Supporting Information

Acceptor-only Oligomers with High Coplanarity enable Efficient and Stable Organic Solar Cells

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Contents

Experimental Procedures

General Information. All reactions and operations of this work are carried out in argon atmosphere, and all raw materials are purchased from commercial suppliers. Chloroform, Y6 and other materials were purchased from Alfa, Aldrich, Derthon, SunaTech Inc., Solarmer Materials Inc., and Shanghai Haohong Scientific Co.,Ltd. And used without further purification. Indium-tin oxide (ITO) glass was purchased from Delta Technologies Limited. 1,3-Bis(2-ethylhexyl)-5,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[1,2-c:4,5-c']dithiophene-4,8-dione(BDD-2Sn) and 1,3-bis(thiophen-2-yl)-5,7-bis(2-ethyl-hexyl)benzo-[1,2-c:4,5-c′]dithiophene-4,8-dione (BDD) were purchased from Solarmer Materials Inc. $Pd(dba)_3$ and $P(o\text{-}Tol)_3$ was obtained from J&K. The chemical reagent of PEDOT:PSS aqueous solutions (PVP AL 4083) was purchased from Energy Chemical. The sputtering target of silver (Ag ,99.999%) was procured from ZhongNuo Advanced Material (Beijing)

Technology Co., Ltd.

1H spectrum was recorded on Bruker ADVANCE 400 NMR spectrometer in deuterated solvent. Using the residual protonated solvent as the internal standard, report the 1H NMR chemical shift in ppm from the tetramethylsilane (TMS) reference material to the next field. Thermogravimetric analysis (TGA) was performed on the PerkinElmer TGA 7 instrument for thermal analysis at a heating rate of 10 °C/min under nitrogen.

Optical characterizations. UV-vis absorption spectra were recorded on an Agilent series UV-Vis-NIR spectrophotometer. All film samples were spin-cast on quartz slice substrates. The photoluminescence spectra (PL) were measured by photoluminescence spectroscopy (Hitachi F-7000).

Electrochemical characterizations. Cyclic voltammetry (CV) was performed by a Zahner IM6e electrochemical work station, using Ag/AgCl as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. Polymers were drop-cast onto the electrode from chloroform solutions to form thin films. 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as the supporting electrolyte. The scan rate was 0.05 V s^{-1}. The EHOMO and ELUMO are calculated as refer to the eqs (1) and (2).

$$E_{HOMO} = -(E_{ox} + 4.71)\ eV \quad (1),$$

$$E_{LUMO} = -(E_{red} + 4.71)\ eV \quad (2).$$

Surface energy characterization. The water and diiodomethane contact angle images of neat films were recorded by using a KRÜSS DSA 100 instrument under atmospheric condition.

DSC measurements. DSC was measured by TA DSC Q2000 differential scanning calorimeter, with the samples being heated to 300 °C and then cooled to 40 °C at a heating/cooling rate of 10 °C/min.

AFM characterizations. The specimen for AFM measurements was prepared using the same procedures those for fabricating devices but without PDINO/Ag on top of the active layer.

Device Fabrication and Characterizations. All PM6:oligomer:Y6 devices were manufactured with the structure of Glass ITO/poly(3,4-

ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS)/activelayer/PDINO/Ag. The conductive ITO substrates were sequentially cleaned with ultrasonication in acetone, detergent, water and isopropanol. After drying the ITO substrates and treating the surface with UV ozone for 20 min, The PEDOT:PSS precursor was spin-coated at 4000 rpm. for 50s onto the ITO surface. After being baked at 150 ° C for 20 min in air, the PEDOT:PSS-coated substrates were transferred into a nitrogen-filled glove box. The PM6:Y6 with a D/A weight ratio of 1:1.2 was dissolved in chloroform solvent with a total weight concentration of 16.5 mg/mL with the addition of 0.5% 1-CN as an additive. The oligomers of AA and AAA were added in PM6:Y6 blend. The concentration of oligomers in the solution of active layer is 1~2 $mg \cdot mL^{-1}$ (the corresponding weight ratio of PM6:oligomer:Y6 is 1:0.13:1.2 for 1 $mg \cdot mL^{-1}$, 1:0.19:1.2 for 1.5 $mg \cdot mL^{-1}$ and 1:0.26:1.2 for 2 $mg \cdot mL^{-1}$). Then the blend solution was stirred for over 5 h at 40 ℃ and spin-coating onto the PEDOT:PSS at 3000 rpm for 40 s, followed by thermal annealing at 100 °C for 10 min in a nitrogen-filled glove box. The interlayer of PDINO (2.0 mg mL^{-1} in methanol) is usually deposited on the active layer by rotating coating at 3000 rpm for 30 s. Subsequently, the structure of Ag (100 nm) is deposited on the intermediate layer by thermal evaporation under a vacuum chamber with a mask to complete device fabrication. The effective area of a battery is 0.04 cm^2. The device structure of PM6: BTP-eC9 is the same as above, except that the concentration of PM6: BTP-eC9 is 17.6 $mg \cdot mL^{-1}$ and the additive is 0.5% DIO.

Electron and Hole mobility measurements.

Hole and electron mobilities were measured using the space charge limited current (SCLC) method, with hole-only device of ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS)/active layer /MoO_3/Ag for hole mobility measurement and the electron-only devices used a diode configuration of ITO/ZnO/active layer/PDINO/Al by taking current-voltage curve in the range of -5-5 V. The SCLC mobilities were calculated by MOTT-Gurney equation, which is described by: $J = 9\varepsilon_0\varepsilon_r u V^2/8L^3$, where J is the current density, L is the film thickness of active layer, ε_0 is the permittivity of free space (8.85×10^{-12} $F \cdot m^{-1}$), ε_r is the relative dielectric constant of the transport medium, u is the hole or electron mobility, V is the internal voltage in the device and $V = V_{appl}-V_r-V_{bi}$, where V_{appl} is the applied

voltage to the device, V_r is the voltage drop due to contact resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.

Detailed EQE measurements. Highly Sensitive EQE was measured by using an integrated system (PECT-600, Enlitech), where the photocurrent was amplified and modulated by a lock-in instrument. The-FTPS-spectra-were-calibrated by a germanium detector.

GIWAXS measurements. The GIWAXS measurement was carried out at the PLS-II 6A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea. The X-rays coming from the in-vacuum undulator (IVU) were monochromate (wavelength l = 1.10994 Å) using a double crystal monochromator and focused both horizontally and vertically (450 (H) x 60 (V) um^2 in FWHM @ the sample position) using K-B type mirrors. The grazing incidence wide-angle X-ray scattering (GIWAXS) sample stage was equipped with a 7-axis motorized stage for the fine alignment of the sample, and the incidence angles of the X-ray beam were set to be 0.11°-0.13° for the neat and blend films. The GIWAXS patterns were recorded with a 2D CCD detector (Rayonix SX165) and an X-ray irradiation time within 100 s, dependent on the saturation level of the detector. Diffraction angles were calibrated using a sucrose standard (monoclinic, P21, a=10.8631 Å, b =8.7044 Å, c=7.7624 Å, and b=102.938 Å) and the sample-to-detector distance was ~231 mm.

Synthetic procedures

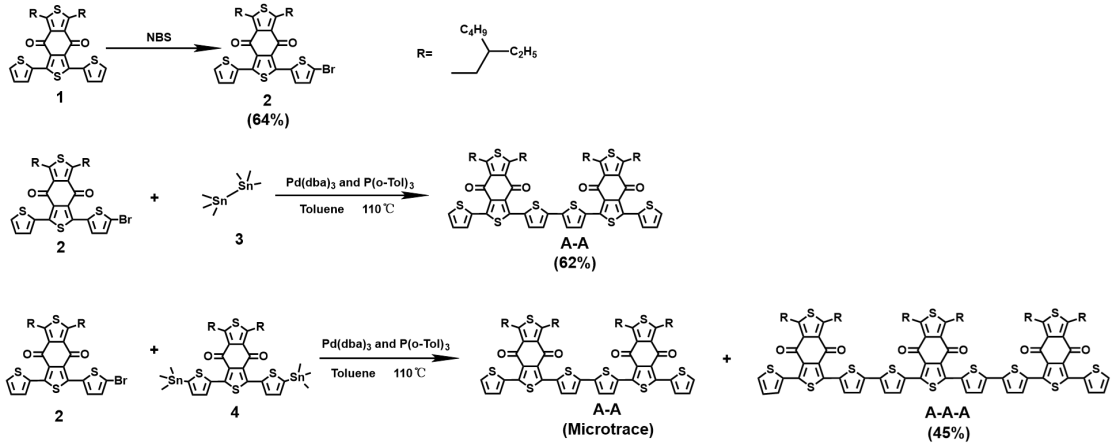
Synthesis of compound 2. To a solution of compound 1 (0.456 g, 0.748 mmol) dissolved in 30 mL THF was added N-bromosuccinimide (0.160 g, 0.898 mmol) in portions over a course of 30 min without light and stirred for another 12 h at room temperature. Then 100 mL water was added in it to quench the reaction. The mixture was extracted with CH_2Cl_2. The resulting organic phase was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed off under reduced pressure and the yellow residue was purified by silica gel chromatography, eluting with N-hexane:CH_2Cl_2 (4:1) to give yellow solid (0.287 g, yield 63 %).

Synthesis of compound AA. In a 50mL two-neck round-bottom flask, the mixture of

compound 2 (100 mg,0.145 mmol), compound 3 (23.74 mg, 0.0726 mmol), $Pd(dba)_3$ (1.995 mg, 0.0022 mmol) and P(o-Tol)$_3$ (2.6517 mg 0.0087 mmol) in toluene was degassed in N_2 atmosphere and stirred at reflux temperature for 12 h. After cooling to room temperature, the mixture was poured into water (150 mL) and extracted with CH_2Cl_2 (30 mL×3). Combine the organic phase and dry with anhydrous $MgSO_4$. Remove the solvent under decompression. The orange-red residue was purified by silica gel chromatography and eluted with N-hexane: CH_2Cl_2 (4:1) to obtain orange-red 44.2 mg 62%). 1H NMR (400 MHz, $CDCl_3$) δ (ppm) of AA: 7.76 (dd, J = 5.7, 4.0 Hz, 4H), 7.51 (d, J = 5.1 Hz, 2H), 7.32 (d, J = 4.0 Hz, 2H), 7.15 – 7.12 (m, 2H), 3.34 (t, J = 8.9 Hz, 8H), 1.82 – 1.75 (m, 4H), 1.46 – 1.29 (m, 32H), 0.93 (ddd, J = 14.7, 9.1, 5.0 Hz, 24H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 153.47, 142.18, 142.01, 140.40, 133.34, 133.08, 133.02, 132.59, 132.39, 131.51, 130.59, 129.38, 127.15, 124.44, 77.28, 76.97, 76.65, 41.22, 33.65, 33.61, 32.79, 32.73, 31.47, 30.10, 29.67, 28.82, 28.78, 26.04, 25.98, 22.99, 14.10, 10.91, 10.86, 0.99. MALDL-MS (m/z): Calcd. for [$C_{68}H_{78}O_4S_8$], 1214.37; found 1216.19.

Synthesis of compound AAA. In a 50 mL two-neck round-bottom flask, a mixture of compound 2 (100 mg, 0.145 mmol), compound 4 (70.03 mg, 0.0726 mmol), and $Pd(dba)_3$ (2.0583 mg 0.0023 mmol) and P(o-Tol)$_3$ (2.6517 mg 0.0087 mmol) in toluene was degassed under the N_2 atmosphere and stirred at refluxing temperature for 12 h. After cooled to room temperature, the mixture was poured into water (150 mL), and extracted with CH_2Cl_2 (30 mL× 3). The organic phases were combined and dried over with anhydrous $MgSO_4$. The solvents were removed off under reduced pressure. The red residue was purified by silica gel chromatography, eluting with N-hexane:CH_2Cl_2 (4:1) to give purplish red solid of AA (microtrace) and AAA (58.69 mg, 45%). 1H NMR (400 MHz, $CDCl_3$) δ (ppm) of AAA: 7.75 (dd, J = 7.7, 4.2 Hz, 63H), 7.50 (d, J = 5.5 Hz, 24H), 7.31 (d, J = 4.4 Hz, 33H), 7.29 – 7.28 (m, 4H), 7.29 – 7.09 (m, 133H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 177.52, 177.40, 177.38, 153.34, 153.29, 153.24, 142.07, 141.79, 140.60, 140.48, 133.08, 132.99, 132.94, 132.88, 132.18, 131.61, 131.56, 131.51, 130.57, 129.38, 127.09, 124.38, 77.29, 76.97, 76.66, 41.18, 33.66, 32.83, 32.74, 29.67, 28.83, 26.09, 25.99, 23.02, 14.15, 10.93, 10.86, 0.99. MALDL-MS (m/z): Calcd. for [$C_{102}H_{116}O_6S_{12}$],1821.55; found 1823.50.

Results and Discussion



Scheme S1. Synthetic route for AA and AAA.

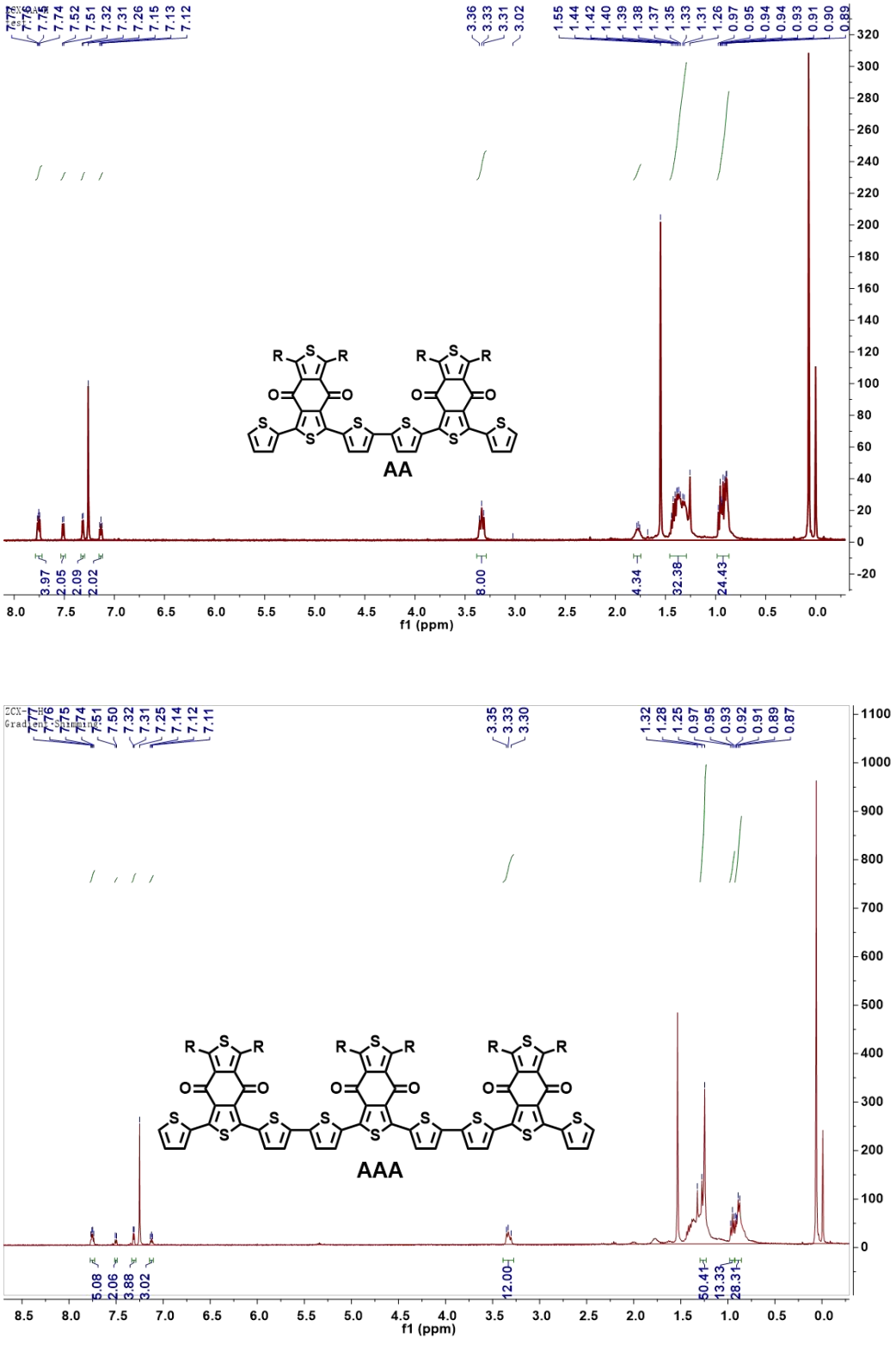


Figure S1. The ^{1}H NMR spectrum of AA and AAA in $CDCl_3$ solution.

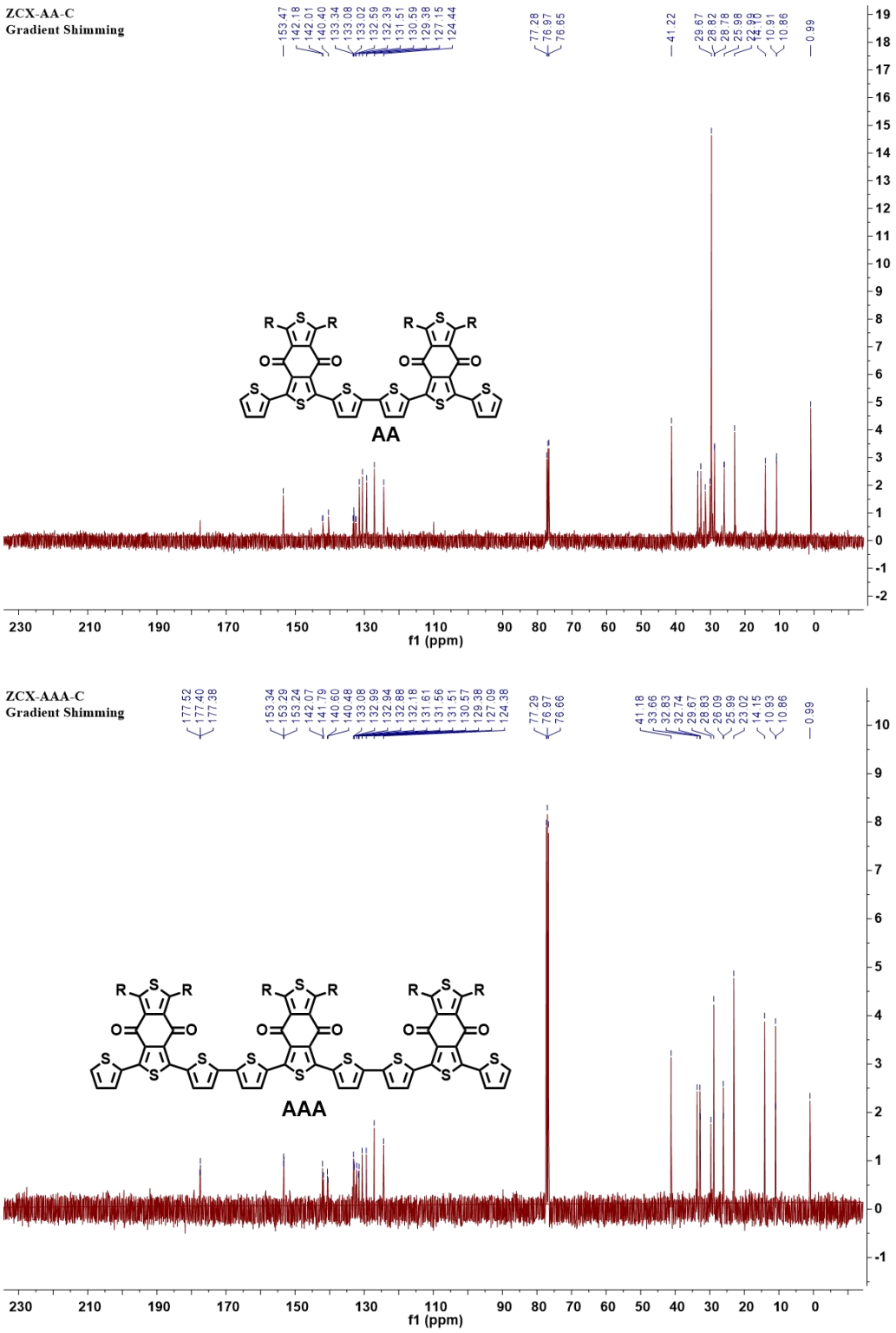


Figure S2. The ^{13}C NMR spectrum of AA and AAA in $CDCl_3$ solution.

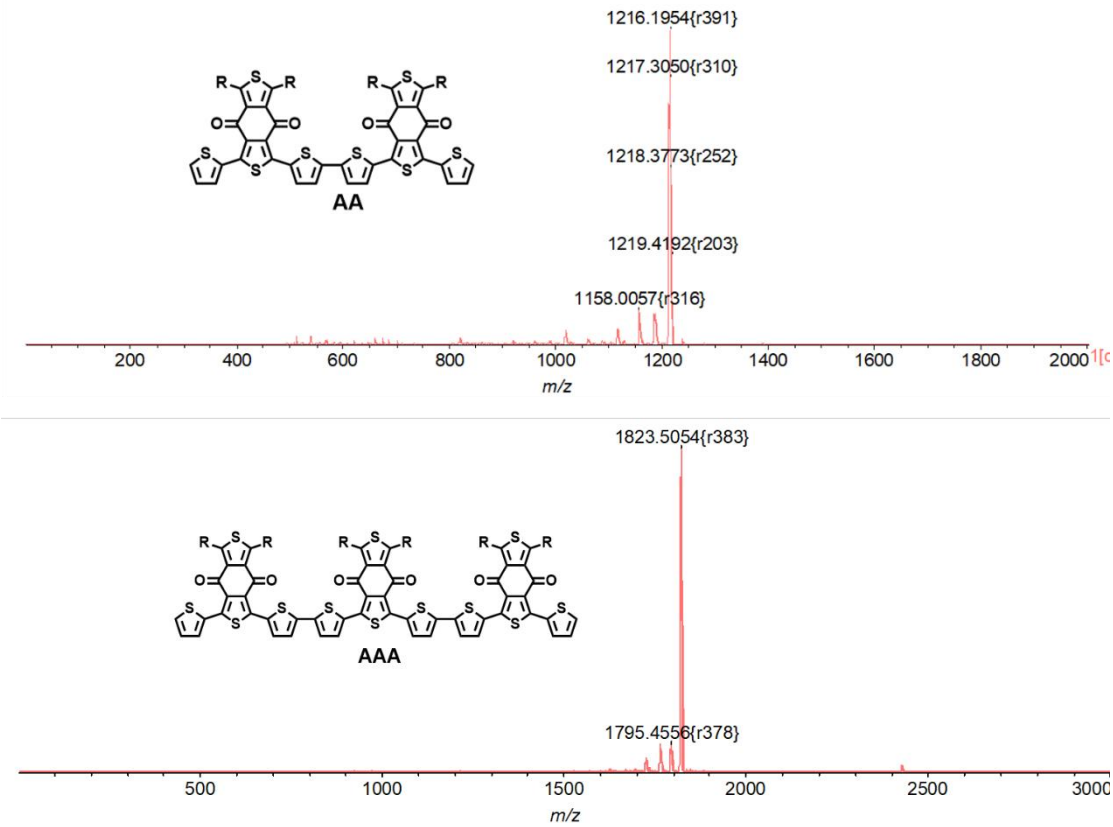


Figure S3. The mass spectra of AA, and AAA.

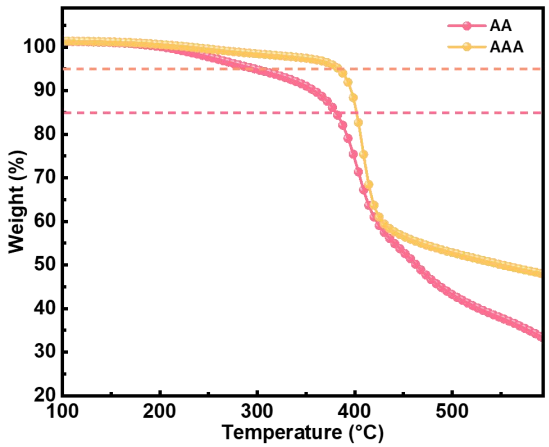


Figure S4. TGA analysis (heating ramp: 10°C min^{-1}) of AA, AAA.

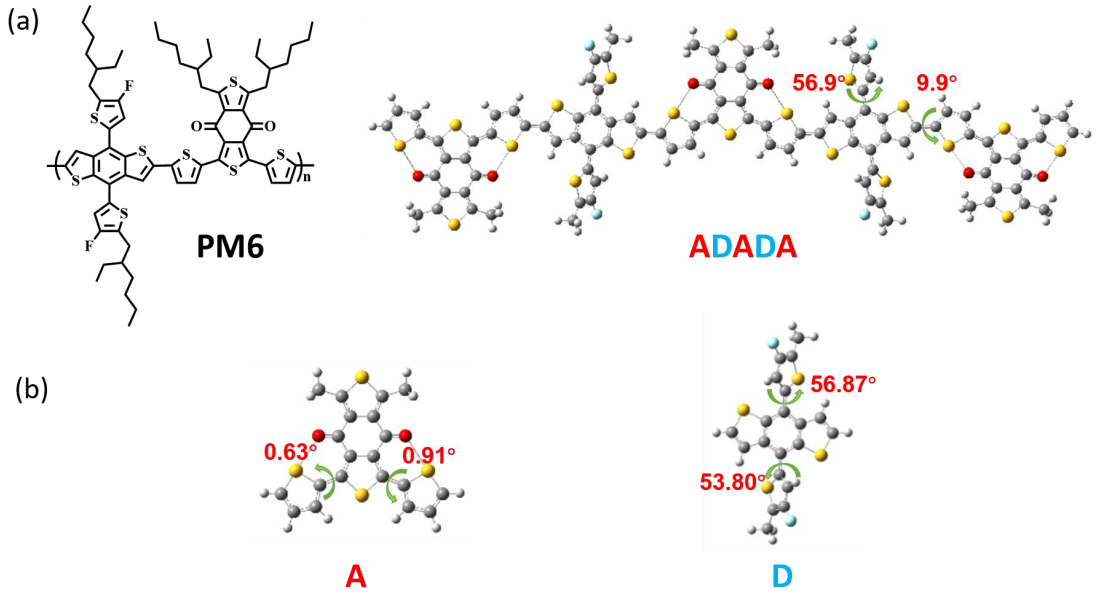


Figure S5. Torsion angles of A and D.

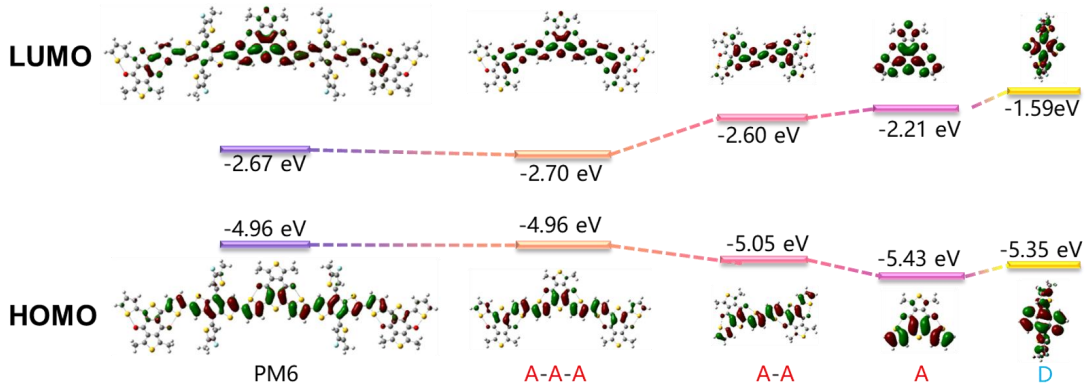


Figure S6. Energy levels and wave function distributions of the frontier orbits for PM6, AAA, AA, A and D unit.

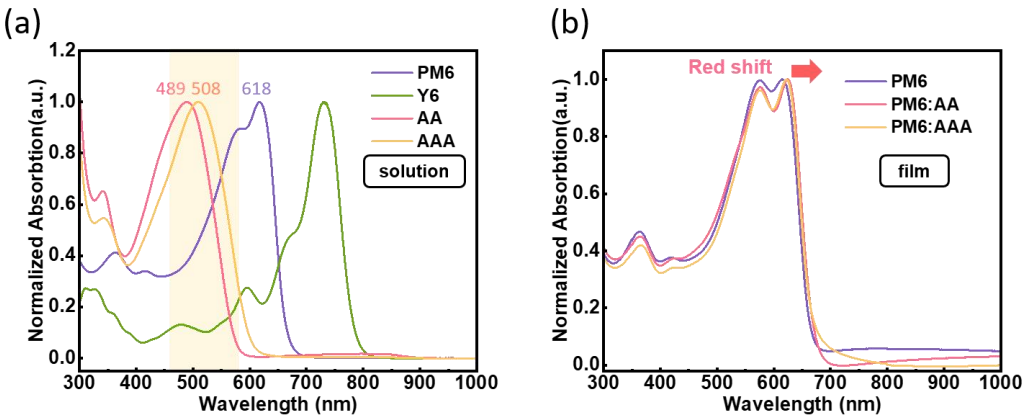
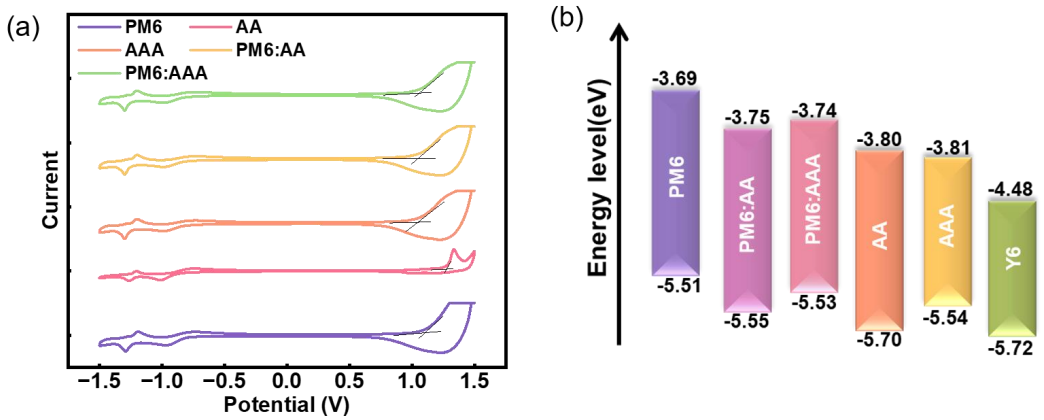


Figure S7. (a) UV-vis absorption spectra of PM6, AA, AAA and Y6 in chloroform. (b) UV-vis absorption spectra of PM6, PM6:AA and PM6:AAA in film.



Supplementary notes: The PM6:AA and PM6:AAA (2:1)-based blends show only one oxidation peak.

Figure S8. (a) Cyclic voltammograms of PM6, AA, AAA and blend of PM6:AA, PM6: AAA. (b) Electronic energy levels of the related materials.

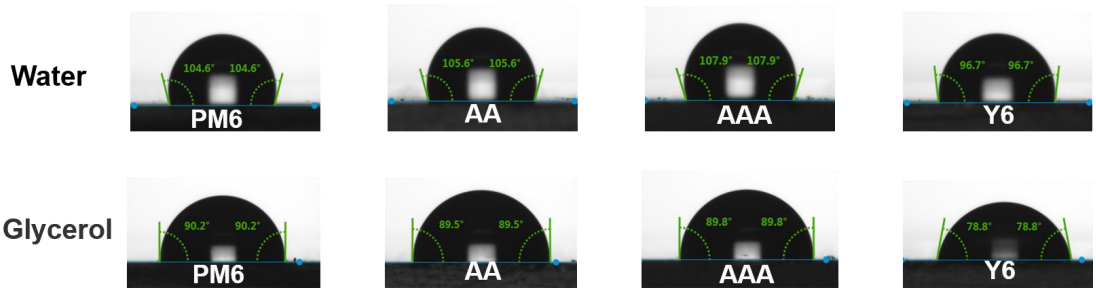


Figure S9. Contact angles of drops of water and glycerol for surface energy analysis of PM6, AA, AAA, Y6

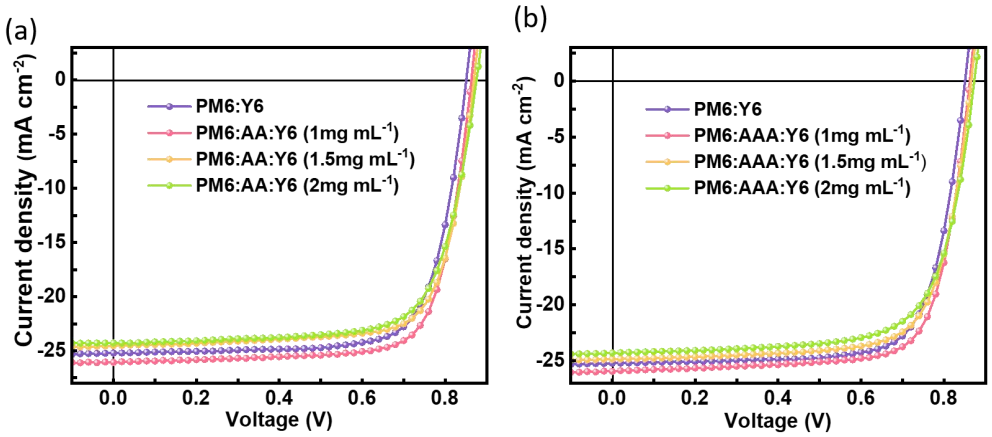


Figure S10. (a) J−V curves of PM6:AA:Y6-based devices with different concentration of oligomers. (b) J−V curves of PM6:AAA:Y6-based devices with different concentration of oligomers.

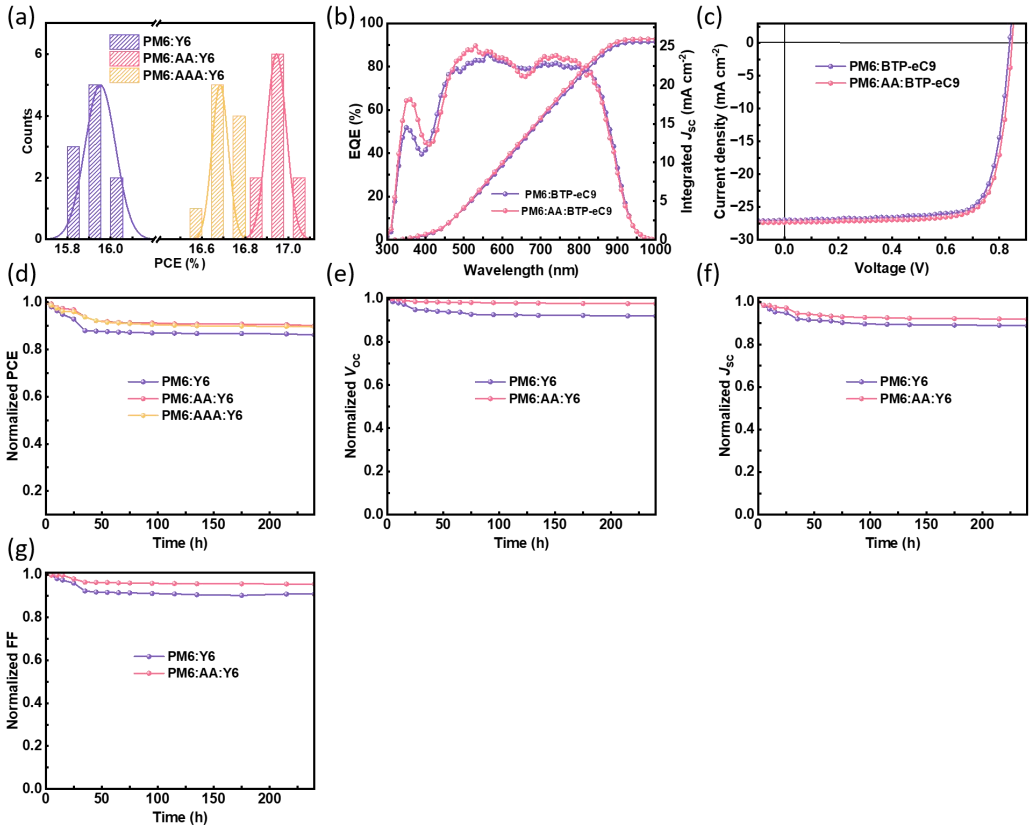


Figure S11. (a) Histogram of the PCEs for 10 devices. (b) EQE curves of the PM6:AA:BTP-eC9 blend cells. (c) J–V curves of the PM6:AA:BTP-eC9-based devices. (d) Photostability test of unencapsulated OSCs based on PM6:Y6, PM6:AA:Y6 and PM6:AAA:Y6 devices, stored in N_2 atmosphere under continuous 1-sun-euivalent white LED illumination. (e), (f), (g) Photostability test of the PM6:Y6 and PM6:AA:Y6 devices.

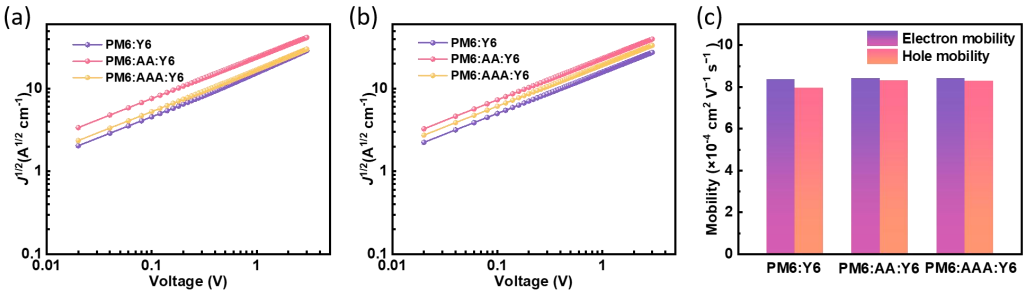


Figure S12. (a) J1/2−V plots of hole-only devices. (b) J1/2−V plots of electron-only devices (in dark). (c) Hole and electron mobility comparison bar graph.

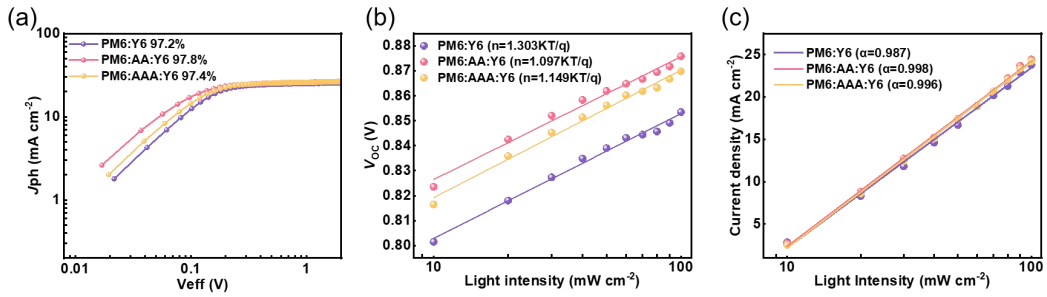


Figure S13. (a) The plot of J_{ph} as a function of V_{eff} for the PM6: oligomer: Y6 devices. (b) Dependence of V_{OC} on the light intensity of the OSC devices. (c) Dependence of J_{SC} on the light intensity of the OSC devices.

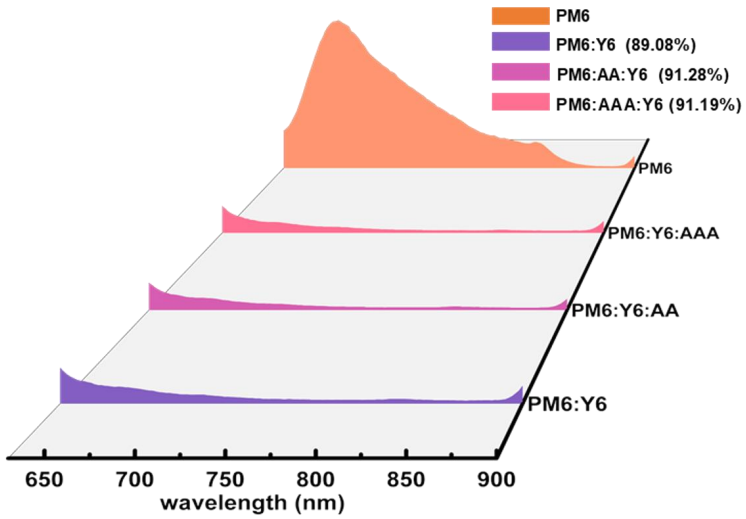


Figure S14. Photoluminescence (PL) spectra of the neat film of PM6 and the five blend films of PM6:Y6, PM6:AA:Y6 and PM6: AAA:Y6.

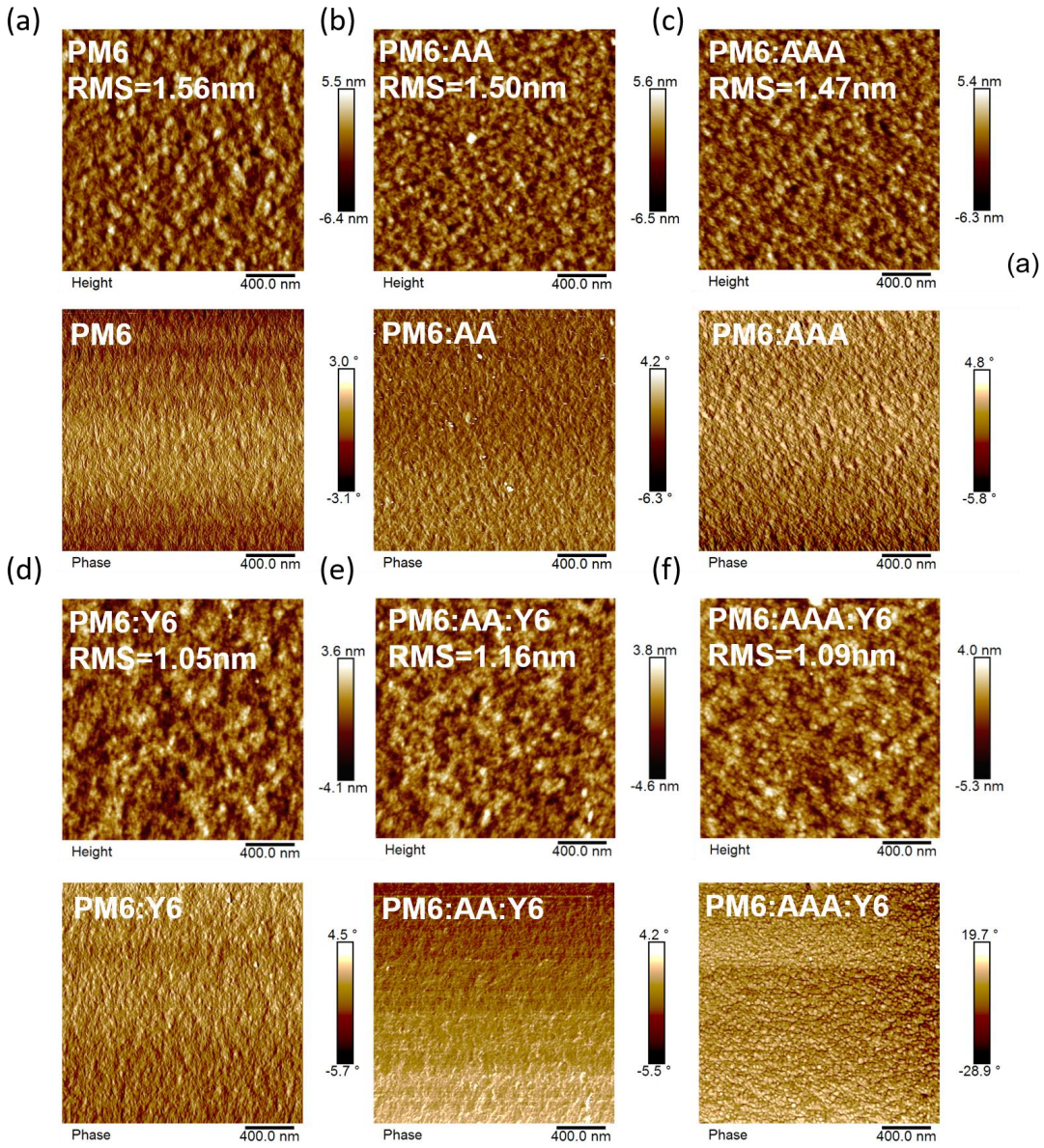


Figure S15. AFM height images and phase images of the neat and blend films.

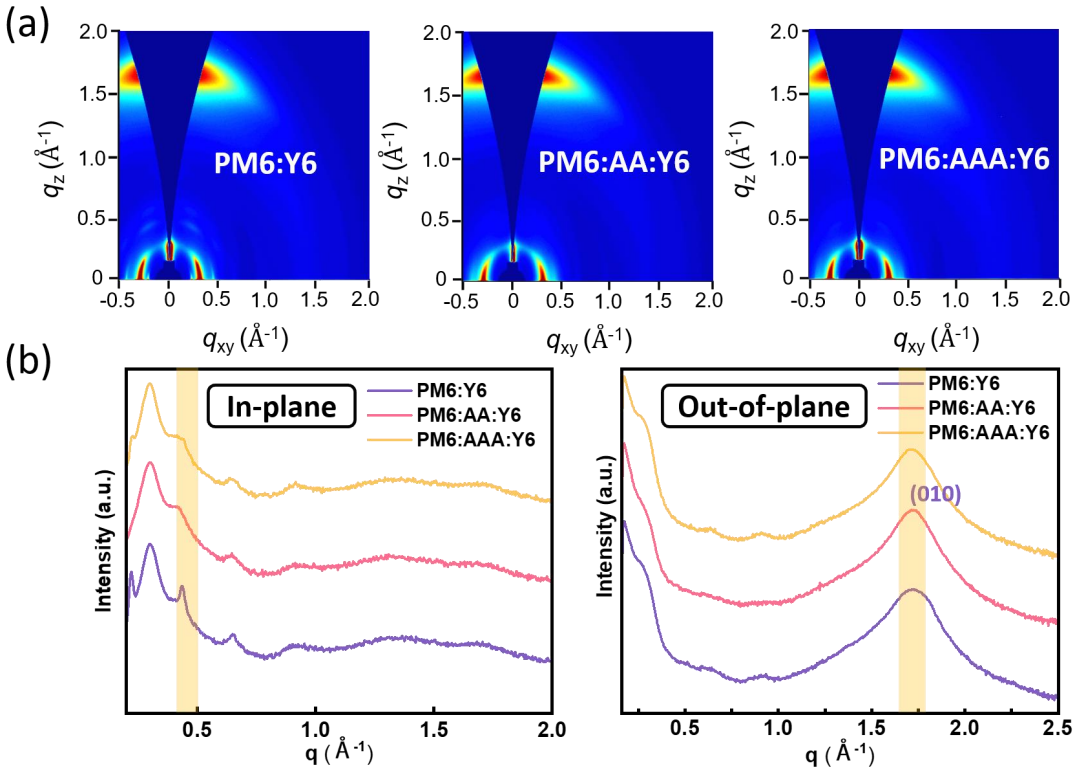


Figure S16. (a) 2D GIWAXS images of PM6:Y6, PM6:AA:Y6 and PM6:AAA:Y6. (b) 1D plots extracted from the 2D patterns along OOP and IP directions

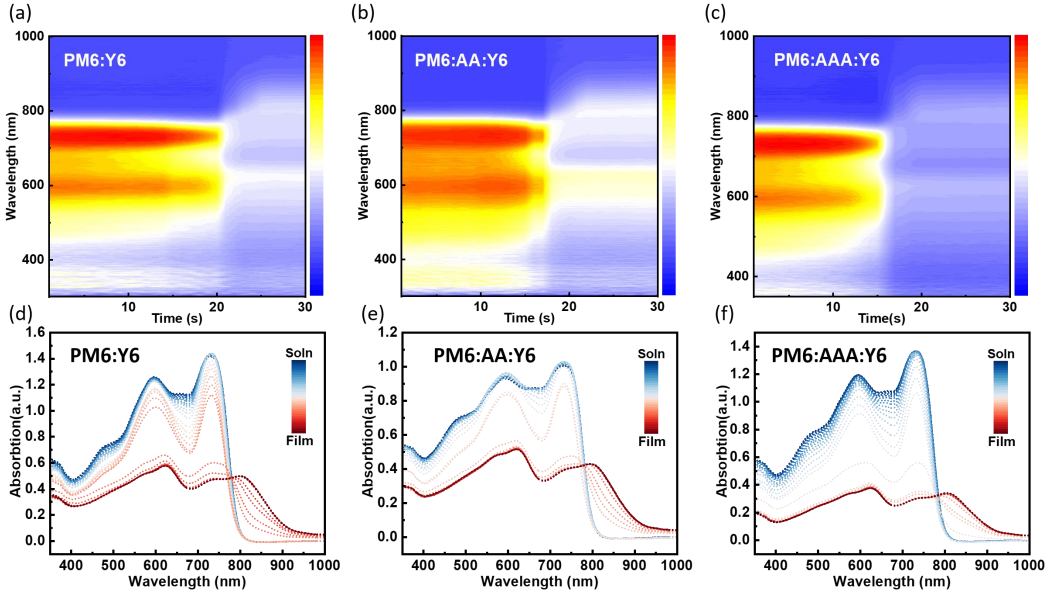


Figure S17. (a-c) Time-resolved UV/Vis absorption spectra as a function of annealing time of PM6:Y6, PM6:AA:Y6, PM6:AAA:Y6 films. (d-f) In situ UV-visible absorption of PM6:Y6, PM6:AA:Y6, PM6:AAA:Y6 from solution to film.

Table S1: Detailed optical and electrochemical parameters of PM6, AA, AAA, and Y6.

Material	λ_{max} soln [nm]	λ_{max} film [nm]	λ_{onset} film [nm]	E_g^{opt}[a] [eV]	HOMO [eV]	LUMO [eV]
PM6	618	615	680	1.82	-5.51	-3.69
PM6:AA	617	624	694	1.80	-5.55	-3.75
PM6:AAA	617	622	694	1.79	-5.53	-3.74
Y6	730	818	996	1.24	-5.72	-4.48
AA	489	540	650	1.90	-5.70	-3.80
AAA	508	578	716	1.73	-5.54	-3.81

[a] Calculated from the formula: $E_g^{opt} = 1240/\lambda_{onset}$.

Table S2. Information from the top surface measured by water and glycerol contact angle.

Flim	θ_{water}[°]	$\theta_{glycerol}$ [°]	γ[mN m^{-1}]	**Blend film**	$\chi/K(\gamma D^{-2} - \gamma A^{-2})^{-2}$
PM6	104.62	90.18	23.76	PM6:Y6	0.3959
AA	105.62	89.48	23.06	PM6:AA	0.0052
AAA	107.92	89.76	22.49	PM6:AAA	0.0174
AA	105.62	89.48	23.06	AA:Y6	0.4922
AAA	107.92	89.76	22.49	AAA:Y6	0.5795
Y6	96.71	78.75	30.29	-	-

Table S3. Photovoltaic parameters of PM6:oligomer:Y6-based devices with different concentration of AA and AAA.

Active Layer	oligomers	V_{OC}(V)	J_{SC}(mA cm^{-2})	FF(%)	PCE(%)
PM6:Y6	-	0.851	25.20	74.35	15.94
PM6:AA:Y6	1mg/mL	0.863	26.06	75.35	16.95
PM6:AA:Y6	1.5mg/mL	0.869	24.53	74.29	15.84
PM6:AA:Y6	2mg/mL	0.875	24.27	71.99	15.30
PM6:AAA:Y6	1mg/mL	0.862	25.94	74.68	16.70
PM6:AAA:Y6	1.5mg/mL	0.866	24.83	73.11	15.71
PM6:AAA:Y6	2mg/mL	0.872	24.29	70.84	15.02

Table S4. Hole and electron mobilities of PM6:oligomer:Y6-based devices in the dark.

Device	μ_h ($cm^2 V^{-1} s^{-1}$)	μ_e ($cm^2 V^{-1} s^{-1}$)	μ_e/μ_h
PM6:Y6	7.970×10^{-4}	8.375×10^{-4}	1.051
PM6:AA:Y6	8.327×10^{-4}	8.429×10^{-4}	1.012
PM6:AAA:Y6	8.300×10^{-4}	8.414×10^{-4}	1.014

Table S5. Summarized parameters for the ordering structures of films.

Active Layer	π-π stacking cell axis (010)			
	FWHM ($Å^{-1}$)	q ($Å^{-1}$)	d-spacing (Å)	CCL (Å)
PM6:Y6	0.26327	1.7210	3.6508	23.866
PM6:AA:Y6	0.22379	1.7133	3.6674	28.076
PM6:AAA:Y6	0.23746	1.7190	3.6551	26.460