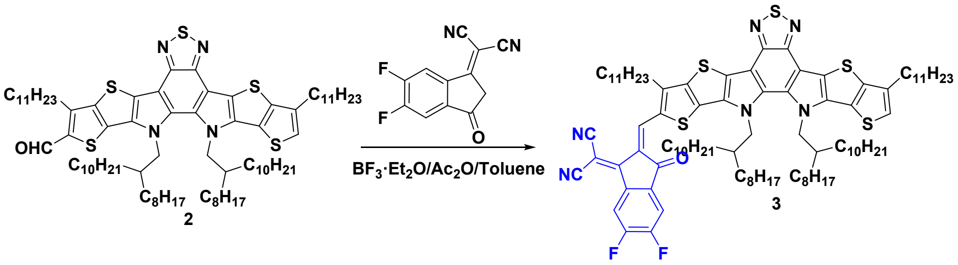

Figure S3. Synthesis of compound **3**.

To the flask was added compound **2**(0.350 g 0.262 mmol), 2F-IC(0.082 g 0.314 mmol), BF$_3$·Et$_2$O(0.1 mL), Ac$_2$O(0.2 mL) and toluene(20 mL). After stirring for 10 mins, the reaction solution was poured into methanol and filtered. The compound **3** was obtained by column chromatography(PE:DCM=3:1). Dark green solid(0.228g, yield 56%). ^{1}H NMR (400 MHz, Chloroform-d) δ 9.15 (s, 1H), 8.56 (dd, J = 10.0, 6.4 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.10 (s, 1H), 4.71 (d, J = 7.6 Hz, 2H), 4.62 (d, J = 7.8 Hz, 2H), 3.23 (t, J = 8.0 Hz, 2H), 2.83 (t, J = 7.8 Hz, 2H).

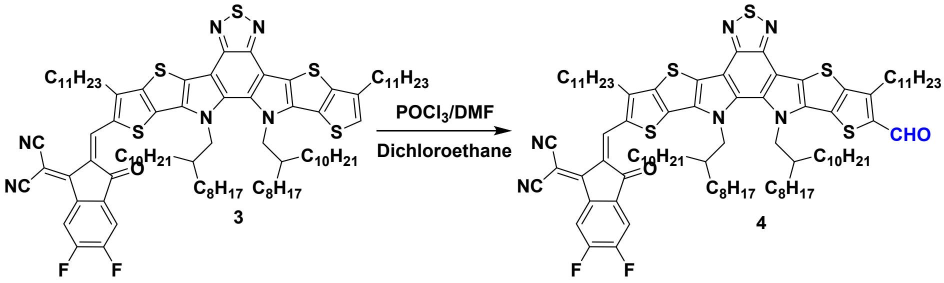

Figure S4. Synthesis of compound **4**.

Under argon protection, the flask was added with compound **3**(0.180 g 0.142 mmol), DMF(0.2 mL), dichloroethane(10 mL) and added POCl$_3$(0.2 mL) under ice water bath. After stirring for 1 hour, the reaction was carried out under the ice bath for 6 hours. The reaction solution was poured into methanol and filtered. The compound **4** was obtained by column chromatography(PE:DCM=3:1). Dark green solid(0.150 g yield 81%). ^{1}H NMR (400 MHz, Chloroform-d) δ 10.16 (s, 1H), 9.16 (s, 1H), 8.57 (dd, J = 10.0, 6.4 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 4.72 (d, J = 7.7 Hz, 2H), 4.65 (d, J = 7.8 Hz, 2H), 3.28 – 3.15 (m, 4H), 2.07 (q, J = 6.6 Hz, 3H), 1.91 (dt, J = 20.2, 7.5 Hz, 5H), 1.61 – 1.43 (m, 10H), 1.43 – 1.36 (m, 5H), 1.36 – 1.21 (m, 35H), 1.21 – 1.08 (m, 22H), 0.95 (d, J = 8.4 Hz, 42H), 0.91 – 0.68 (m, 35H).

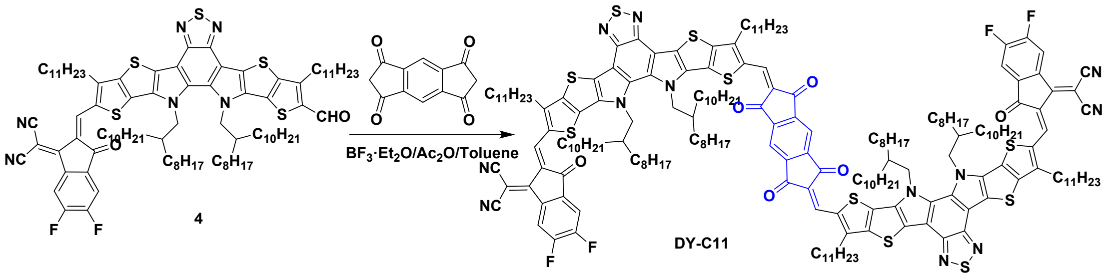

Figure S5. Synthesis of giant molecule **DY-C11**.

To the flask was added compound **4**(0.100 g 0.063 mmol), s-indacene-1,3,5,7(2H,6H)-tetraone (0.008 g 0.037 mmol), BF$_3$·Et$_2$O(0.1 mL), Ac$_2$O(0.2 mL) and toluene(10 mL). After stirring for 30 mins, the reaction solution was poured into methanol and filtered. The compound DY-C11 was obtained by column chromatography gradient elution(PE:DCM=3:1-1.5:1). Black solid(0.070 mg, yield 66%). ^{1}H NMR (400 MHz, Chloroform-d) δ 9.19 (s, 1H), 8.59 (ddd, J = 10.0, 6.5, 3.6 Hz, 1H), 8.48 (d, J = 10.7 Hz, 1H), 8.34 (d, J = 10.2 Hz, 1H), 7.72 (td, J = 7.5, 2.1 Hz, 1H), 4.78 (d, J = 7.4 Hz, 4H), 3.25 (t, J = 8.0 Hz, 4H), 2.20 – 2.08 (m, 2H), 1.98 – 1.84 (m, 4H), 1.56 (s, 20H), 1.40 (s, 5H), 1.37 –

1.22 (m, 35H), 1.22 – 1.09 (m, 25H), 1.01 (s, 34H), 0.93 – 0.70 (m, 29H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.58, 187.49, 158.35, 153.77, 151.54, 147.50, 147.46, 145.26, 145.14, 137.83, 137.72, 137.39, 136.17, 134.45, 133.67, 133.45, 131.24, 130.07, 122.30, 119.89, 114.83, 114.39, 113.91, 113.81, 113.34, 77.59, 77.27, 76.95, 55.77, 39.40, 32.27, 32.22, 32.16, 32.14, 32.12, 31.44, 31.13, 30.81, 30.16, 30.13, 30.08, 30.04, 30.00, 29.94, 29.92, 29.89, 29.86, 29.80, 29.74, 29.67, 29.56, 29.54, 27.54, 25.93, 23.16, 23.11, 23.05, 23.03, 14.49, 14.46, 14.44, 14.42, 1.11. HRMS (MALDI-FTICR-MS) m/z: $[M]^+$ calcd. for $C_{200}H_{266}F_4N_{12}O_6S_{10}$, found $[M]^+$: 3327.7920.

The DY-BO was synthesized by the similar method of DY-C11.

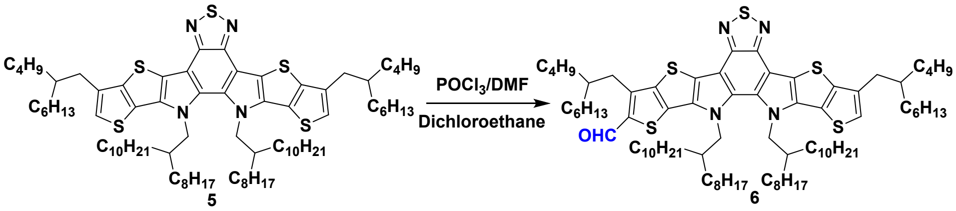

Figure S6. Synthesis of compound **6**.

Under argon protection, the flask was added with compound **5**(0.522 g 0.391 mmol), DMF(0.043 mL), dichloroethane(25 mL) and $POCl_3$(0.052 mL) under ice water bath. After stirring for 1 hour, the reaction was carried out under the ice bath for 6 hours. Extraction of reaction solution with dichloromethane/water, and concentrate the organic phase. The compound **6** was obtained by column chromatography(PE:DCM=5:1). Yellow oil(0.347 mg, yield 68%). ^{1}H NMR (400 MHz, Chloroform-d) δ 10.11 (s, 1H), 7.03 (s, 1H), 4.60 (t, J = 7.4 Hz, 4H), 3.10 (d, J = 7.4 Hz, 2H), 2.75 (d, J = 7.1 Hz, 2H), 2.12 – 1.95 (m, 7H), 1.49 – 1.33 (m, 23H), 1.34 – 1.23 (m, 33H), 1.16 (t, J = 7.1 Hz, 18H), 1.03 (ddd, J = 22.8, 10.6, 5.6 Hz, 28H), 0.94 – 0.71 (m, 55H).

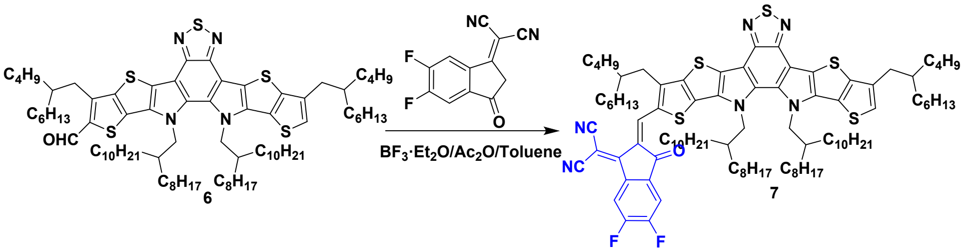

Figure S7. Synthesis of compound **7**.

To the flask was added compound **6**(0.347 g 0.262 mmol), 2F-IC(0.070g 0.304 mmol), $BF_3·Et_2O$(0.1 mL), Ac_2O(0.2 mL) and toluene(20 mL). After stirring for 10 mins, the reaction solution was poured into methanol and filtered. The compound **7** was obtained by column chromatography(PE:DCM=3:1). Dark green solid(0.240 g, yield 60%). ^{1}H NMR (400 MHz, Chloroform-d) δ 9.14 (s, 1H), 8.56 (dd, J = 10.1, 6.4 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.07 (s, 1H), 4.71 (d, J = 7.7 Hz, 2H), 4.62 (d, J = 7.9 Hz, 2H), 3.19 (d, J = 7.6 Hz, 2H), 2.76 (d, J = 7.1 Hz, 2H), 2.09 (s, 4H), 2.00 (t, J = 6.8 Hz, 3H), 1.70 – 1.59 (m, 5H), 1.36 (d, J = 5.2 Hz, 14H), 1.34 – 1.20 (m, 49H), 1.14 (dd, J = 11.3, 6.0 Hz, 18H), 1.04 (p, J = 7.2 Hz, 21H), 1.00 – 0.91 (m, 30H), 0.91 – 0.75 (m, 58H).

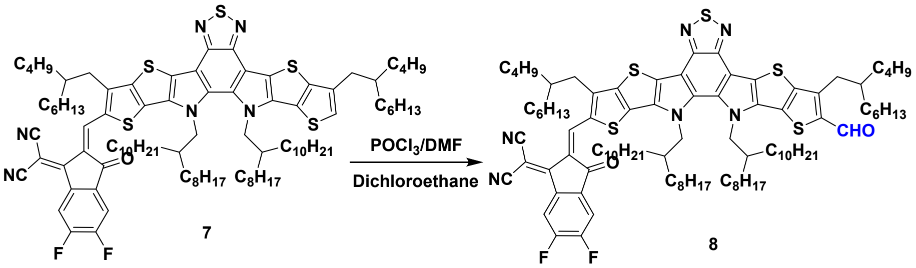

Figure S8. Synthesis of compound **8**.

Under argon protection, the flask was added with compound **7**(0.240 g 0.152 mmol), DMF(0.3 mL), dichloroethane(20 mL) and POCl$_3$(0.3 mL) under ice water bath. After stirring for 1 hour, the reaction was carried out under the ice bath for 6 hours. The reaction solution was poured into methanol and filtered. The compound **8** was obtained by column chromatography(PE:DCM=3:1). Dark green solid(0.182 g yield 75%). ^{1}H NMR (400 MHz, Chloroform-d) δ 10.14 (s, 1H), 9.16 (s, 1H), 8.58 (dd, J = 10.0, 6.4 Hz, 1H), 7.69 (t, J = 7.4 Hz, 1H), 4.72 (d, J = 7.6 Hz, 2H), 4.65 (d, J = 7.8 Hz, 2H), 3.20 (d, J = 7.6 Hz, 2H), 3.12 (d, J = 7.3 Hz, 2H), 2.05 (d, J = 24.0 Hz, 7H), 1.47 – 1.35 (m, 15H), 1.35 – 1.20 (m, 49H), 1.15 (s, 17H), 0.99 (d, J = 40.6 Hz, 39H), 0.90 – 0.77 (m, 36H).

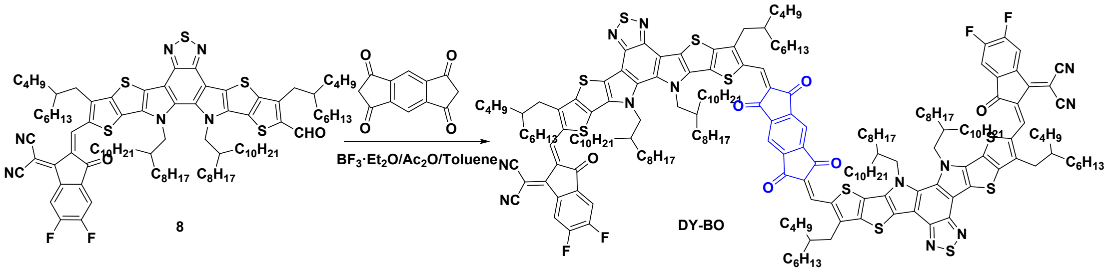

Figure S9. Synthesis of giant molecule **DY-BO**.

To the flask was added compound **8**(0.182 g 0.113 mmol), s-indacene-1,3,5,7(2H,6H)-tetraone (0.021g 0.068 mmol), BF$_3$·Et$_2$O(0.2 mL), Ac$_2$O(0.2 mL) and toluene(20 mL). After stirring for 30 mins, the reaction solution was poured into methanol and filtered. The compound DY-BO was obtained by column chromatography gradient elution (PE:DCM=3:1-1.5:1). Black solid(0.102 mg, yield 53%). ^{1}H NMR (400 MHz, Chloroform-d) δ 9.18 (d, J = 3.0 Hz, 1H), 8.59 (ddd, J = 9.9, 6.5, 3.3 Hz, 1H), 8.49 (d, J = 7.7 Hz, 1H), 8.36 (s, 1H), 7.72 (td, J = 7.5, 2.5 Hz, 1H), 4.80 (d, J = 7.5 Hz, 4H), 3.19 (dd, J = 13.5, 7.6 Hz, 4H), 2.22 (t, J = 7.6 Hz, 1H), 2.12 (s, 4H), 2.01 (d, J = 6.3 Hz, 1H), 1.56 (s, 10H), 1.52 – 1.44 (m, 6H), 1.40 (d, J = 6.1 Hz, 8H), 1.36 – 1.22 (m, 29H), 1.17 (dt, J = 13.9, 7.5 Hz, 22H), 1.10 – 0.93 (m, 36H), 0.93 – 0.74 (m, 31H). ^{13}C NMR (101 MHz, Chloroform-d) δ 188.49, 187.71, 185.77, 158.83, 153.46, 151.43, 151.36, 147.54, 147.51, 146.85, 145.36, 137.74, 137.34, 135.94, 135.62, 135.27, 134.41, 134.21, 134.18, 133.53, 131.22, 130.00, 122.23, 119.99, 115.05, 114.51, 113.77, 113.27, 68.81, 55.75, 40.28, 40.17, 39.36, 34.79, 34.38, 34.10, 33.77, 33.73, 33.45, 32.12, 32.09, 32.08, 32.05, 32.01, 30.74, 29.99, 29.91, 29.84, 29.81, 29.76, 29.65, 29.61, 29.59, 29.56, 29.43, 29.41, 29.04, 26.85, 26.80, 25.84, 23.33, 23.30, 22.95, 22.91, 22.89, 14.34, 14.32, 14.30. HRMS (MALDI-FTICR-MS) m/z: $[M]^+$ calcd. for $C_{204}H_{274}F_4N_{12}O_6S_{10}$, found $[M]^+$: 3383.8648.

2. ^{1}H, ^{13}C NMR and Mass spectra.

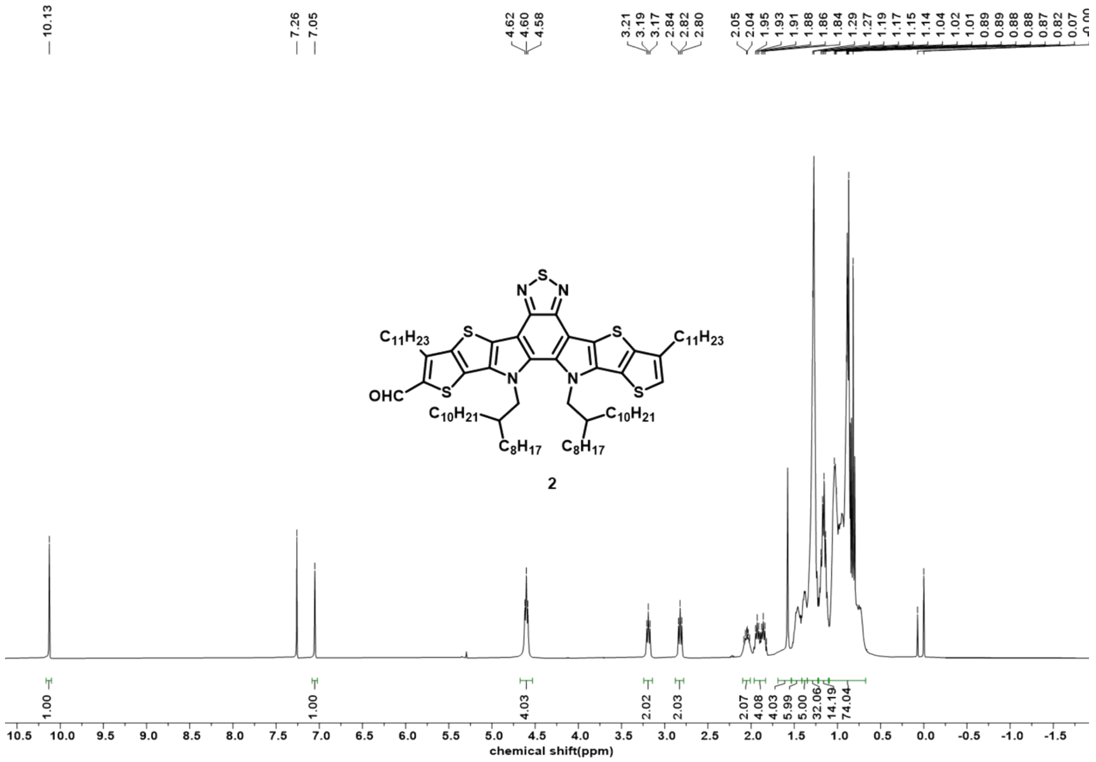

Figure S10. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

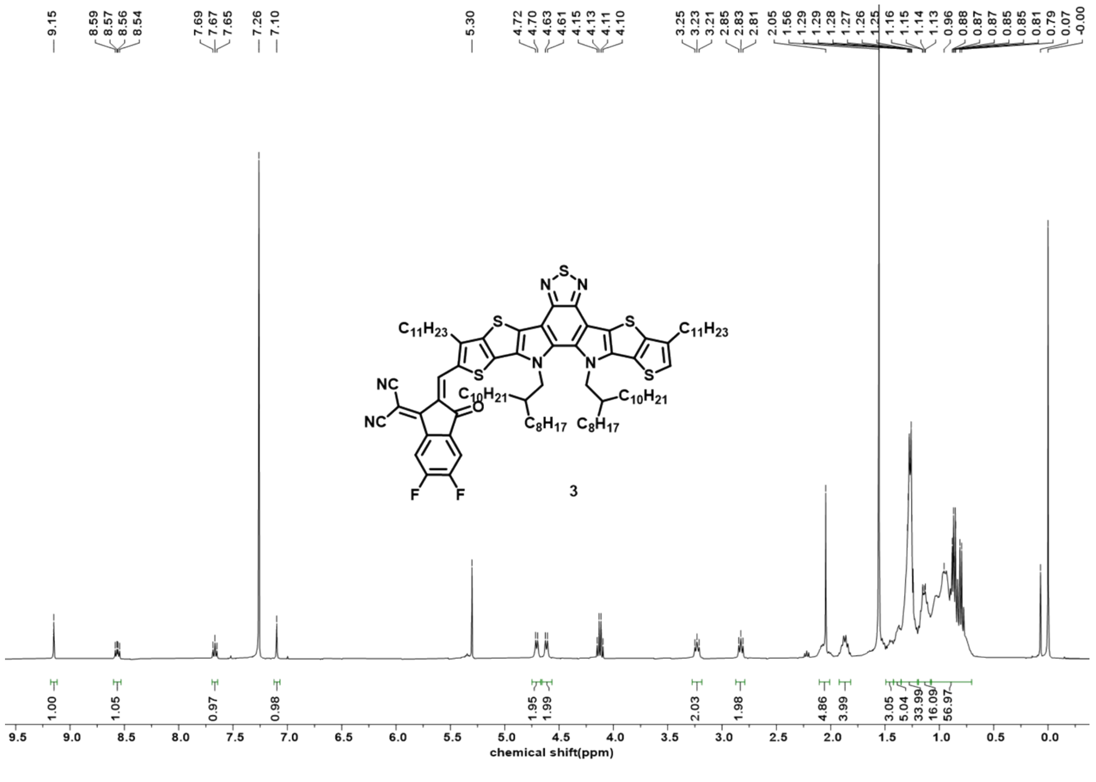

Figure S11. ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

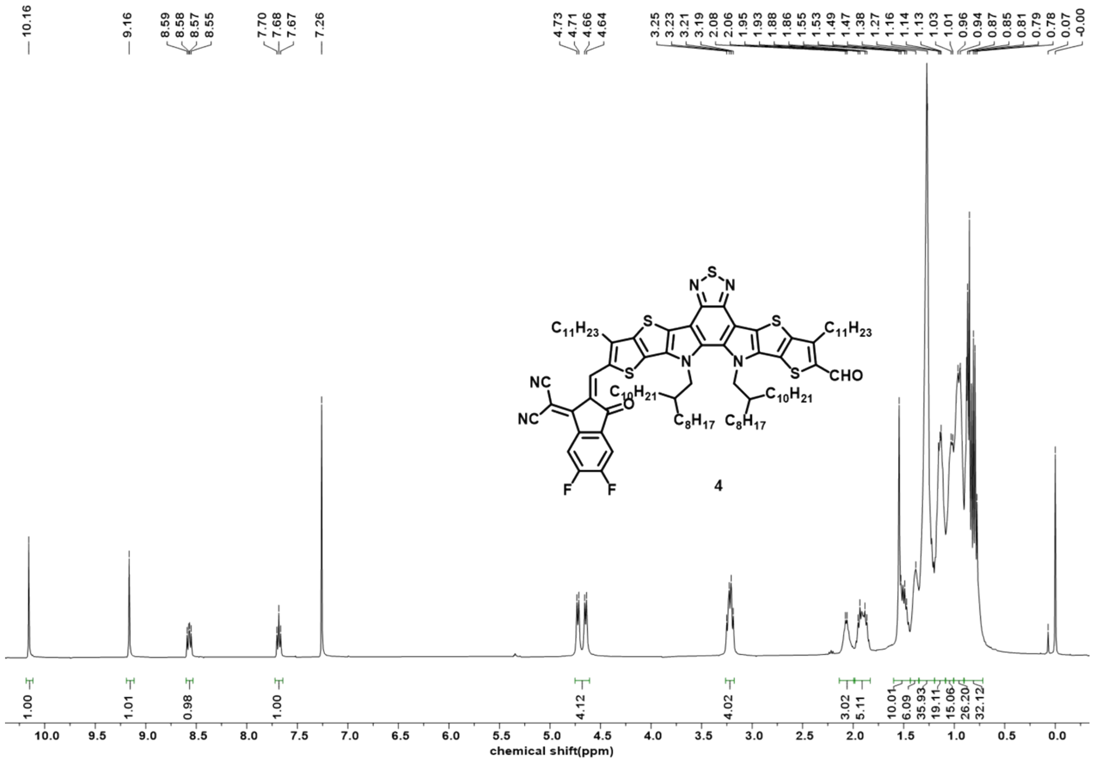

Figure S12. ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

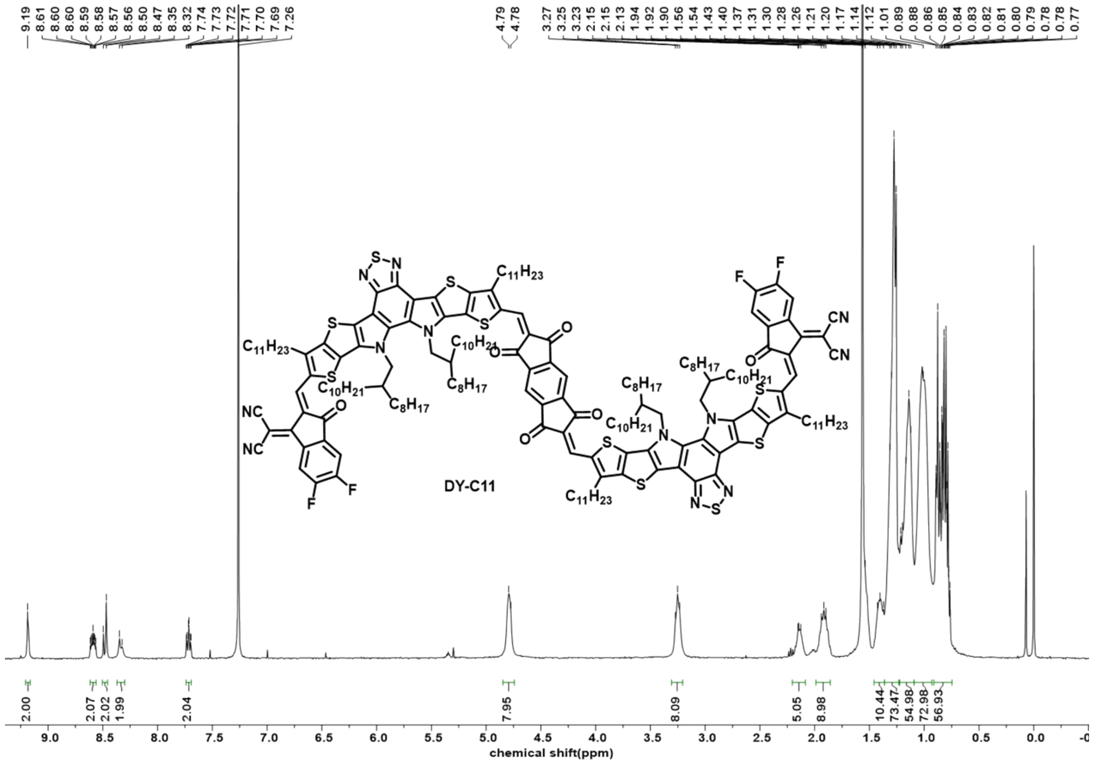

Figure S13. ^{1}H NMR spectrum of giant molecule DY-C11 in $CDCl_3$.

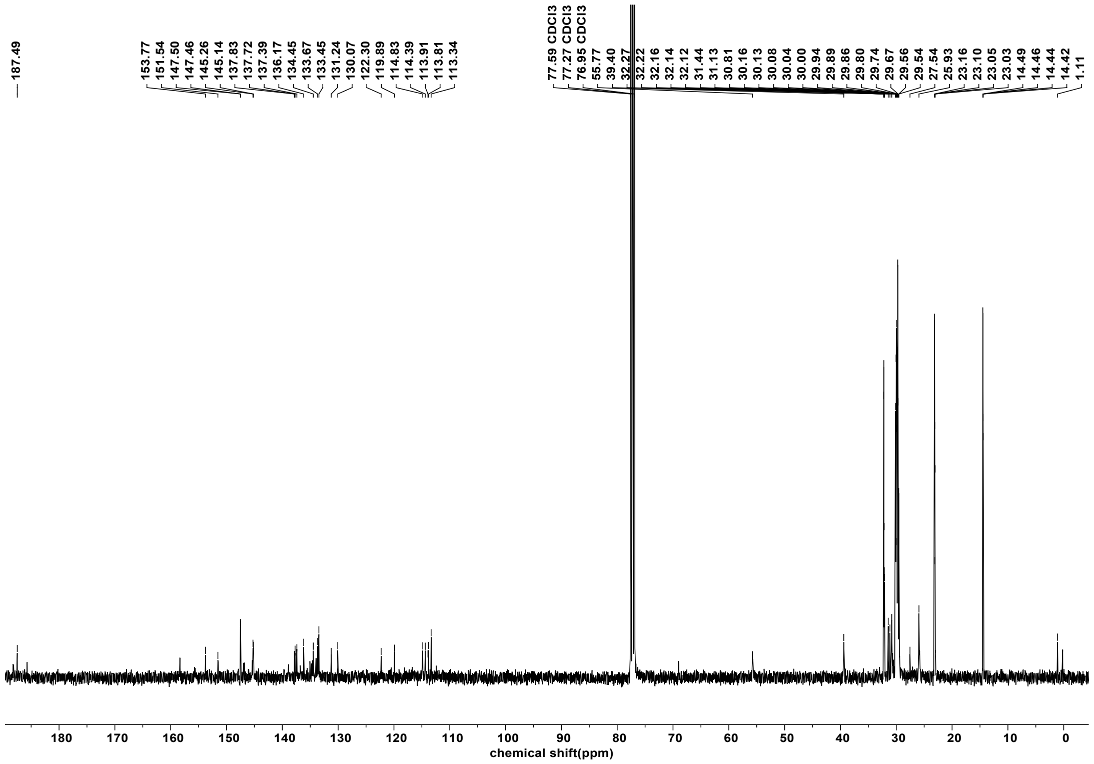

Figure S14. ^{13}C NMR spectrum of giant molecule DY-C11 in $CDCl_3$.

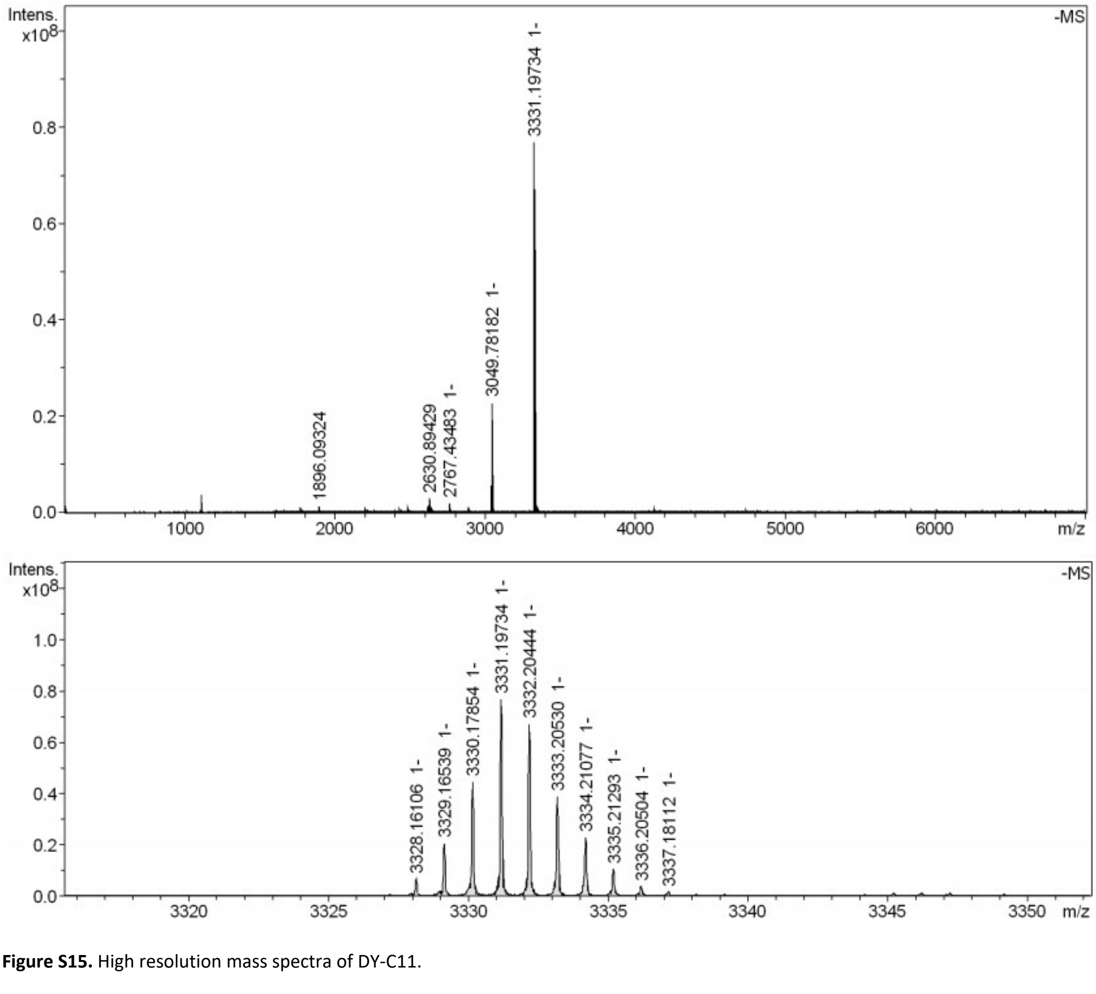

Figure S15. High resolution mass spectra of DY-C11.

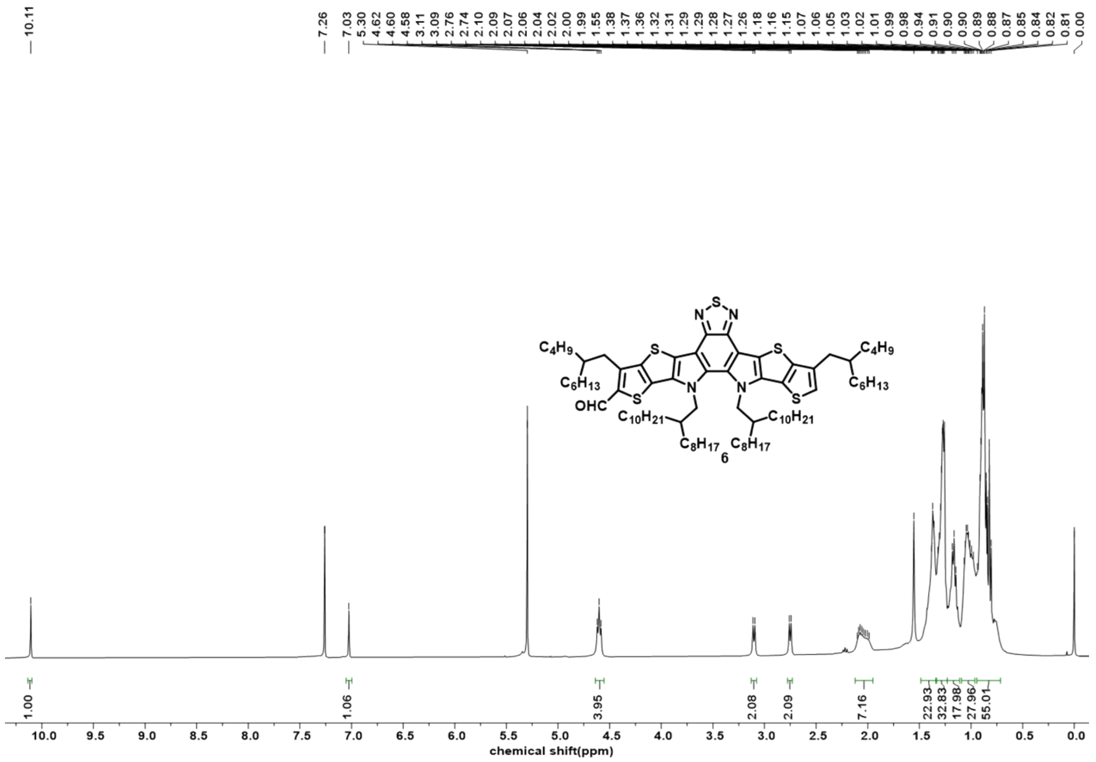

Figure S16. ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

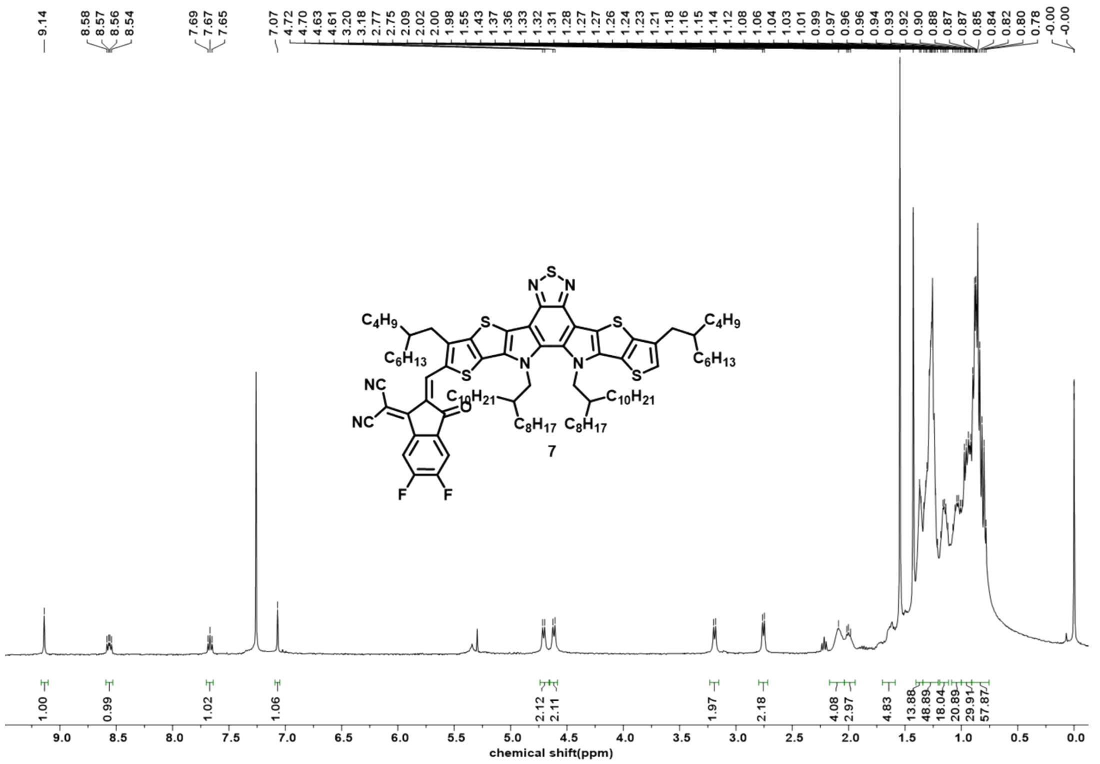

Figure S17. ^{1}H NMR spectrum of compound **7** in $CDCl_3$.

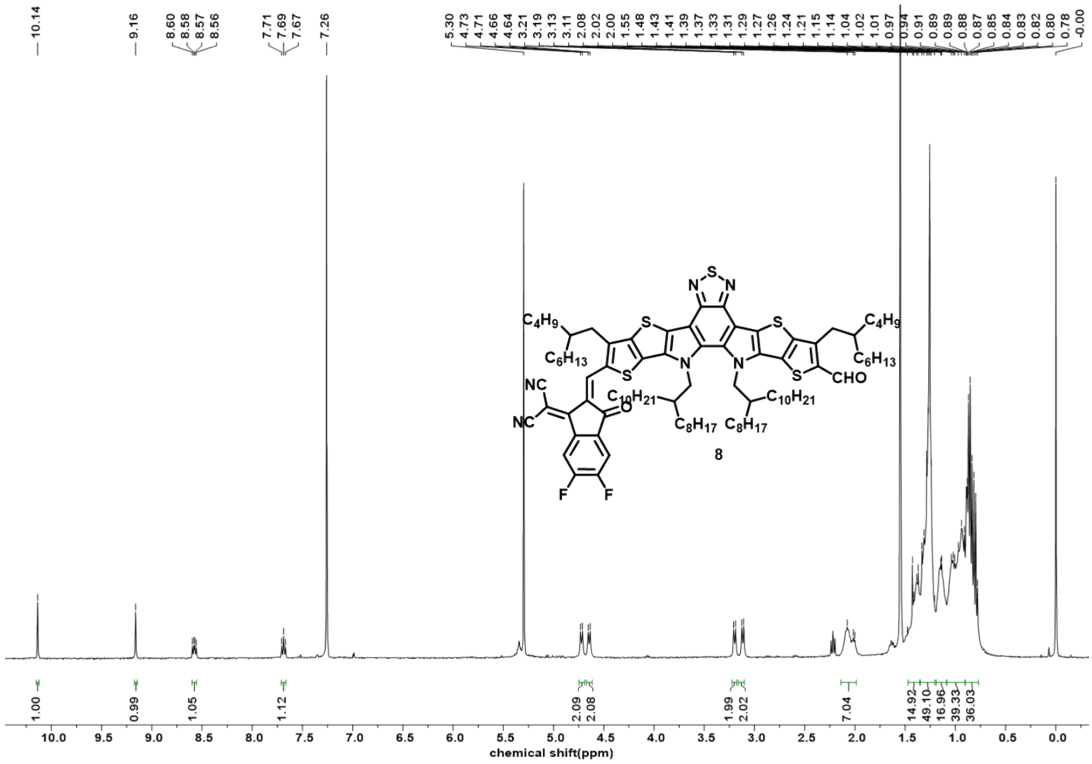

Figure S18. ^1H spectrum of compound **8** in $CDCl_3$.

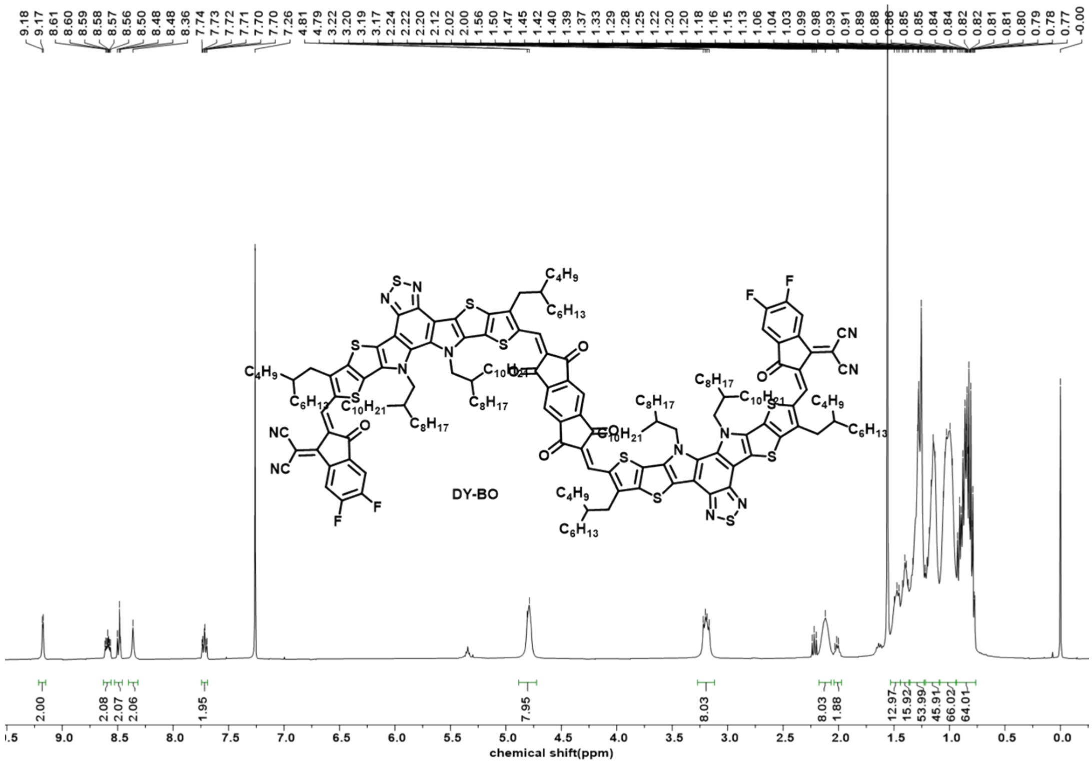

Figure S19. ^1H spectrum of giant molecule DY-BO in $CDCl_3$.

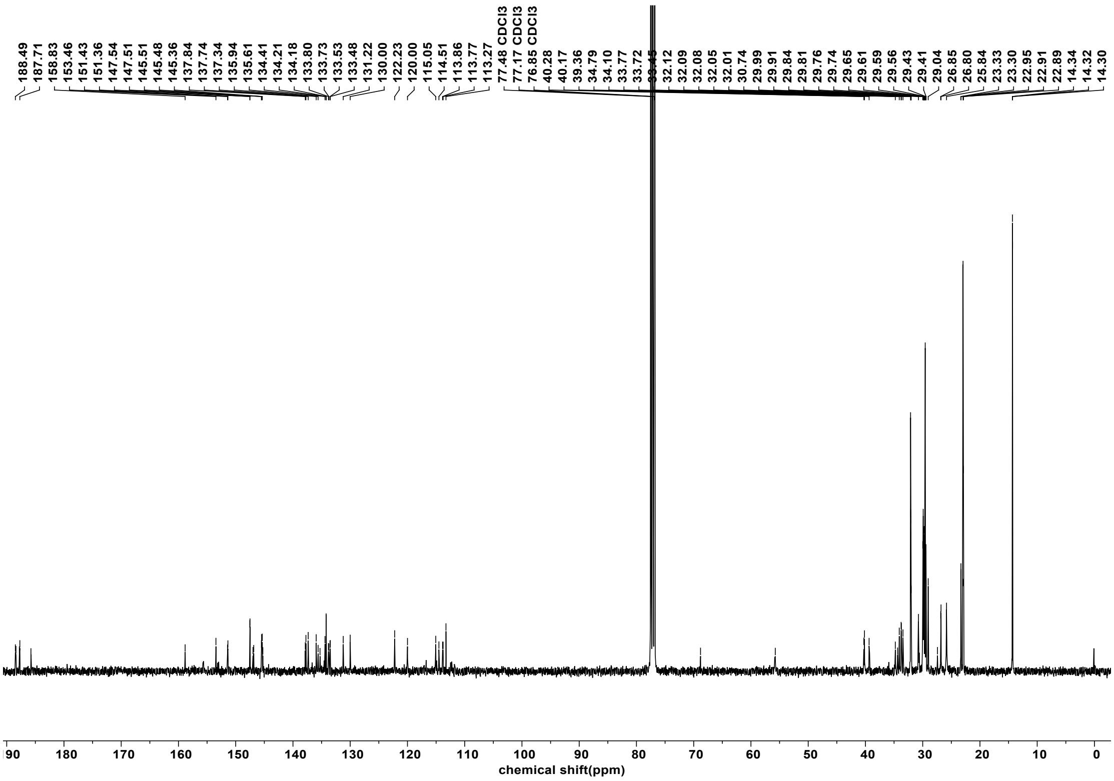

Figure S20. ^{13}C NMR spectrum of giant molecule DY-BO in $CDCl_3$.

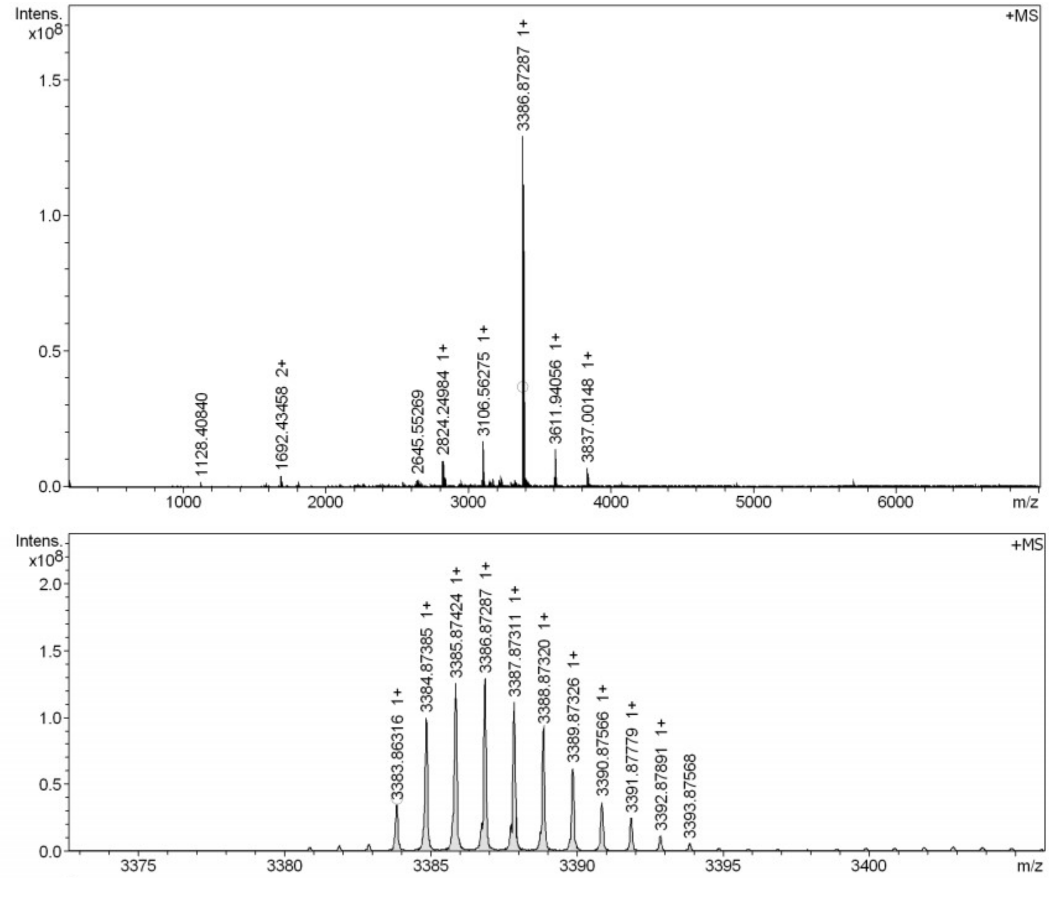

Figure S21. High resolution mass spectra of DY-BO.

3. Instruments and Measurements.

^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AV-400 spectrometer in a deuterated chloroform solution at 298 K, unless specified otherwise. Chemical shifts are reported as δ values (ppm) with tetramethylsilane (TMS) as the internal reference. The molecular mass was confirmed using an Autoflex III matrix-assisted laser desorption ionization mass spectrometer (MALDI-TOF MS). UV-Vis absorption spectra were recorded on the SHIMADZU UV-2600 spectrophotometer. The cyclic voltammetry results were obtained with a computer-controlled CHI 660E electrochemical workstation.

Density Functional Theory (DFT) Calculations. Calculation level WB97XD/def2SVP was chosen for structural optimisation and B3PW91/def2TZVP for single point calculation. Energy correlations such as molecular orbitals are viewed with Multiwfn.[2, 3] Original text of procedures used: Gaussian16：Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

The morphologies of the PM6/acceptor blend films were investigated by atomic force microscopy (AFM, Agilent Technologies, 5500 AFM/SPM System, USA) in contacting mode with a 5 µm scanner.

Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) measurements were accomplished with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.2º. GIWAXS samples are prepared on silicon substrate by spin coating.

4. Device fabrication and characterization.

The optimized solar cell devices were fabricated with a conventional structure of Glass/ITO/PEDOT: PSS (40 nm)/Active layer/PDINN (5nm)/Ag. Pre-patterned ITO coated glass substrates were washed with deionized water and isopropyl alcohol in an ultrasonic bath for 15 mins each. After blow-drying with high-purity nitrogen, all ITO substrates are cleaned in the ultraviolet ozone cleaning system for 25 mins. Subsequently, a thin layer of PEDOT: PSS was deposited through spin-coating on pre-cleaned ITO-coated glass at 4500 rpm for 30 s and dried subsequently at 150°C for 15 mins in atmospheric air. Then the photovoltaic layers were spin-coated in a glovebox from a solution of PM6: acceptor (14 mg/mL with 0.5 vol% 1-chloronaphthalene (CN) with the PM6/acceptor weight ratios of 1:0.9 in CF. The optimal active layers were fabricated by spin-coating at about 3500 rpm for the 30s. At a rate of 3000 rpm for 40 s, a PDINN layer was deposited on the top of the active layer. Finally, the top Ag electrode of 100 nm thickness was thermally evaporated through a mask onto the cathode buffer layer under a vacuum of 1.5×10^{-4} mbar. Current density–voltage (J–V) curves of the devices were performed by a Keithley 2400 source meter in a glove box with a nitrogen atmosphere. The simulated sunlight was calibrated by an AM 1.5G solar simulator (Enlitech, SS-F5, Taiwan), which was measured with a calibrated Si diode from National Renewable Energy Laboratory. The EQE curves were tested by an EnLi Technology (Taiwan) EQE measurement system.

Electron mobility and hole mobility measurements. The electron mobility device adopted the ITO/ZnO/active layer/PDINN/Ag structure, and the hole mobility device adopted the ITO/PEDOT: PSS/Active layer/MoO_3/Ag structure. The electron and hole mobilities were calculated according to the space charge limited current (SCLC) method by the equation: $J = 9\mu\varepsilon_r\varepsilon_0V^2/8d^3$, where J is the current density, µ is the electron or hole mobility, V is the internal voltage in the device, ε_r is the relative dielectric constant of active layer material, ε_0 is the permittivity of empty space, and d is the thickness of the active layer.

5. Additional Figures and Tables.

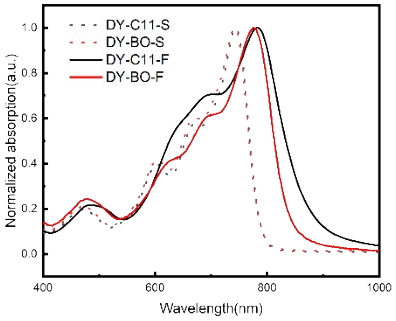

Figure S22. Absorption spectra of DY-C11 and DY-BO in chloroform solution(-S) and in film(-F).

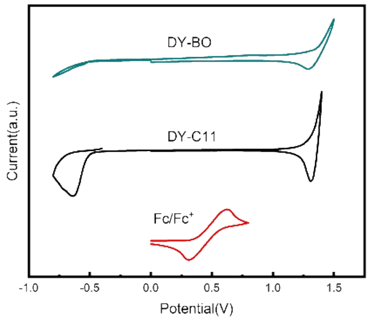

Figure S23. Cyclic voltammetry curves of DY-C11 and DY-BO.

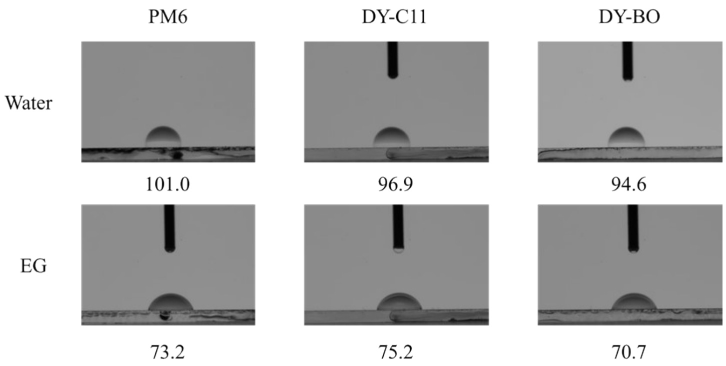

Figure S24. Contact angle images of water and ethylene glycol droplets on the neat films of PM6, DY-C11 and DY-BO.

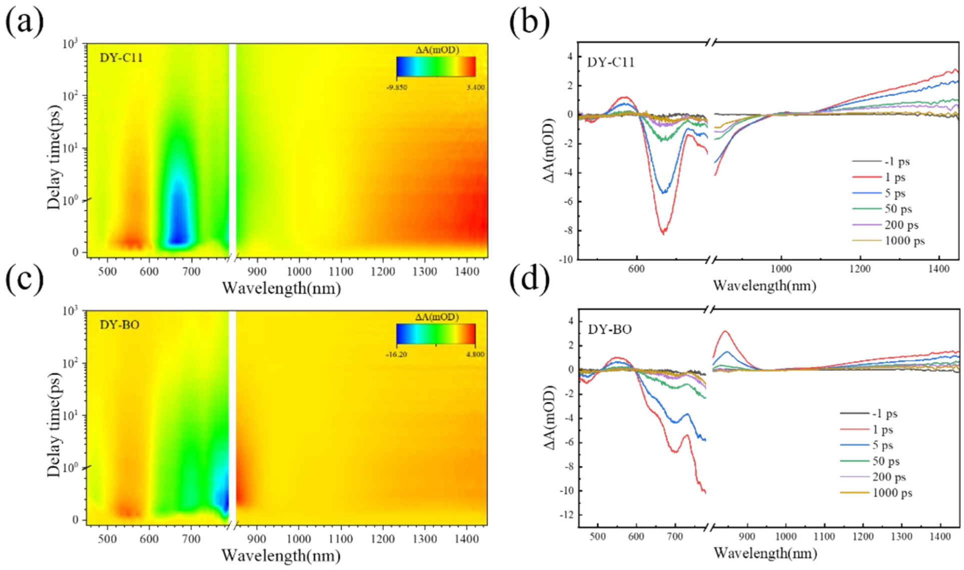

Figure S25. 2D TA spectra images of DY-C11 and DY-BO. Corresponding TA spectra at different time delays of DY-C11 and DY-BO.

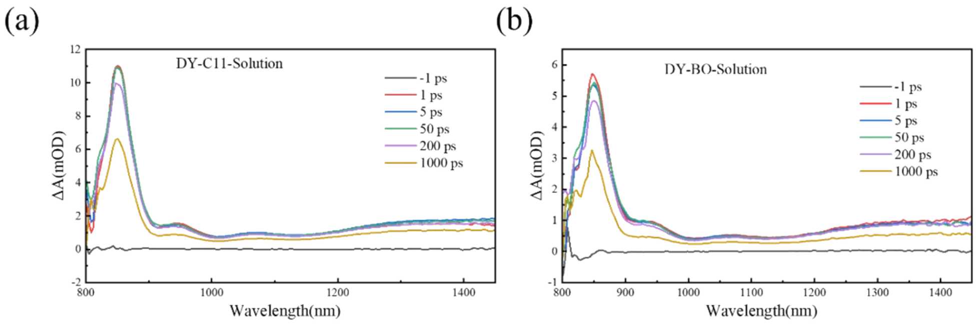

Figure S26. TAS spectra of DY-C11 and DY-BO solutions at different time delays.

Table S1. Contact angle and statistical data of surface tension and interaction parameter.

Materials	Water	EG	γd/ (mN m^{-1})	γp/ (mN m^{-1})	γ/ (mN m^{-1})	χ/ K(γD^{-2}-$\gamma A^{-2})^{2}$
PM6	101.0	73.2	23.10	0.96	24.07	/
DY-C11	96.9	75.2	16.12	3.46	19.58	0.232
DY-BO	94.6	70.7	18.90	3.41	22.31	0.033

Table S2. GIWAXS parameters of the blend films.

Samples	OOP(010)			
	q(A^{-1})	$d_{\pi-\pi}$(A)	FWHM	CCL(A)
PM6:DY-C11	1.74	3.61	0.539	10.49
PM6:DY-BO	1.70	3.70	0.532	10.63

Table S3. The detailed biexponential function estimate result of HT kinetics.

condition	A1(%)	t1(ps)	A2(%)	t2(ps)	tavg(ps)
PM6:DY-C11	89	0.19	11	22.61	21.22
PM6:DY-BO	96	0.24	4	19.36	14.97

Table S4. The molar absorption coefficient of DY-C11 and DY-BO.

	DY-C11 in solution(M^{-1} cm^{-1})	DY-C11 in film(cm^{-1})	DY-BO in solution(M^{-1} cm^{-1})	DY-BO in film(cm^{-1})
molar absorption coefficient	3.39×10^{5}	3.89×10^{4}	3.35×10^{5}	3.70×10^{4}

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2. T. Lu and F. Chen, *Journal of Computational Chemistry*, 2012, **33**, 580-592.
3. T. Lu, *The Journal of Chemical Physics*, 2024, **161**.