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Supporting Information

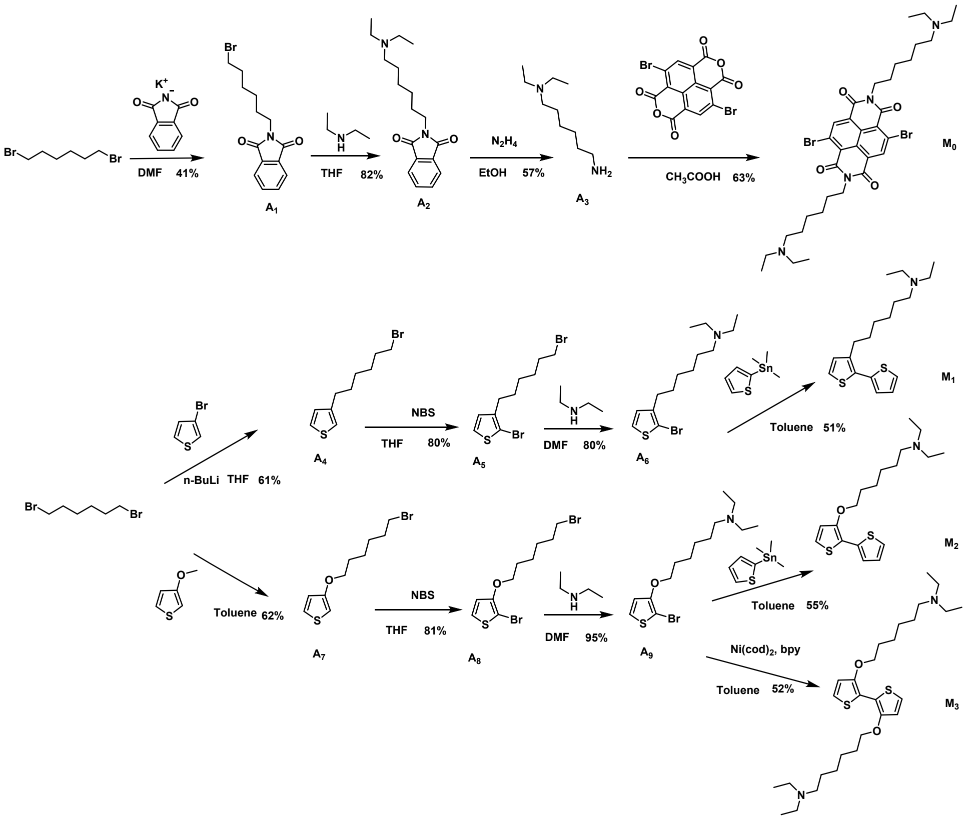
Direct Arylation Polycondensated Conjugated Polyelectrolytes as Universal Electron Transport Layers for Highly Efficient Polymer Solar Cells

Zhicheng Hu,[a,†] Zhiming Chen,[a,†] Jianhua Jing,[a] Yuanying Liang,[a] Yuanqing Bai,[a] Xiaocheng Liu,[a] Fei Huang[a,b,*] and Yong Cao[a]

[a] Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou, 510640, P. R. China

[b] South China Institute of Collaborative Innovation, Dongguan, 523808, PR China

Synthesis of Monomers



Scheme S1 Synthetic routes of monomers

Synthesis of 2-(6-bromohexyl)isoindoline-1,3-dione (A_1):

Potassium phthalimide (50.0 g, 270 mmol), 1,6-dibromohexane (197.6 g, 810 mmol) and 250 mL N,N-dimethylformamide were added into a 500 mL of round bottom flask. After purging N_2 for 15 minutes, the mixture was heated to 100 °C and stirred for 24 hours. The reaction was cooled to room temperature, extracted by water and dichloromethane. The organic layer was then concentrated and purified by column chromatography. The product $\mathbf{A_1}$ was obtained as a white solid (34.5g, 41%). ^{1}H-NMR (500 MHz, $CDCl_3$, δ): 7.86-7.83 (m, 2H), 7.73-7.70 (m, 2H), 3.69 (t, 2H, J = 6.9 Hz), 3.40 (t, 2H, J = 6.9 Hz), 1.88-1.61(m, 4H), 1.49-1.37 (m, 4H).

Synthesis of 2-(6-(diethylamino)hexyl)isoindoline-1,3-dione (A_2):

$\mathbf{A_1}$ (31.02 g, 100 mmol), diethylamine (29.2 g, 400 mmol), and 60 mL of tetrahydrofuran were added into a 250 mL of round bottom flask. After purging N_2 for 15 minutes, the mixture was heated to 60 °C and refluxed for 26 hours. After cooling to room temperature, the reaction was concentrated under vacuum evaporation. Afterwards, water and dichloromethane were added and the organic layer was separated and concentrated to obtain a white solid $\mathbf{A_2}$ (25.8g, 83%), which was directly used in the next step.

Synthesis of N^1,N^1-diethylhexane-1,6-diamine (A_3):

$\mathbf{A_2}$ (24.2g, 80 mmol), 80% hydrazine hydrate (25.0g, 400 mmol) and 280 mL of ethanol were added into a 500 mL of round bottom flask. After purging N_2 for 15 minutes, the mixture was heated to 90 °C and refluxed for 19 hours. After cooling to room temperature, the reaction was filtrated. The filter cake was washed with ethanol for two times. The combined filtrate was concentrated to obtain $\mathbf{A_3}$ as a yellow liquid (7.92 g, 57%). ^{1}H-NMR (500 MHz, DMSO-d_6, δ):3.70 (s, 2H), 2.54 (t, J = 7.0 Hz, 2H), 2.40 (q, J = 7.1 Hz, 4H), 2.34-2.27 (m, 2H), 1.43-1.17 (m, 8H),0.91 (t, J = 7.1 Hz, 6H).

Synthesis of 4,9-dibromo-2,7-bis(6-(diethylamino)hexyl)benzo [lmn][3,8]phenanthroline-1,3,6,8(2H, 7H)-tetraone (M_0):

$\mathbf{A_3}$ (7.75g, 45 mmol), 4,9-dibromoisochromeno [6,5,4-def]isochromene -1,3,6,8-tetrasone (6.4g, 15 mmol), and 150 mL of acetic acid were added into a 250 mL of round bottom flask. After purging N_2 for 20 minutes, the mixture was heated to 130 °C and refluxed for 3 hours. After cooling to room temperature, the mixture was poured into sodium carbonate solution slowly. The precipitate was then filtered, which was purified by column chromatography. The crude M_0 was washed with acetone to obtain a pure $\mathbf{M_0}$ as a yellow solid (6.95g, 63%).^{1}H-NMR (500 MHz, $CDCl_3$, δ):8.97 (s, 2H), 4.22-4.14 (m, 4H), 2.52 (q, J = 7.2 Hz, 8H), 2.45-2.38 (m, 4H), 1.79-1.69 (m, 4H), 1.45 (ddd, J = 15.4, 13.1, 7.4 Hz, 8H), 1.36 (tt, J = 10.4, 4.2 Hz, 4H), 1.01 (t, J = 7.1 Hz, 12H). ^{13}C-NMR (126 MHz, $CDCl_3$) 160.75, 139.08, 128.35, 127.74, 125.35, 124.09, 52.75, 46.83, 41.50, 27.88, 27.33, 27.04, 11.44.

Synthesis of 3-(6-bromohexyl)thiophene (A_4):

3-bromothiophene (5.7 g, 35 mmol) and 30 mL of anhydrous tetrahydrofuran were added into a 150 mL of round bottom flask, then the mixture was cooled to -78 °C under the protection of N_2. n-butyllithium solution (14 mL, 2.5 M) was added dropwisely and the reaction was stirred at -78 °C for 1 hour. Afterwards, 1,6-dibromohexane (12.2 g, 50 mmol) was added, the mixture was gradually warmed to room temperature and stirred for 12 hours. Then the mixture was concentrated under vacuum evaporation and extracted with water and dichloromethane. The organic layer was then concentrated and purified by column chromatography to obtain $\mathbf{A_4}$ as a colorless oil (5.2 g, 61%).^{1}H-NMR (500 MHz, $CDCl_3$, δ):7.25 (t, 1H), 6.94 (t, 2H), 3.44 (t, 2H), 2.67 (t, 2H,), 1.89 (m, 2H), 1.67 (m, 2H), 1.5 (m, 2H), 1.36 (m, 2H).

Synthesis of 2-bromo-3-(6-bromohexyl)thiophene (A_5):

$\mathbf{A_4}$ (5 g, 20 mmol) and 30 mL of tetrahydrofuran were added into a 100 mL of round bottom flask. Then the flask was placed in an ice-water bath. After purging N_2 for 15 minutes, N-bromosuccinimide (3.67 g, 20 mmol) was added. The reaction system was then slowly warmed to room temperature and stirred for 12 hours. After that, the mixture was concentrated and extracted with water and dichloromethane. The organic layer was concentrated and purified by column chromatography to obtain $\mathbf{A_5}$ as a yellow oil (5.22 g, 80%).^{1}H-NMR (500 MHz, $CDCl_3$, δ):7.19 (d, J = 5.6 Hz, 1H), 6.78 (d, J = 5.0 Hz, 1H), 3.40 (t, J = 6.8 Hz, 2H), 2.62-2.53 (m, 2H), 1.91-1.81 (m, 2H), 1.65-1.52 (m, 2H), 1.52-1.41 (m, 2H), 1.41-1.29 (m, 2H).

Synthesis of 6-(2-bromothiophen-3-yl)-N, N-diethylhexan-1-amine (A_6):

$\mathbf{A_5}$ (5.22 g, 16 mmol), diethyl amine (4 mL, 40 mmol) and 30 mL of N, N-dimethylformamide were added into a 100 mL of round bottom flask. After purging N_2 for 15 minutes, the mixture was refluxed for 12 hours. After cooling to room temperature, the mixture was concentrated under reduced pressure and extracted with water and dichloromethane. The organic layer was then concentrated and purified by column chromatography to obtain $\mathbf{A_6}$ as a yellow oil (4.83g, 95%). $\mathbf{A_6}$ was directly used in the next step.

Synthesis of 6-([2,2'-bithiophen]-3-yl)-N, N-diethylhexan-1-amine (M_1):

$\mathbf{A_6}$ (1.00 g, 3 mmol), 2-trimethyltinthiophene (2.22 g, 9 mmol) and 30 mL of toluene were added into a 100 mL of round bottom flask. After purging N_2 for 15 minutes, $Pd_2(dba)_3$ (250 mg, 0.3 mmol) and $P(o\text{-}tol)_3$ (500 mg, 1.5 mmol) were added into the solution. The mixture was then purged with N_2 for 15 minutes. Afterwards, the reaction solution was refluxed for 12 hours. After cooling to room temperature, the mixture was concentrated and extracted with water and dichloromethane. The organic layer was then concentrated and purified by column chromatography to obtain $\mathbf{M_1}$ as a yellow oil (482 mg, 51%).^{1}H-NMR (500 MHz, $CDCl_3$, δ):7.31-7.28 (m, 1H), 7.19-7.15 (m, 1H), 7.12-7.08 (m, 1H), 7.06 (td, J = 4.8, 2.6 Hz, 1H), 6.92 (dd, J = 6.8, 3.0 Hz, 1H), 2.78-2.71 (m, 2H), 2.53 (q, J = 7.1 Hz,4H), 2.41 (dd, J = 14.8, 7.0 Hz, 2H), 1.63 (dt, J = 15.4, 7.6 Hz, 2H), 1.49-1.21 (m, 6H), 1.06-0.99 (m, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$, δ):139.53, 136.19, 130.56, 129.86, 127.34, 126.03, 125.31, 123.78, 52.73, 46.81, 30.68, 29.40, 29.04, 27.46, 11.36. MS (TOF): Calcd., m/z =321.16, Found, m/z=322.12

Synthesis of 3-((6-bromohexyl)oxy)thiophene (A_7):

3-Methoxythiophene (3.43 g, 30 mmol), 6-bromo-n-hexanol (10.86 g, 60 mmol) and 40 mL of toluene were added into a 100 mL of round bottom flask. After purging N_2 for 15 minutes, p-toluenesulfonic acid (258 mg, 1.5 mmol) was added and the reaction solution was refluxed for 12 hours. After cooling to room temperature, the mixture was concentrated under reduced pressure and extracted with water and dichloromethane. Then the organic layer was concentrated and purified by column chromatography to obtain $\mathbf{A_7}$ as a colorless oil (4.90 g, 62%). $\mathbf{A_7}$ was directly used in the next step.

Synthesis of 2-bromo-3-((6-bromohexyl)oxy)thiophene (A_8):

$\mathbf{A_7}$ (4.90 g, 18 mmol) and 30 mL of tetrahydrofuran were added into a 100 mL of round bottom flask. Then the flask was placed in an ice-water bath. After purging N_2 for 15 minutes, N-bromosuccinimide (3.31g, 18mmol) was added. Afterwards, the reaction was slowly warmed to room temperature and stirred overnight. The mixture was then concentrated under reduced pressure and extracted with water and dichloromethane. The organic layer was concentrated and purified by column chromatography to obtain $\mathbf{A_8}$ as a yellow oil (4.92g, 81%).

Synthesis of 6-((2-bromothiophen-3-yl)oxy)-N, N-diethylhexan-1-amine (A_9):

$\mathbf{A_8}$ (4.92 g, 14 mmol), diethylamine (3 ml, 30 mmol) and 30 mL of N,N-dimethylformamide were added into a 100 mL of round bottom flask. After purging N_2 for 15 minutes, the mixture was refluxed for 12 hours. After cooling to room temperature, the mixture was concentrated under reduced pressure and extracted with water and dichloromethane. The organic layer was then concentrated and purified by column chromatography to obtain $\mathbf{A_9}$ as a yellow oil (4.57g, 95%).^{1}H-NMR (500 MHz, $CDCl_3$, δ):7.20-7.16 (m, 1H), 6.76-6.71 (m, 1H), 4.03 (t, J = 6.5 Hz, 2H), 2.52 (q, J = 7.2 Hz, 4H), 2.46-2.36 (m, 2H), 1.81-1.71 (m, 2H), 1.52-1.48 (m, 2H), 1.46 (ddd, J = 10.4, 7.4, 4.6 Hz, 2H), 1.39-1.30 (m, 2H), 1.02 (t, J = 7.2 Hz, 6H).

Synthesis of 6-([2,2'-bithiophen]-3-yloxy)-N, N-diethylhexan-1-amine (M_2):

$\mathbf{A_9}$ (334 mg, 1 mmol), 2-trimethyltinthiophene (741 mg, 3 mmol) and 30 mL toluene were added into a 100 mL round bottom flask. After purging N_2 for 15 minutes, $Pd_2(dba)_3$ (90 mg, 0.1 mmol) and $P(o\text{-}tol)_3$ (180 mg, 0.6 mmol) were added into solution. Then the reaction solution was purged with N_2 for 15 minutes again. Afterwards, the reaction was refluxed for 12 hours and cooled to room temperature. The mixture was concentrated under reduced pressure and extracted with water and dichloromethane. The organic layer was concentrated and purified by column chromatography to obtain **M_2** as a yellow oil (184 mg, 55%). ^{1}H-NMR (500 MHz, $CDCl_3$, δ):7.22 (ddd, *J* = 4.8, 3.3, 1.2 Hz, 1H), 7.20-7.16 (m, 1H), 7.04 (d, *J* = 5.5 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.84 (d, *J* = 5.5 Hz, 1H), 4.10 (t, *J* = 6.4 Hz, 2H), 2.52 (dt, *J* = 11.4, 5.1 Hz, 4H), 2.42 (dd, *J* = 8.8, 6.7 Hz, 2H), 1.89-1.79 (m, 2H), 1.60-1.44 (m, 4H), 1.41-1.32 (m, 2H), 1.02 (dd, *J* = 8.9, 5.4 Hz, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$, δ):152.45, 135.26, 126.67, 123.50, 122.41, 121.33, 117.43, 115.48, 71.75, 52.90, 46.90, 29.64, 27.42, 26.95, 26.04, 11.64. MS (TOF): Calcd., m/z =337.16, Found, m/z=338.13.

Synthesis of 6,6'-([2,2'-bithiophene]-3,3'-diylbis(oxy)) bis(N,N-diethylhexan-1-amine) (M_3):

Bis(1,5-cyclooctadiene)nickel (0.4 g, 1.45 mmol), 2,2-bipyridine (0.23 g, 1.45mmol), 1,5-cyclooctadiene (120 μL, 0.97 mmol) and 4 mL of anhydrous N,N-dimethylformamide were added into a 25 mL of round bottom flask. After purging N_2 for 15 minutes, the flask was heated to 80 °C for 1 hour. After cooling to room temperature, **A_9** (0.34 g, 1 mmol) in 6mL of toluene was slowly added into the solution. Afterwards, the flask was stirred at 80 °C overnight. The mixture was then concentrated under reduced pressure and extracted with water and dichloromethane. The organic layer was concentrated and purified by column chromatography to obtain **M_3** as a colorless oil (120 mg, 52%). ^{1}H-NMR (500 MHz, $CDCl_3$, δ):7.06 (d, *J* = 5.5 Hz, 2H), 6.83 (d, *J* = 5.6 Hz, 2H), 4.09 (t, *J* = 6.4 Hz, 4H), 2.52 (q, *J* = 7.2 Hz, 8H), 2.45-2.39 (m, 4H), 1.85 (dt, *J* = 14.5, 6.5 Hz, 4H), 1.62-1.44 (m, 8H), 1.40-1.31 (m, 4H), 1.02 (t, *J* = 7.2 Hz, 12H). ^{13}C-NMR (126 MHz, $CDCl_3$, δ):151.91, 121.64, 116.04, 114.11, 71.87, 52.90, 46.89, 29.68, 27.45, 26.88, 26.09, 11.61. MS (TOF): Calcd., m/z =508.82, Found, m/z =509.9.

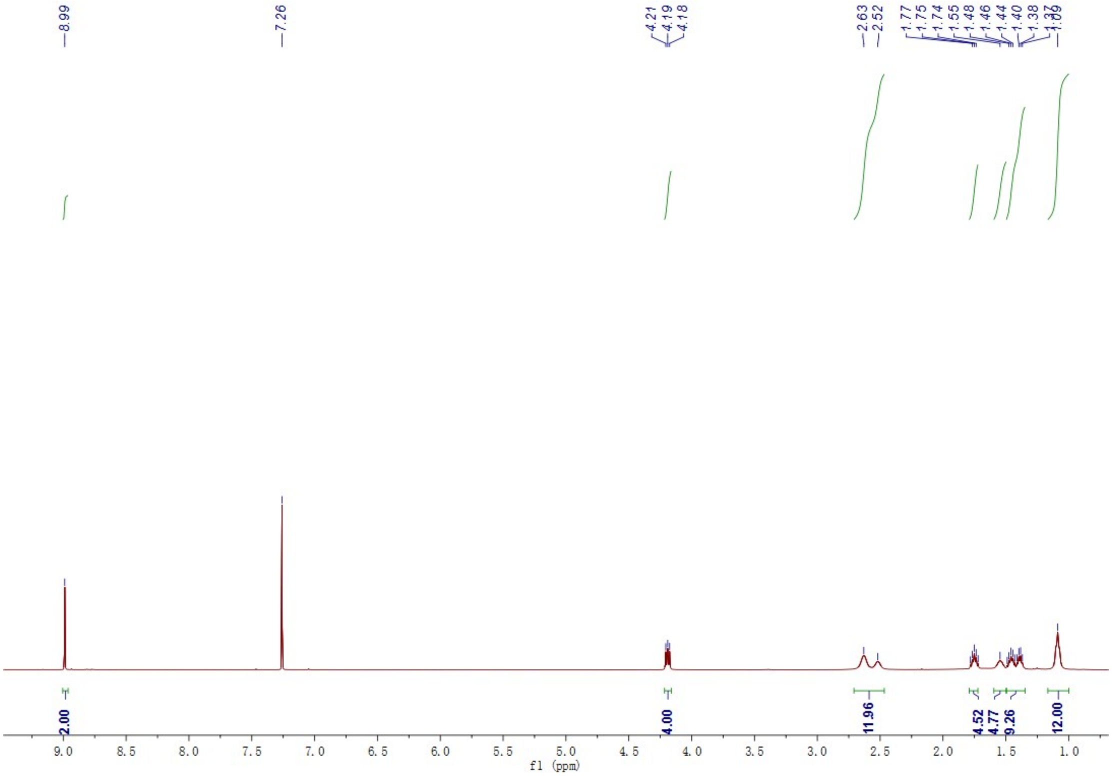


Figure S1 ^{1}H-NMR spectrum of M_0

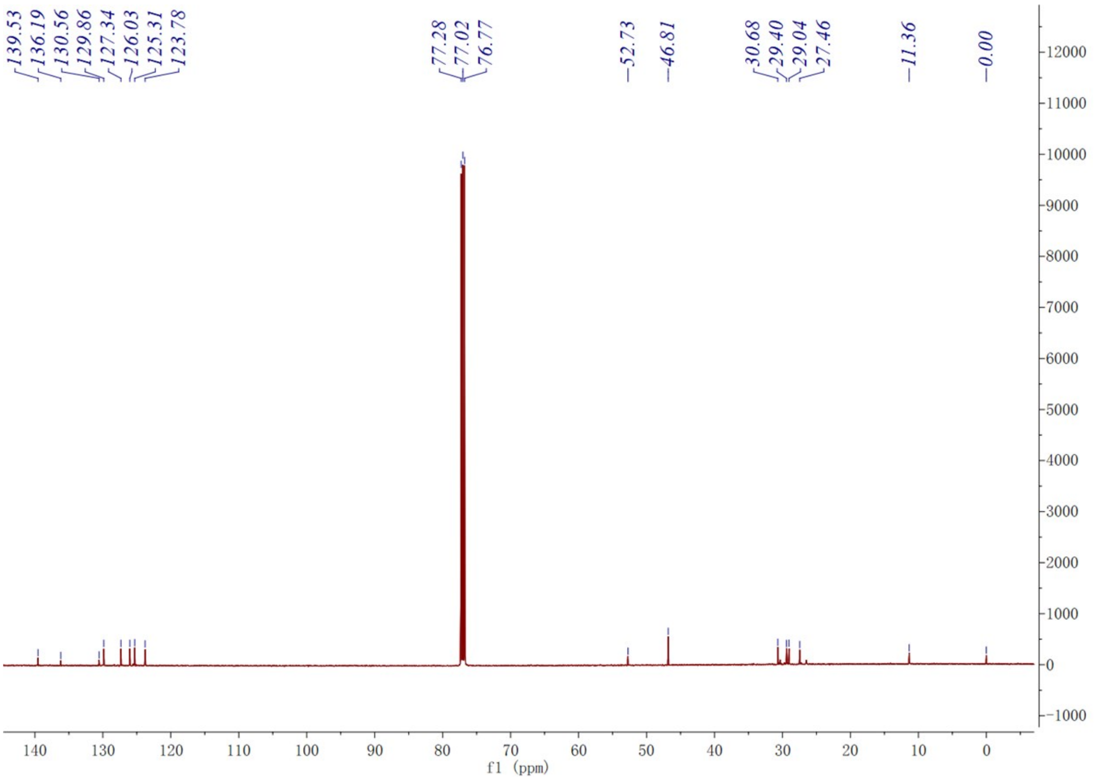


Figure S2 ^{13}C-NMR spectrum of M_0

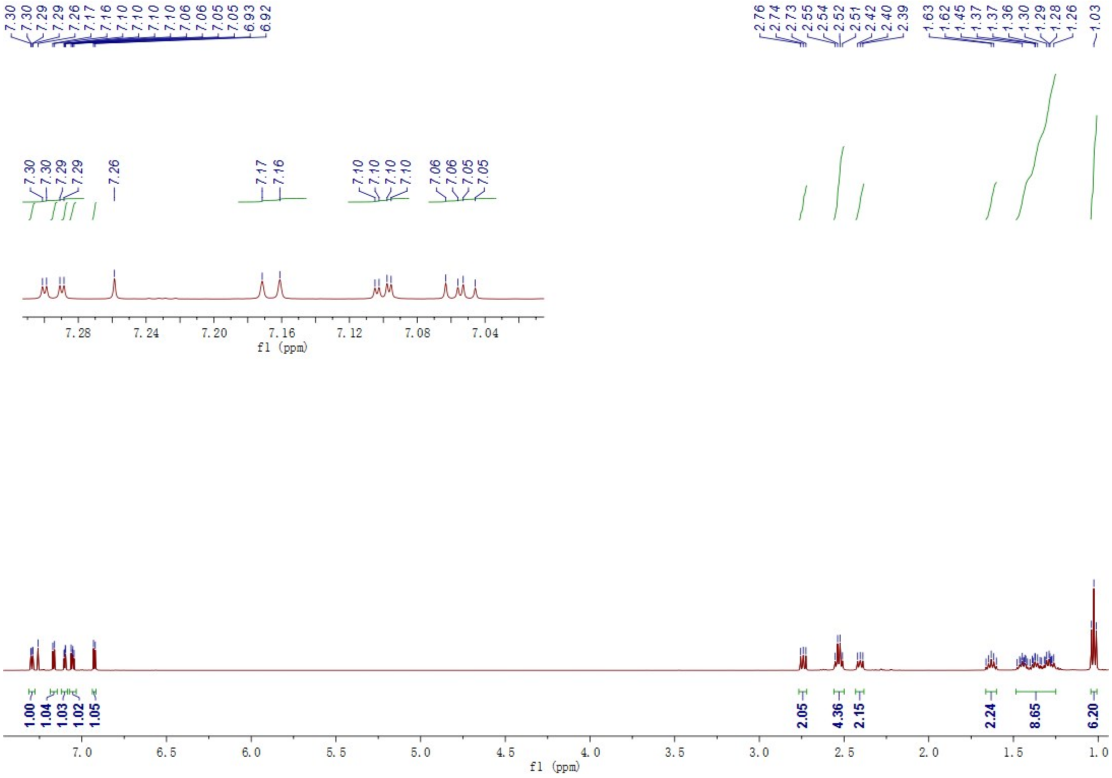


Figure S3 ^{1}H-NMR spectrum of M_1

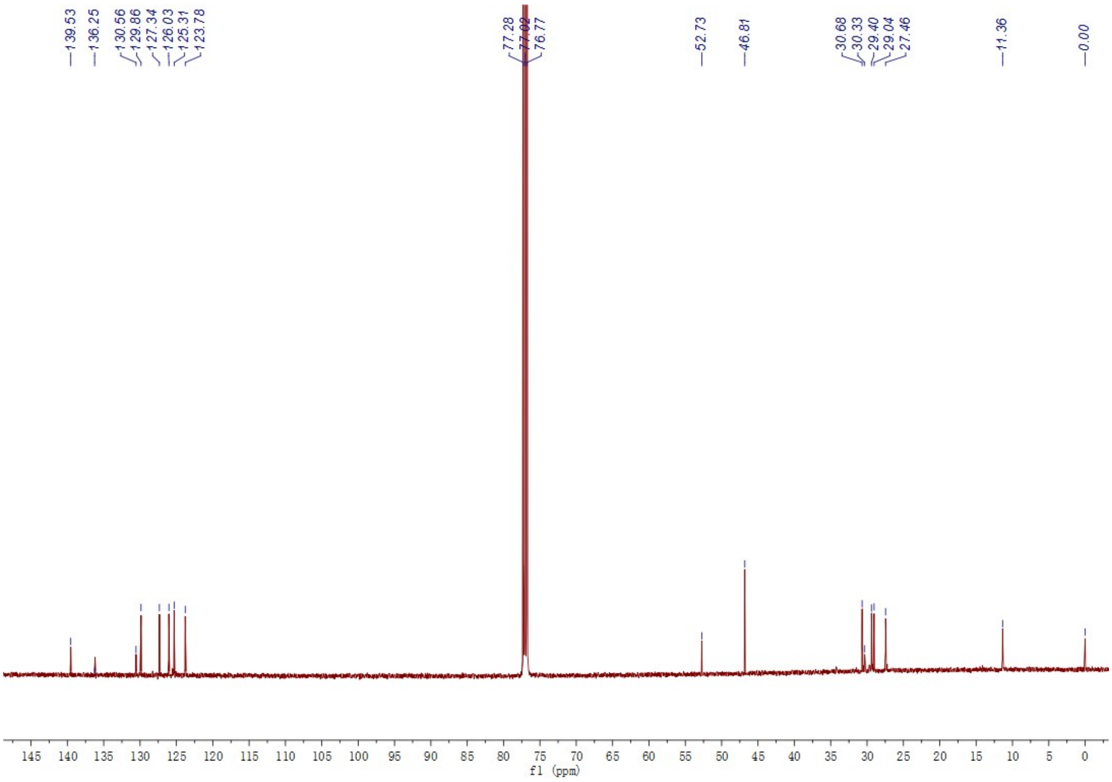


Figure S4 ^{13}C-NMR spectrum of M_1

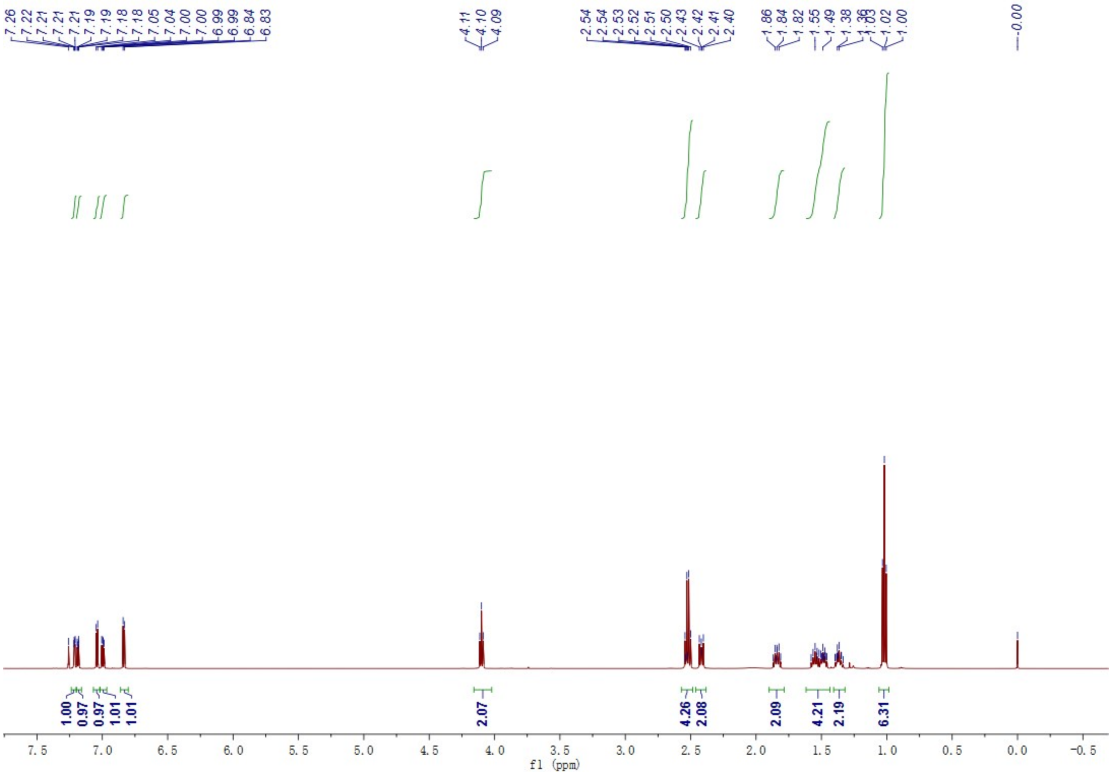


Figure S5 ^{1}H-NMR spectrum of M_2

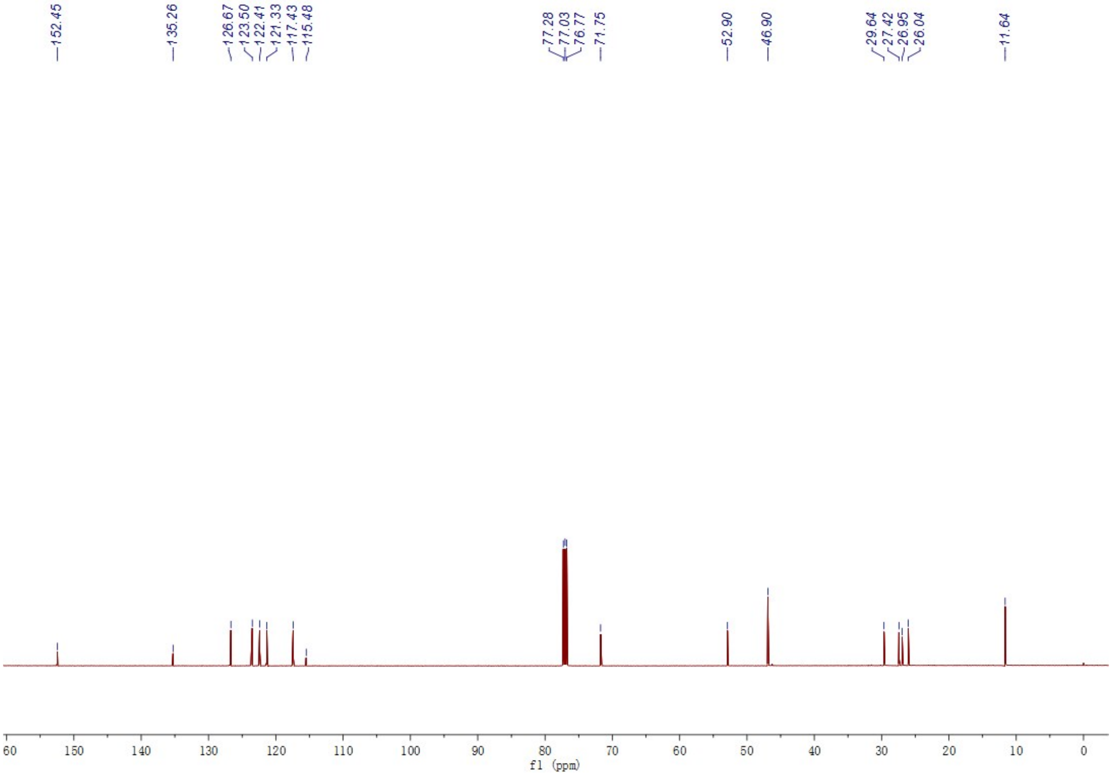


Figure S6 ^{13}C-NMR spectrum of M_2

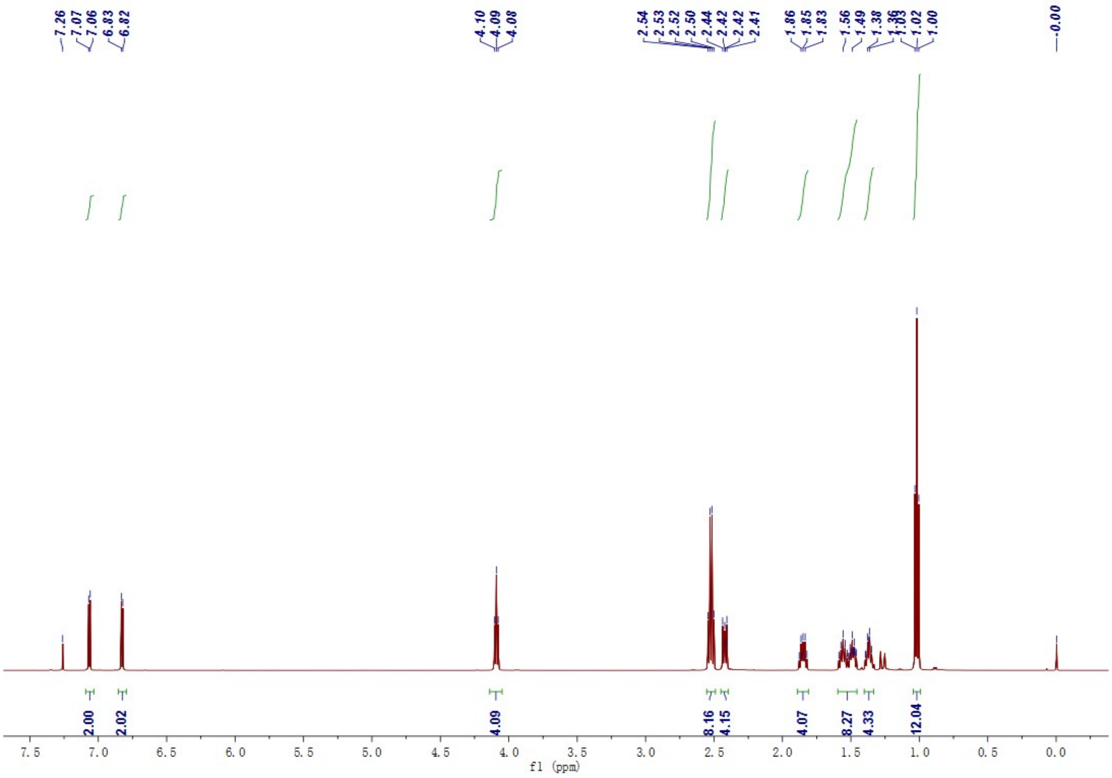


Figure S7 ^{1}H-NMR spectrum of M_3

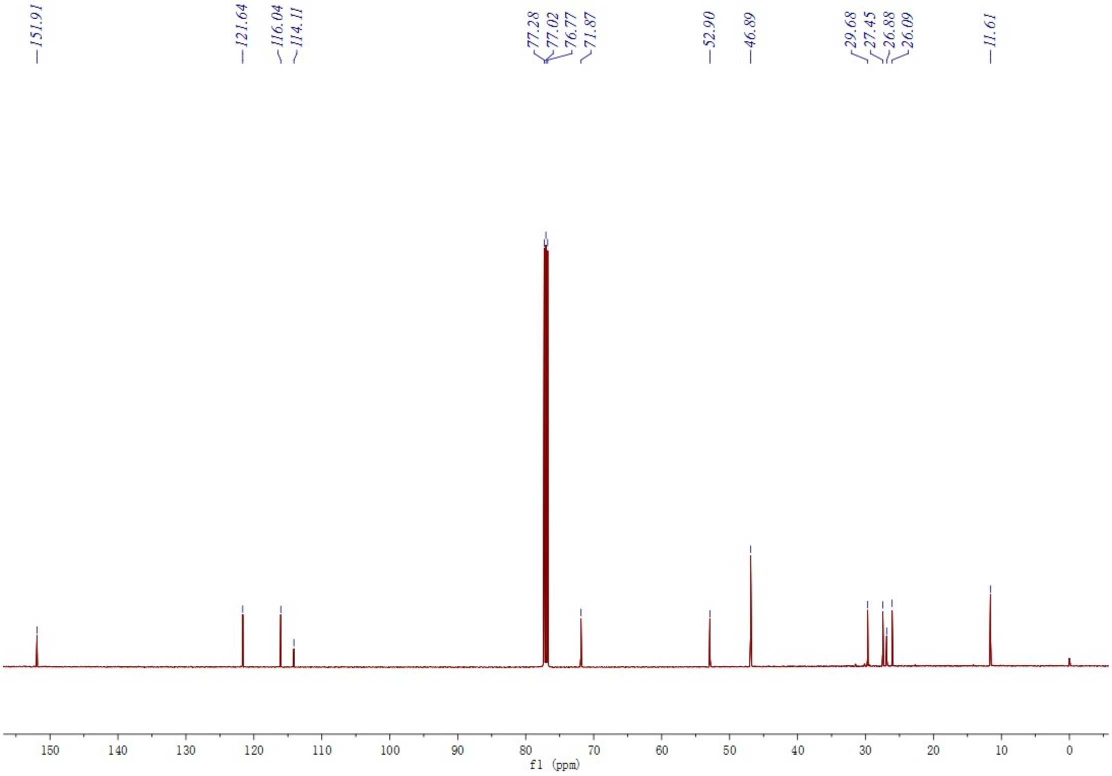


Figure S8 ^{13}C-NMR spectrum of M_2

MW Averages

Mp: 40333
Mn: 20670
Mv: 44464
Mw: 59733
Mz: 177219
Mz+1: 430745
PD: 2.8898

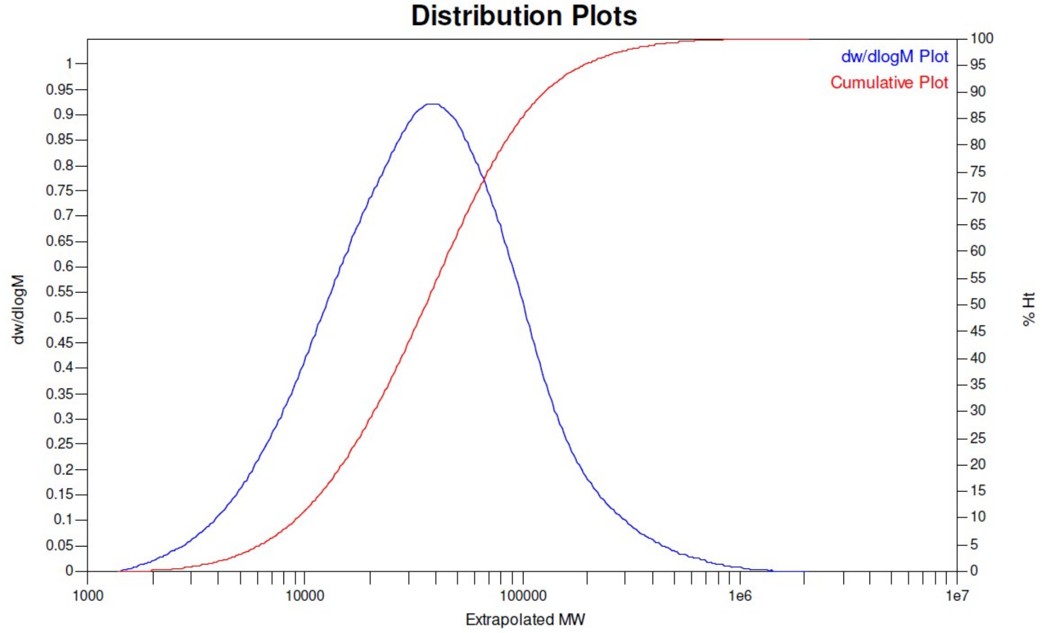


Figure S9 GPC plot of PNDTN

MW Averages

Mp: 42044
Mn: 29106
Mv: 58674
Mw: 58491
Mz: 161138
Mz+1: 2728701
PD: 2.0095

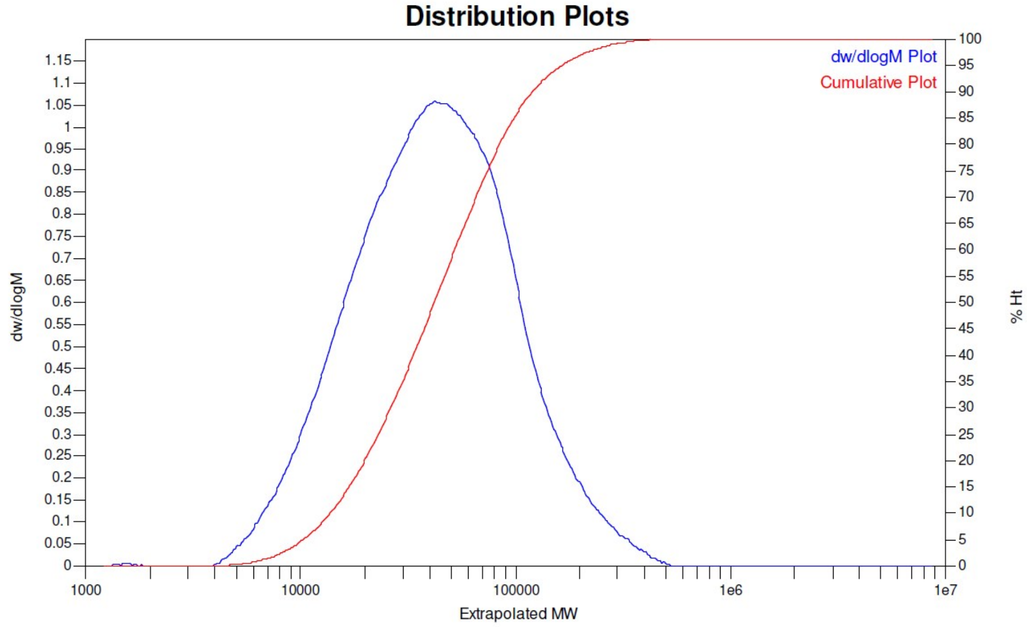
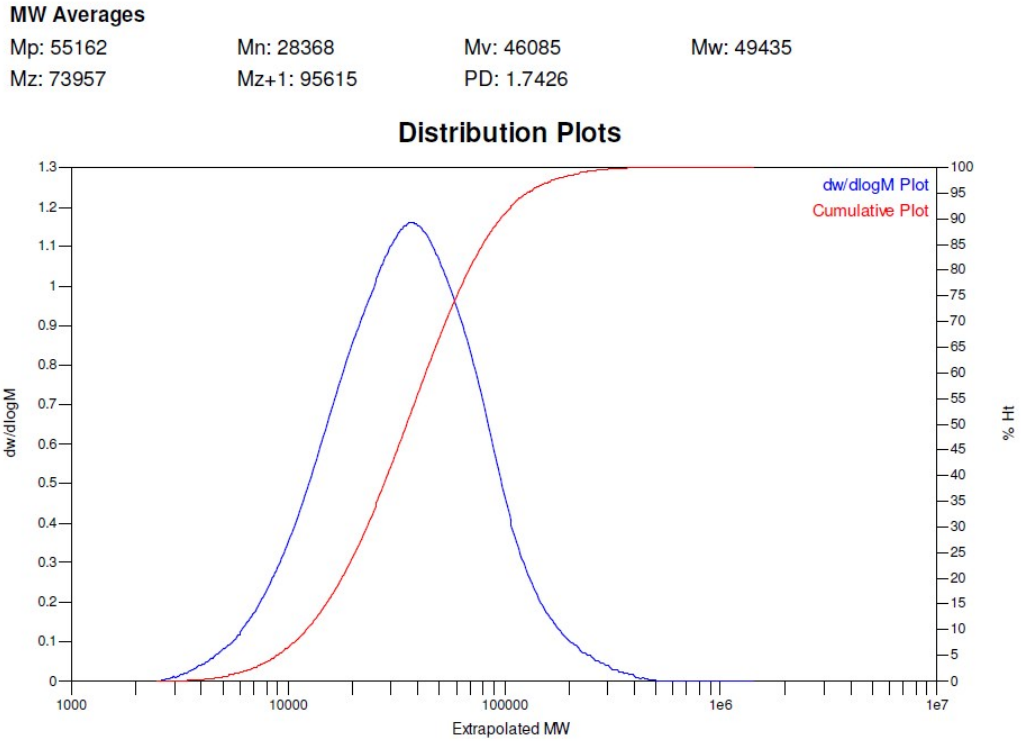


Figure S10 GPC plot of PNDTON



MW Averages

Mp: 55162 Mn: 28368 Mv: 46085 Mw: 49435

Mz: 73957 Mz+1: 95615 PD: 1.7426

Figure S11 GPC plot of PNDTOON

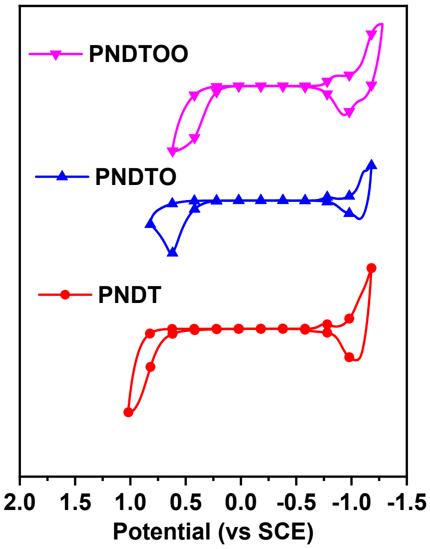


Figure S12 CV characteristics of CPEs

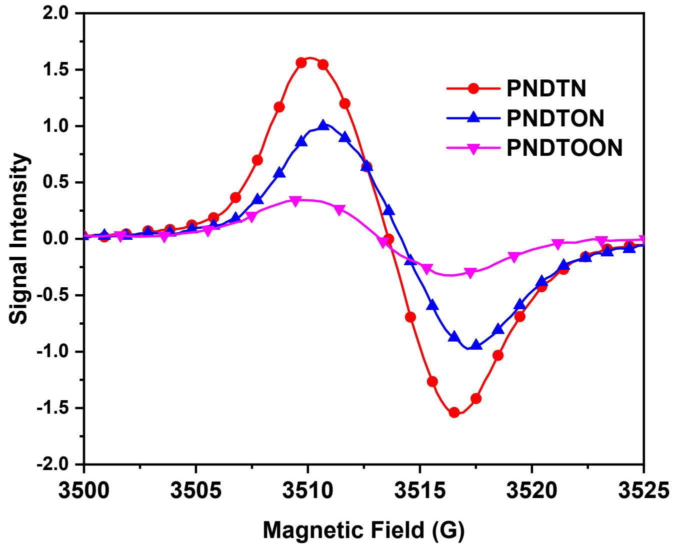


Figure S13 EPR spectra of PNDTN, PNDTON and PNDTOON in solid state.

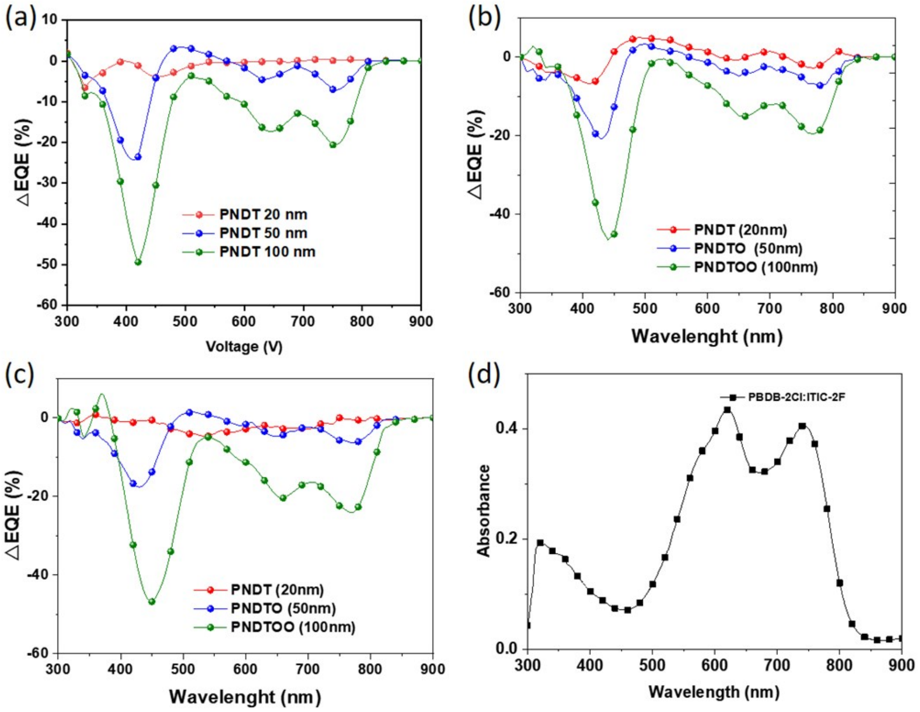


Figure S14 EQE loss (ΔEQE) between devices with 10-nm and thicker ETMs; (d) absorption spectra of PBDB-2Cl:ITIC-2F film

Table S1 Work functions of ETM/Ag electrodes

	Electrode	*Thickness of ETM*			
		10 nm	*20 nm*	*50 nm*	*100 nm*
Work function (eV)	*Bare Ag*	*4.60*			
	PNDT/Ag	*4.02*	*3.98*	*3.95*	*3.92*
	PNDTO/Ag	*3.94*	*3.92*	*3.89*	*3.90*
	PNDTOO/Ag	*3.99*	*4.02*	*3.99*	*3.98*