Electronic Supplementary Information for

Aggregation state tuning via controlling molecular weights of D-A₁-A₂ type polymer donors for efficient organic photovoltaics

Shanlu Wang,‡^a Tianyi Chen,‡^a Shuixing Li,*^a Lei Ye,^b Yuang Fu,^c Xinhui Lu,^c Haiming Zhu,^b Lijian Zuo,^a Minmin Shi^a and Hongzheng Chen*^a

^aState Key Laboratory of Silicon Materials, MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China. E-mail: <u>lishuixing89@163.com</u>; <u>hzchen@zju.edu.cn</u>

^bDepartment of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China. ^cDepartment of Physics, Chinese University of Hong Kong, New Territories, Hong Kong, 999077, P. R. China.

‡S. Wang and T. Chen contributed equally to this work.

Materials and Methods

Materials: All chemicals and reagents are commercially purchased and are used without further purification.

Synthetic scheme for the polymer donors and acceptor L8-Cl.



Monomer synthesis

Compound 2: Dithieno[3,2-f:2',3'-h]quinoxaline: Compound 1 (benzo[2,1-*b*:3,4*b'*]dithiophene-4,5-dione (1.11 g, 5 mmol) and ethylenediamine (0.36 g, 6 mmol) were dissolved in 50 mL of ethanol under argon, the solution was heated to reflux for 12 hours. Then, 40 mL of acetic acid was added to the reaction solution and the protection of argon was removed, and the reaction was heated to reflux for 9 hours. After cooling the reaction to room temperature, it was added to water and extracted with dichloromethane. The crude product was further purified by column chromatography with pure dichloromethane as the eluent, yielding pale yellow solid (650 mg, 54%). ¹H NMR (400 MHz, Chloroform-*d*) δ = 8.90 (s, 2H), 8.29 (d, *J* = 5.3 Hz, 2H), 7.58 (d, *J* = 5.3 Hz, 2H).

Compound 3: 6,9-dibromodithieno[3,2-f:2',3'-h]quinoxaline: Dithieno[3,2-f:2',3'-h] quinoxaline (650 mg, 2.7 mmol) and N-bromosuccinimide (2.4 g, 13.5 mmol) were dissolved in 12.5 mL of chloroform, 12.5 mL of acetic acid was added to the solution, and the solution was heated to reflux for 12 hours. Then the reaction was washed with water and extracted with dichloromethane. The crude product was further purified by column chromatography, yielding a gray solid (569 mg, 53 %).

¹H NMR (500 MHz, Chloroform-*d*): $\delta = 8.92$ (s, 2H), 8.31 (s, 2H).

Compound 6: 2-octyldodecyl thiophene-3-carboxylate: Thiophene-3-carboxylic acid (5.13 g, 40 mmol), 2-octyldodecan-1-ol (11.94 g, 40 mmol), dicyclohexylcarbodiimide (4.13 g, 20 mmol) and 4-dimethylaminopyridine (1.22 g, 10 mmol) was dissolved in 50 mL of dichloromethane, the mixture was stirred at room temperature for 48 hours under argon protection. Then the reaction was washed with water and extracted with dichloromethane. The crude product was further purified by column chromatography with petroleum ether and dichloromethane (v:v = 4:1) as the eluent, yielding a transparent oily liquid(7.45 g, 46%).

¹H NMR (500 MHz, Chloroform-*d*) $\delta = 8.09$ (dd, J = 3.0, 1.1 Hz, 1H), 7.52 (dd, J = 5.0, 1.1 Hz, 1H), 7.30 (dd, J = 5.1, 3.1 Hz, 1H), 4.18 (d, J = 5.7 Hz, 2H), 1.74 (dt, J = 11.2, 5.7 Hz, 1H), 1.36 - 1.24 (m, 32H), 0.88 (t, J = 6.8 Hz, 6H). ¹³C NMR (126 MHz, Chloroform-*d*) $\delta = 162.98, 134.08, 132.41, 127.91, 125.91, 67.51, 37.42, 31.92, 31.91, 31.43, 29.96, 29.65, 29.60, 29.56, 29.35, 29.31, 26.76, 22.68, 14.12.$

Compound 7: 2-octyldodecyl 2-(trimethylstannyl)thiophene-3-carboxylate: Compound 6 (2.45 g, 6 mmol) was dissolved in 40 mL of tetrahydrofuran under argon. The solution was cooled to -78 °C and lithium diisopropylamide (6 mmol, 3 mL, 2 M) was slowly added dropwise into mixture. The mixture was kept at -78 °C for one hour, then trimethylstannyl chloride (6 mmol, 6 mL, 1 M) was added. The solution was slowly warmed to room temperature, and the reaction was carried out for 12 hours. The reaction solution was quenched by KF aqueous solution and extracted with dichloromethane. After removing the solvent, 2.872 g of the product was obtained.

¹H NMR (400 MHz, Chloroform-*d*) δ = 7.63 (d, *J* = 4.8 Hz, 1H), 7.55 (d, *J* = 4.8 Hz, 1H), 4.17 (d, *J* = 5.8 Hz, 2H), 1.75 (p, *J* = 5.8 Hz, 1H), 1.30 - 1.25 (m, 32H), 0.89 - 0.86 (m, 6H), 0.38 (s, 9H).

Compound 8: bis(2-octyldodecyl) 2,2'-(dithieno[3,2-f:2',3'-h] quinoxaline-6,9-diyl) bis (thiophene-3-carboxylate): Compound 3 (502.72 mg, 1.26 mmol), compound 7 (2.87 g, 5.03 mmol) and bis(triphenylphosphine)palladium(II) chloride (50 mg) were dissolved in 48 mL of toluene, 12 mL of DMF was added into reaction under argon. The mixture was heated to 110 °C for 48 hours. Then the reaction solution was cooled to room temperature. The mixture was washed with water and extracted with dichloromethane. The crude product was further purified by column chromatography with petroleum ether and dichloromethane (v:v = 1:1) as the eluent, and the pure product was obtained as an orange solid(673 mg, 51%).

¹H NMR (500 MHz, Chloroform-*d*) δ =8.90 (s, 2H), 8.59 (s, 2H), 7.57 (d, *J* = 5.4 Hz, 2H), 7.32 (d, *J* = 5.4 Hz, 2H), 4.20 (d, *J* = 5.7 Hz, 4H), 1.66 (p, *J* = 5.6 Hz, 2H), 1.26 - 1.13 (m, 64H), 0.88 - 0.83 (m, 12H). ¹³C NMR (126 MHz, Chloroform-*d*) δ = 163.24, 143.07, 142.07, 138.89, 136.12, 134.90, 134.06, 130.76, 129.24, 125.64, 125.08, 67.94, 53.44, 37.32, 31.93, 31.90, 31.25, 29.91, 29.65, 29.59, 29.55, 29.36, 29.30, 26.73, 22.70, 22.68, 14.14.

Compound 9: bis(2-octyldodecyl) 2,2'-(dithieno[3,2-f:2',3'-h]quinoxaline-6,9-diyl) bis(5-bromothiophene-3-carboxylate): Compound 8 (324 mg, 0.307 mmol) and Nbromosuccinimide (120 mg, 0.675 mmol) were dissolved in 15 mL of chloroform, 5 mL of acetic acid was added. The solution was heated to reflux for 24 hours in dark. The mixture was washed with water and extracted with dichloromethane. The crude product was further purified by column chromatography with petroleum ether and dichloromethane (v:v = 1:1) as the eluent, then the product were further purified by recrystallization from chloroform and methanol, yielding a orange solid (152 mg, 41 %). ¹H NMR (400 MHz, Chloroform-*d*) $\delta = 8.90$ (s, 2H), 8.55 (s, 2H), 7.50 (s, 2H), 4.18 (d, J = 5.6 Hz, 4H), 1.65 (q, J = 5.9 Hz, 2H), 1.29 - 1.12 (m, 64H), 0.86 (td, J = 6.9, 4.0 Hz, 12H). ¹³C NMR (101 MHz, Chloroform-*d*) $\delta = 162.03$, 143.27, 143.09, 138.70, 136.25, 134.87, 133.00, 132.96, 129.46, 126.04, 112.11, 68.25, 37.28, 31.93, 31.90, 31.23, 29.89, 29.65, 29.60, 29.54, 29.36, 29.30, 26.71, 22.70, 22.68, 14.13.

Synthesis of Polymer PQC-TL/M/H:

PQC-TL: Compound **9** (85 mg, 0.07 mmol), compound 10 (28.7 mg, 0.07 mmol) and Pd (PPh₃)₄ (3 mg) were dissolved in 3.5 mL of toluene under argon. The reaction was heated to 110 °C for 18 hours. Then the mixture was cooled down and was added to 150 mL methanol drop by drop. The crude product was further purified by soxhlet extraction from methanol, acetone, hexane, chloroform. After removing the solvent, a dark red solid was obtained (69 mg, 85%). (N% = 5.892, C% = 70.773%, H% = 0.554)

PQC-TM/H: The synthetic route is similar to PQC-TL, replacing the catalyst with $Pd_2(dba)_3$ and $P(o-tol)_3$. Compound **9** (58 mg, 0.048 mmol), compound **10** (19.6 mg, 0.048 mmol), 2.20 mg $Pd_2(dba)_3$ and 7.28 mg $P(o-tol)_3$ were dissolved in 2.5 mL of toluene under argon. The reaction was heated to 110 °C for 30 hours and 46 hours, respectively. Then the mixture was cooled down and was added to 150 mL methanol drop by drop. The crude product was further purified by soxhlet extraction from methanol, acetone, hexane, and chloroform. After removing the solvent, dark red solids were obtained (45 mg and 43 mg).

Synthesis of acceptor L8-CI: Compound 11 (211mg, 0.2 mmol), Compound 12 (229 mg, 1 mmol) and 0.6 mL pyridine were dissolved in 25 mL of chloroform under argon. The reaction was heated to 65 °C for 24 hours. Then the mixture was cooled and the crude product were purified by column chromatography with petroleum ether and dichloromethane (v:v = 1:1) as the eluent, yielding a brown solid (158 mg, 56%).

¹H NMR (400 MHz, Chloroform-*d*) δ = 9.14 (s, 2H), 8.72 – 8.60 (m, 2H), 7.87 (dd, *J* = 4.8, 3.2 Hz, 2H), 7.69 (ddd, *J* = 7.2, 5.1, 1.7 Hz, 2H), 4.79 (d, *J* = 6.8 Hz, 4H), 3.16

(d, J = 7.3 Hz, 4H), 2.17 - 2.03 (m, 4H), 1.48 - 0.98 (m, 48H), 0.84 (dt, J = 11.2, 6.7 Hz, 12H), 0.80 - 0.63 (m, 12H).

Supporting Methods

General Characterizations.¹H NMR spectra were measured on a Bruker Advance III 400 (400 MHz) nuclear magnetic resonance (NMR) spectroscope. MALDI-TOF MS spectra were obtained on a Walters Maldi Q-TOF Premier mass spectrometry. UV-vis-NIR absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Cyclic voltammetry (CV) was done on a CHI600A electrochemical workstation with Pt disk, Pt plate, and standard calomel electrode (SCE) as working electrode, counter electrode. and reference electrode. respectively, in 0.1 mol/L а tetrabutylammoniumhexafluorophosphate (Bu₄NPF₆) acetonitrile solution. The CV curves were recorded versus the potential of SCE, which was calibrated by the ferrocene-ferrocenium (Fc/Fc^+) redox couple (4.8 eV below the vacuum level). The equation of EEA/IP = -e(Ered/ox+4.41) (eV) was used to calculate the EA and IP levels (the redox potential of Fc/Fc^+ is found to be 0.39 eV). HT-GPC curves were measured by 1260 Infinity II HT GPC. AFM images were obtained on a VeecoMultiMode atomic force microscopy in the tapping mode. SNOM images were obtained on Anasys nano IR2-s (Bruke). GIWAXS measurements were conducted at a Xeuss 3.0 SAXS/WAXS laboratory beamline at Vacuum Interconnected Nanotech Workstation (Nano-X) in China with Ka X-ray of Cu source (operated at 50kV, 0.06 mA, 1.542 Å). GIWAXS patterns were recorded by a two dimensional X-ray detector (Eiger2 R 1M, Dectris). The grazing incident angle were 0.18°. Samples were prepared by spin coating identical chloroform blend solutions as those used in OPVs on Si substrates. GISAXS measurements with Ka X-ray of Cu source (8.05 keV, 1.54 Å) and a Pilatus3R 300 K detector were conducted at a Xeuss 2.0 SAXS laboratory beamline. Samples were prepared by spin coating identical chloroform blend solutions as those used in OPVs on Si substrates. The grazing incident angle were 0.2°. TRPL were detected using a home-setup microfluorescence system. TRPL decay kinetics were collected using a TCSPC module (PicoHarp 300) and a SPAD detector (IDQ, id100). Samples were kept in a N₂ filled cell at room temperature for all optical measurements.

Device Fabrication and Measurement. Organic photovoltaics (OPVs) were fabricated on glass substrates commercially pre-coated with a layer of ITO with the conventional structure of ITO/PEDOT:PSS/Active Layer/PDINN/Ag. Prior to fabrication, the substrates were cleaned using detergent, deionized water, acetone and isopropanol consecutively for 15 min in each step, and then treated in an ultraviolet ozone generator for 10 min before being spin-coated at 4500 rpm with a layer of 20 nm thick PEDOT:PSS (Clevios 4083). After baking the PEDOT:PSS layer in air at 150 °C for 20 min, the substrates were transferred to a glovebox. The active layer was spincoated from chloroform solution (16.5 mg/mL, D:A = 1:1.2, 0.5% CN at 3000 rpm for 30 s to form a 95nm active layer. Then an extra pre-annealing at 90 °C for 10 min was performed. Then a 5 nm thick PDINN film was deposited as the cathode buffer layer by the spin-coating of a solution of 1 mg/mL in methanol. Finally, the Ag (100 nm) electrode was deposited by thermal evaporation to complete the device with an active area of 9.25 mm², then a mask with an area of 4.73 mm² (certified by National Institute of Metrology, China) was used to measure the efficiencies. The J-V measurement was performed via the solar simulator (SS-X50, Enlitech) along with AM 1.5G spectra whose intensity was calibrated by the certified standard silicon solar cell (KG2, SRC-2020, Enlitech) at 100 mV/cm². Devices were tested in N_2 -filled glove box. The scan direction is -0.1 V to 1.0 V, with a scan step of 0.01 V and dwell time is 1 ms. The EQE data were obtained by using the solar- cell spectral-response measurement system (RE-R, Enlitech). The charge carrier mobilities of the donor:L8-Cl films were measured using the space-charge-limited current (SCLC) method. Hole-only devices with a structure of ITO/PEDOT:PSS/Active layer/MoO₃/Ag and electron-only devices with a structure of ITO/ZnO/Active layer/PDINN/Ag were fabricated.

Supplementary Figures



Fig. S1 High temperature Gel Permeation Chromatography spectra of PQC-TL, PQC-TM and PQC-TH.



Fig. S2 Geometries of QC-T via density functional theory (DFT) calculations at the B3LYP/6-31G level.



Fig. S3 Electrochemical cyclic voltammetry curves of PQC-TL, PQC-TM, PQC-TH, L8-Cl and Fc/Fc⁺.



Fig. S4 Normalized UV-vis absorption spectra of PQC-TL, PQC-TM, PQC-TH and L8-Cl in chloroform solutions.



Fig. S5 Normalized UV-vis absorption spectra of PQC-TL:L8-Cl, PQC-TM:L8-Cl and PQC-TH:L8-Cl blend films.



Fig. S6 $J^{0.5}$ - V curves of (a) hole-only and (b) electron-only devices.



Fig. S7 The dependence of J-V curves on various light intensities.



Fig. S8 The dependence of $V_{\rm OC}$ on light intensities.



Fig. S9 AFM height/phase images of PQC-TL, PQC-TM and PQC-TH pristine films and PQC-TL:L8-Cl, PQC-TM:L8-Cl and PQC-TH:L8-Cl blend films.



Fig. S10 IR spectra of PQC-T and L8-Cl neat films.



Fig. S11 2D GIWAXS images of PQC-TL, PQC-TM, PQC-TH and L8-Cl pristine films.



Fig. S12 2D GISAXS images of PQC-TL:L8-C1, PQC-TM:L8-C1 and PQC-TH:L8-C1 blend films.



Fig. S13 1 H NMR spectrum of compound 2



Fig. S14 ¹H NMR spectrum of compound 3



Fig. S15 ¹H NMR spectrum of compound 6



Fig. S16 ¹³C NMR spectrum of compound 6



Fig. S17 1 H NMR spectrum of compound 7



Fig. S18 ¹H NMR spectrum of compound 8



Fig. S19 ¹³C NMR spectrum of compound 8



Fig. S20 ¹HNMR spectrum of compound 9



Fig. S21 ¹³C NMR spectrum of compound 9







Fig. S23 MALDI-TOF mass spectrum of compound 9

Supplementary Tables

D:A	Annealing	Additive	$V_{OC}(\mathbf{V})$	J_{SC}	FF(%)	PCE(%)
	(°C)			(mA cm ⁻²)		
1:1.2	90	/	0.937	18.24	60.88	10.40
1:1.2	90	0.3%DIO	0.912	20.56	63.26	11.86
1:1.2	90	0.15%CN	0.925	20.29	64.28	12.06
1:1.2	90	0.3%CN	0.921	20.84	66.06	12.68
1:1.2	90	0.45%CN	0.914	20.75	65.29	12.43
1:1	90	0.3%CN	0.924	20.48	65.19	12.39
1:1.4	90	0.3%CN	0.913	21.01	64.78	12.48
1:1.2	/	0.3%CN	0.935	17.00	59.36	9.47
1:1.2	80	0.3%CN	0.923	20.89	64.20	12.43
1:1.2	100	0.3%CN	0.918	20.64	65.98	12.55

 Table S1 Photovoltaic parameters of OPVs based on PQC-TL:L8-Cl films under various optimization conditions

D:A	Annealing	Additive	$V_{OC}(\mathbf{V})$	J_{SC}	FF(%)	PCE(%)
	(°C)			(mA cm ⁻²)		
1:1.2	90	/	0.923	23.88	60.25	13.29(13.08±0.12)
1:1.2	90	0.3%DIO	0.902	24.39	65.47	14.40(14.24±0.14)
1:1.2	90	0.15%CN	0.915	24.64	64.43	14.52(14.32±0.17)
1:1.2	90	0.3%CN	0.906	24.73	67.05	15.01(14.73±0.19)
1:1.2	90	0.45%CN	0.900	24.61	65.98	14.61(14.49±0.10)
1:1	90	0.3%CN	0.911	23.02	65.25	13.70(13.44±0.21)
1:1.4	90	0.3%CN	0.901	24.77	66.09	14.76(14.60±0.16)
1:1.2	/	0.3%CN	0.933	18.75	55.92	9.78(9.37±0.30)
1:1.2	80	0.3%CN	0.909	24.32	66.96	14.80(14.50±0.13)
1:1.2	100	0.3%CN	0.898	24.62	66.88	14.78(14.37±0.15)

 Table S2 Photovoltaic parameters of OPVs based on PQC-TM:L8-Cl under various

 optimization conditions

D:A	Annealing	Additive	$V_{OC}(\mathbf{V})$	J_{SC}	FF(%)	PCE(%)
	(°C)			(mA cm ⁻²)		
1:1.2	90	/	0.903	20.12	49.12	8.92
1:1.2	90	0.3%DIO	0.880	22.39	54.28	10.69
1:1.2	90	0.15%CN	0.897	21.88	53.19	10.44
1:1.2	90	0.3%CN	0.889	22.93	55.31	11.29
1:1.2	90	0.45%CN	0.881	22.60	55.40	11.09
1:1	90	0.3%CN	0.893	22.10	55.42	10.94
1:1.4	90	0.3%CN	0.890	22.84	55.29	11.23
1:1.2	/	0.3%CN	0.901	20.07	50.35	9.10
1:1.2	80	0.3%CN	0.893	22.91	54.29	11.10
1:1.2	100	0.3%CN	0.885	22.55	54.28	10.83

Table S3 Photovoltaic parameters of OPVs based on PQC-TH:L8-Cl under variousoptimization conditions

Table S4 Summary of hole and electron mobilities of PQC-TL:L8-Cl, PQC-TM:L8-Cl andPQC-TH:L8-Cl Devices

Sample	$\mu_{\rm h}(imes 10^{-5} { m cm}^2 { m V}^{-1} { m s}^{-1})$	$\mu_{\rm e}(\times 10^{-5} {\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})$	$\mu_{ m h}/\mu_{ m e}$
PQC-TL:L8-C1	7.85 ± 0.89	2.44±0.29	3.21
PQC-TM:L8-C1	5.72±0.72	10.14±1.33	0.56
PQC-TH:L8-Cl	3.09±0.36	7.72 ± 0.78	0.40

Table S5 The detailed parameters of PQC-TL:L8-Cl, PQC-TM:L8-Cl and PQC-TH:L8-Clblend films from J_{ph} - V_{eff} curves

Active Layer	$J_{ m sat}$	$J_{ m pha}$	$J_{ m phb}$	P_{diss} (%)	$P_{coll}(\%)$
	$(mA cm^{-2})$	$(mA cm^{-2})$	$(mA cm^{-2})$		
PQC-TL:L8-Cl	21.67	19.67	18.98	90.77	87.59
PQC-TM:L8-Cl	24.05	23.80	23.31	98.96	96.92
PQC-TH:L8-Cl	23.90	21.62	20.39	90.46	85.31

Film	Location	in plane	Intensity	Location	out of plane	Intensity
		d-spacing			d-spacing	
PQC-TL	0.250	25.12	1.647	1.786	3.52	0.986
PQC-TM	0.250	25.12	1.774	1.777	3.54	1.231
PQC-TH	0.250	25.12	1.795	1.777	3.54	1.283
L8-C1	0.439	14.31	0.750	1.731	3.63	1.046
PQC-TL:L8-Cl	0.250	25.12	1.428	1.771	3.55	1.112
PQC-TM:L8-C1	0.250	25.12	1.529	1.768	3.55	1.325
PQC-TH:L8-C1	0.250	25.12	1.548	1.780	3.53	1.342

Table S6 Structure parameters of the various films with different incidence angles obtained

 from GIWAXS data

 Table S7 Fitted data of various films obtained from GISAXS measurement

Film	2Rg(nm)	Xdab(nm)
PQC-TL:L8-Cl	5.2	21.0
PQC-TM:L8-C1	7.2	16.0
PQC-TH:L8-C1	6.2	14.7