Electronic Supplementary Information (ESI) for

Chemical modification of small molecule acceptor with adamantyl side chain for efficient and thermally stable organic solar cells

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Characterization

NMR Measurement：^{1}H-NMR spectra were obtained on a Bruker Advance III 400 (400 MHz), Bruker Advance III 500 (500 MHz) and JEOL 400YH (400 MHz) nuclear magnetic resonance (NMR) spectroscope.

MALDI-TOF MS Measurement: Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum tests were carried out on a Bruker autoflex maX.

TGA Measurement: Thermogravimetric analysis (TGA) was done on a Netzsch STA409PC TG/DSC Thermal Analyzer under N_2 atmosphere at a heating rate of 10°C/min.

DSC Measurement: Differential scanning calorimetry analysis (DSC) was done on a TA DSC Q20 Differential Scanning Calorimeter under N_2 atmosphere at a heating rate of 10 ^{o}C/min.

UV-vis Measurement: UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer.

CV Measurement: Cyclic voltammetry (CV) measurements were carried out on a CHI600A electrochemical workstation with Pt plate (coated with a film of certain organic molecule) as the working electrode, Pt wire as the counter electrode, and standard calomel electrode (SCE) as the reference electrode, respectively, in anhydrous acetonitrile solution containing 0.1 mol/L tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte. Thereby, CV curves were recorded versus the potential of SCE. We calculated the HOMO and LUMO levels of three SMAs employing the equation $E_{\mathrm{LUMO/HOMO}} = -e\,(E_{\mathrm{red/ox}} - E_{\mathrm{Fc/Fc+}}) + (-\,4.8$ eV), in which e was the elementary charge, $E_{\mathrm{red/ox}}$ and $E_{\mathrm{Fc/Fc+}}$ were the onsets of reduction/oxidation waves for SMAs and the couple of neutral ferrocene and its cation (the internal reference, Fc/Fc$^+$), respectively, and −4.8 eV is the absolute energy level of Fc/Fc$^+$.

Device fabrication: Organic solar cells were fabricated on glass substrates commercially pre-coated with a layer of ITO with the conventional structure of ITO/PEDOT:PSS/Donor:Acceptor/PDINN/Ag. Before fabrication, the substrates were cleaned using detergent, deionized water, acetone, and isopropanol consecutively for 20 min in each step and dried up. Then the substrates were treated in an ultraviolet ozone generator for 20 min before being spin-coated at 4500 rpm with a layer of 20 nm thick PEDOT:PSS (Baytron P AI4083). After baking the PEDOT:PSS layer in air at 150 °Cfor 15 min, they were transferred to a glovebox. The optimized active layers were spin-coated from the corresponding chloroform solutions (16.5 mg/mL, PM6: ADAD = 1: 1.25 (by wt.); PM6: BOAD = 1: 1.25 (by wt.); PM6: Y6-BO = 1: 1.25 (by wt.); 0.28% Diiodooctane was used as addition). Then the active layers were annealed at 80°C for 300 s. Then, the PDINN film was deposited as the cathode buffer layer by the spin-coating of a solution of 1 mg/mL PDINN in methanol at 3500 rpm. Finally, the Ag (100 nm) electrode was deposited by thermal evaporation to complete the device with an active area of 6 mm^2.

***J-V* curves and EQE data:** The current density-voltage (*J-V*) curves of OSCs were performed on an Enlitech SSX50 solar simulator under the condition of AM 1.5 G illumination and the light intensity was calibrated by a standard Si solar cell at 100 mV cm^{-2}. The EQE data were measured by a Solar Cell Spectral Response Measurement System (RE-R, Enlitech). All the devices mentioned were tested by a shadow mask with an area of 0.0473 cm^2.

SCLC Mobility Measurement: Using the space-charge-limited current (SCLC) method to measure the charge carrier mobilities of the blend films. Hole-only devices were fabricated in a structure of ITO/PEDOT:PSS/Donor:Acceptor/MoO$_3$/Ag, and electron-only devices were fabricated in a structure of ITO/ZnO/Donor:Acceptor/PDINN/Ag. The device characteristics were extracted by modeling the dark current under forward bias using the SCLC expression described by the Mott-Gurney law: $J = \frac{9}{8}\varepsilon_r\varepsilon_0\mu\frac{V^2}{L^3}$.Here, $\varepsilon_r \approx 3$ is the average dielectric constant of the blend film, ε_0 is the permittivity of the free space, μ is the carrier mobility, L is the thickness of the film (~100 nm), and V is the applied voltage.

Exciton Dissociation Probability (P_{diss}) and Charge Collection Probability (P_{coll}) Calculation: The current density under illumination (J_L) and in the dark (J_D) with the change of voltage were investigated. The photocurrent density (J_{ph}) could be calculated by the equation of $J_{ph} = J_L - J_D$. The voltage in which the generated J_{ph} is zero is called bias voltage (V_{bi}), and the effective voltage (V_{eff}) is defined as $V_{eff} = V_0 - V$ where V_0 is the voltage that makes $J_{ph} \approx 0$ and V is the changeable applied voltage. P_{diss} is decided by the equation $P_{diss} = J_{SC}/J_{sat}$. where J_{sat} is the saturate photocurrent density at high V_{eff}. Similarly, P_{coll} could be estimated by the equation $P_{diss} = J_{max}/J_{sat}$ where J_{max} is the current density when device reaches maximum output power.

PL and TRPL measurement: The steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were both obtained with an FLSP920 Spectro fluorometer at an excitation wavelength of 550 nm.

AFM Measurement: Topographic images of the films were obtained on a VeecoMultiMode atomic force microscopy (AFM). Surface morphologies of PM6:BOAD and PM6:Y6-BO blend films after thermal treatment at 80 °C were observed using Cypher ES environmental atomic force microscope (Asylum Research, Oxford Instruments).

CLSM Measurement: Surface morphologies of PM6:ADAD blend films after thermal treatment at 80 °C were observed using a confocal laser scanning microscope (CLSM, Zeiss LSM900).

Surface Tension Measurement: Contact angle test was conducted on a LAUDA Scientific LSA series video optical contact angle tension measuring instrument. The surface tension values of films are calculated by the Wu method[1]. The Flory-Huggins interaction parameters are deduced from: $\chi^{D-A} = K(\sqrt{\gamma_D} - \sqrt{\gamma_A})^2$.

Estimation of glass-transition temperature: The thermal transition was investigated through the exploitation of discernible shifts in the UV-visible absorption spectrum following the thermal annealing of a diverse array of pristine film samples. This spectral alteration is ascribed to the emergence of structured aggregates, which are intimately associated with the thermal behavior of the molecular constituents within the films. Beyond a certain annealing temperature threshold surpassing the transition temperature, a conspicuous alteration becomes readily apparent in the absorption spectrum. To perform a rigorous quantitative assessment, we employed a metric termed the deviation metric (DMT), which is computed as the sum of squared deviations in absorbance values between the as-cast and annealed film specimens: $DM_T = \sum_{\lambda_{min}}^{\lambda_{max}} [I_{RT}(\lambda) - I_T(\lambda)]^2$, Where λ is the wavelength, and $\lambda_{\min}$ and $\lambda_{\max}$ are the lower and upper bounds of the optical sweep, $I_{RT}(\lambda)$ and $IT(\lambda)$ are the normalized absorption intensities of the as-cast (room temperature) and annealed films, respectively.

GIWAXS measurement: GIWAXS measurements were performed in a Xeuss 3.0 at Vacuum Interconnected Nanotech Workstation (Nano-X) from Suzhou Institution of Nano-Tech and Nano-Bionics, Chinese Academy of Science. The incident angle was set to 0.2 degree. Crystal coherence length (CCL) is calculated by: $CCL = \frac{2\pi K}{FWHM}$, where K is about 0.9 in this case, FWHM is the full width at half maxima in GIWAXS images.

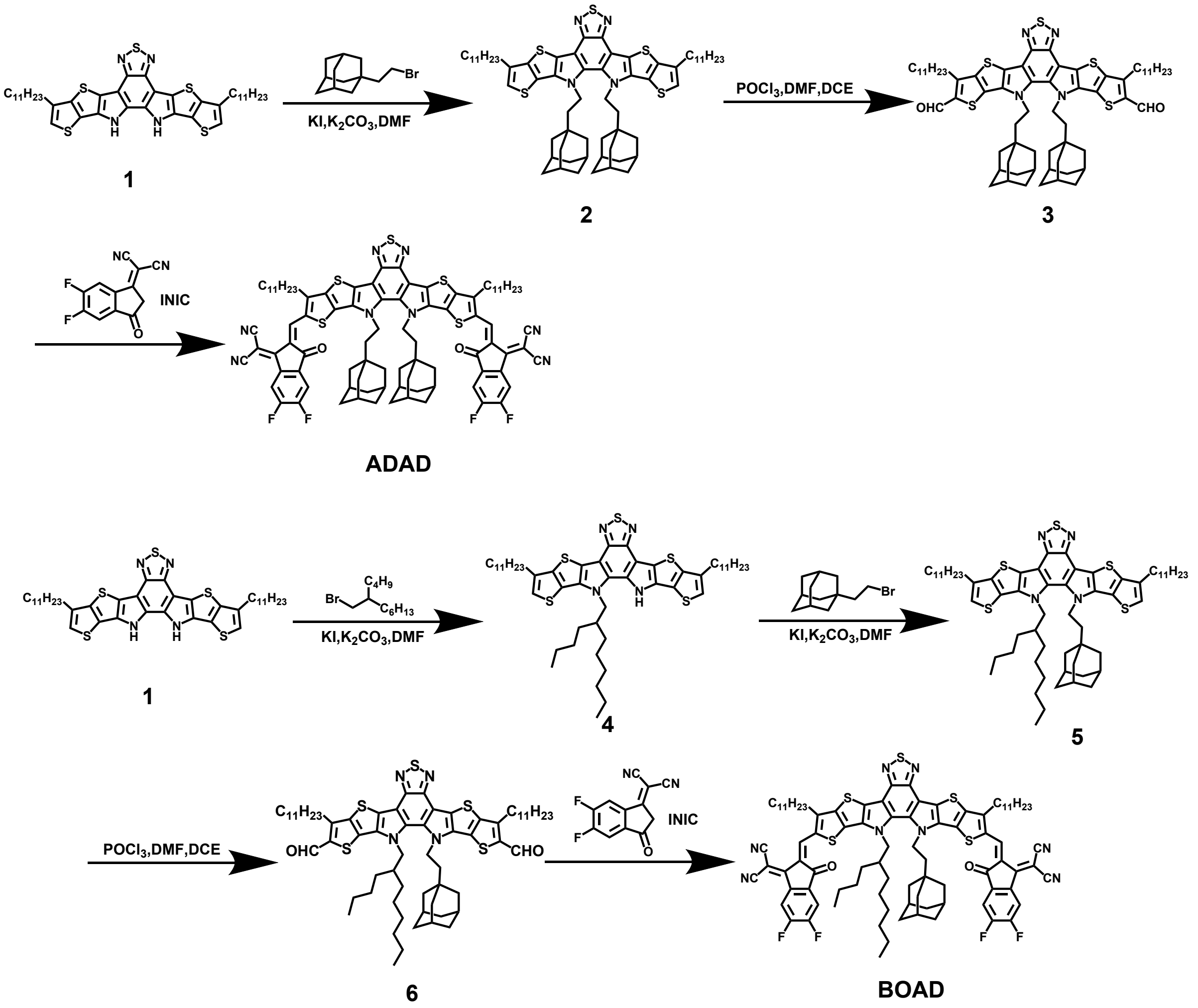
Single Crystal: The crystals of acceptors were grown by solvent diffusion. Acceptor (~20 mg) was dissolved in ~2 mL chloroform and placed in a culture tube (7 × 200 mm) with layered dichloromethane and then methanol upon it. The tube was then sealed tightly and left undisturbed for 20 days. X-ray crystallographic data were collected at Bruker Single Crystal X-RAY Diffraction D8 Venture Photon III. The structure was solved by the intrinsic phasing method (SHELXT) and refined by the least-squares method (SHELXL) integrated in Olex2.

Despite multiple attempts, the obtained crystals were very small and exhibited weak diffraction patterns. As presented in Fig. S9-S12, many data of two single crystals had low resolutions (I/sigma < 3, Rmerge > 15%). Therefore, the data with 2-theta angle above 93 degrees for the BOAD structure and above 100 degrees for the Y6-BO structure were cut off to ensure that the I/sigma values of the remained data were greater than 1.

Through such data processing, we were still able to derive reasonable molecular skeleton models for BOAD and Y6-BO. However, there existed some structural uncertainties for their flexible alkyl side chains.

Materials Synthesis

Compound **1** and INIC were purchased from Derthon Optoelectronics Materials Science Technology Co., Ltd. Other reagents and solvents were purchased from Bidepharm, Sinopharm, Macklin, Rhawn, and J&K Co., Ltd., used without further purification. The synthetic routes for ADAD and BOAD were shown in Scheme S1.



Scheme S1. Detailed synthesis routes of ADAD and BOAD.

Compound **2**

For compound **2**, in a 100 ml flask, compound **1** (0.417 g, 0.56 mmol), 1-(2-bromoethyl)adamantane (0.814 g, 3.35 mmol), potassium iodide (0.741 g, 4.46 mmol), potassium carbonate (1.54 g, 11.1 mmol) and 20 ml DMF were added, and then the solvent was heated to 120 °C and stirring for 20 h. Then the solution was cooled down to room temperature, pour into water and extracted with dichloromethane, washed with brine. After removal of solvent, the crude product was purified using silica gel with the mixture of petroleum ether and dichloromethane as eluent, yielding an orange liquid of compound **2** (0.289 g, 48%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.02 (s, 2H), 4.78 – 4.58 (m, 4H), 2.82 (t, J = 7.7 Hz, 4H), 1.99 (s, 6H), 1.85 (p, J = 7.6 Hz, 4H), 1.77 – 1.68 (m, 6H), 1.67 – 1.57 (m, 18H), 1.54 – 1.47 (m, 4H), 1.46 – 1.34 (m, 8H), 1.32 – 1.25 (m, 24H), 0.91 – 0.84 (m, 6H).

Compound **3**

For compound **3**, in a 100 ml flask, 5 ml dry DMF was added, then phosphorus oxychloride (2 ml, 21.7 mmol) was slowly added dropwise. After stirred for 20 min, compound **2** (0.288 g, 0.27 mmol) dissolved in 20 mL dry dichloroethane was added dropwise, the mixture was heated to 90 °C and stirred for 20 h. Then the solution was cooled down to room temperature, pour into water, neutralized with sodium carbonate and extracted with dichloromethane. After removal of solvent, the crude product was purified using silica gel with the mixture of petroleum ether and dichloromethane as eluent, yielding an orange solid of compound **3** (0.289 g, 95%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.14 (s, 2H), 4.79 – 4.66 (m, 4H), 3.20 (t, *J* = 7.6 Hz, 4H), 2.01 (s, 6H), 1.92 (p, *J* = 7.8 Hz, 4H), 1.77 – 1.70 (m, 6H), 1.67 – 1.57 (m, 18H), 1.52 – 1.43 (m, 8H), 1.40 – 1.34 (m, 4H), 1.30 – 1.25 (m, 24H), 0.89 – 0.85 (m, 6H).

Compound **ADAD**

For compound **ADAD**, in a 100 ml flask, compound **3** (100.0 mg, 0.089 mmol), INIC (82.0 mg, 0.36 mmol), 0.5 ml pyridine and 12 ml chloroform were added, and then the solvent was heated to 70 °C and stirring for 20 h. Then the solution was cooled down to room temperature. After removal of solvent, the crude product was purified using silica gel with the mixture of petroleum ether and dichloromethane as eluent, yielding a black solid of compound **ADAD** (17.5 mg, 12.7%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.04 (s, 2H), 8.50 (dd, *J* = 10.0, 6.5 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 2H), 4.85 – 4.73 (m, 4H), 3.17 (t, *J* = 7.9 Hz, 4H), 2.08 (s, 6H), 1.90 – 1.76 (m, 10H), 1.75 – 1.68 (m, 18H), 1.53 – 1.46 (m, 8H), 1.40 – 1.35 (m, 4H), 1.29 – 1.25 (m, 24H), 0.88 – 0.84 (m, 6H). MALDI-TOF MS *m/z* calcd. for ADAD ($C_{90}H_{90}F_4N_8O_2S_5$): 1552.058. Found: 1552.064.

Compound **4**

For compound **4**, in a 100 ml flask, compound **1** (0.485 g, 0.65 mmol), 5-(bromomethyl)undecane (0.162 g, 0.65 mmol), potassium iodide (0.324 g, 1.95 mmol), potassium carbonate (0.719 g, 5.2 mmol) and 20 ml DMF were added, and then the solvent was heated to 70 °C and stirring for 12 h. Then the solution was cooled down to room temperature, pour into water and extracted with dichloromethane, washed with brine. After removal of solvent, the crude product was purified using silica gel with the mixture of petroleum ether and dichloromethane as eluent, yielding an orange liquid of compound **4** (0.346 g, 58%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (s, 1H), 6.86 (s, 2H), 4.12 – 3.89 (m, 2H), 2.72 – 2.62 (m, 4H), 1.90 (s, 1H), 1.83 – 1.74 (m, 4H), 1.42 – 1.34 (m, 10H), 1.32 – 1.23 (m, 38H), 0.87 (t, *J* = 6.5 Hz, 8H), 0.80 (t, *J* = 6.9 Hz, 4H), 0.75 (t, *J* = 6.8 Hz, 4H).

Compound **5**

For compound **5**, in a 50 ml flask, compound **4** (0.346 g, 0.18 mmol), 1-(2-bromoethyl)adamantane (0.583 g, 2.4 mmol), potassium iodide (0.245 g, 1.48 mmol), potassium carbonate (0.510 g, 3.7 mmol) and 10 ml DMF were added, and then the solvent was heated to 120 °C and stirring for 16 h. Then the solution was cooled down to room temperature, pour into water and extracted with dichloromethane, washed with brine. After removal of solvent, the crude product was purified using silica gel with the mixture of petroleum ether and dichloromethane as eluent, yielding an orange liquid of compound **5** (0.129 g, 65%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.02 (s, 2H), 4.72 – 4.57 (m, 4H), 2.83 (t, *J* = 7.5 Hz, 4H), 2.13 (p, *J* = 5.3 Hz, 1H), 2.00 (s, 3H), 1.86 (p, *J* = 7.1 Hz, 4H), 1.75 – 1.55 (m, 10H), 1.43 – 1.36 (m, 8H), 1.33 – 1.25 (m, 32H), 0.99 – 0.92 (m, 6H), 0.91 – 0.84 (m, 12H), 0.68 – 0.61 (m, 6H).

Compound **6**

For compound **6**, in a 100 ml flask, 5 ml dry DMF was added, then phosphorus oxychloride (1.5 ml, 16.3 mmol) was slowly added dropwise. After stirred for 20 min, compound **5** (0.129 g, 0.12 mmol) dissolved in 20 mL dry dichloroethane was added dropwise, the mixture was heated to 90 °C and stirred for 12 h. Then the solution was cooled down to room temperature, pour into water, neutralized with sodium carbonate and extracted with dichloromethane. After removal of solvent, the crude product was purified using silica gel with the mixture of petroleum ether and dichloromethane as eluent, yielding an orange solid of compound **6** (80.3 mg, 59%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.23 – 10.05 (m, 2H), 4.78 – 4.58 (m, 4H), 3.20 (t, *J* = 7.6 Hz, 4H), 2.09 (p, *J* = 6.2 Hz, 1H), 2.02 (s, 3H), 1.92 (p, *J* = 7.7 Hz, 4H), 1.78 – 1.71 (m, 3H), 1.69 – 1.63 (m, 3H), 1.59 – 1.54 (m, 4H), 1.50 – 1.42 (m, 4H), 1.40 – 1.35 (m, 4H), 1.33 – 1.24 (m, 32H), 1.02 – 0.93 (m, 6H), 0.90 – 0.84 (m, 12H), 0.69 – 0.61 (m, 6H).

Compound **BOAD**

For compound **BOAD**, in a 100 ml flask, compound **6** (80.3 mg, 0.07 mmol), INIC (35.7 mg, 0.16 mmol), 1 ml boron trifluoride diethyl etherate, 1 ml acetic anhydride, 7 ml toluene and 1 ml chloroform were added, and then the solvent was heated to 50 °C and stirring for 1 h. Then the solution was cooled down to room temperature and poured into methanol, the black solid was purified using silica gel with the mixture of petroleum ether and dichloromethane as eluent, yielding a black solid of compound **BOAD** (92.2 mg, 84%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.92 (s, 1H), 8.83 (s, 1H), 8.49 (dd, *J* = 9.7, 6.6 Hz, 1H), 8.32 (dd, *J* = 9.7, 6.6 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.0 Hz, 1H), 4.80 – 4.54 (m, 4H), 3.16 (t, *J* = 7.9 Hz, 2H), 3.00 – 2.85 (m, 2H), 2.28 (s, 3H), 2.16 – 1.92 (m, 15H), 1.88 – 1.66 (m, 4H), 1.52 – 1.41 (m, 4H), 1.38 – 1.19 (m, 32H), 1.11 – 0.92 (m, 6H), 0.90 – 0.74 (m, 12H), 0.71 – 0.56 (m, 6H). MALDI-TOF MS *m/z* calcd. for BOAD ($C_{90}H_{96}F_4N_8O_2S_5$): 1558.106. Found: 1558.127.

Supplementary NMR Figures

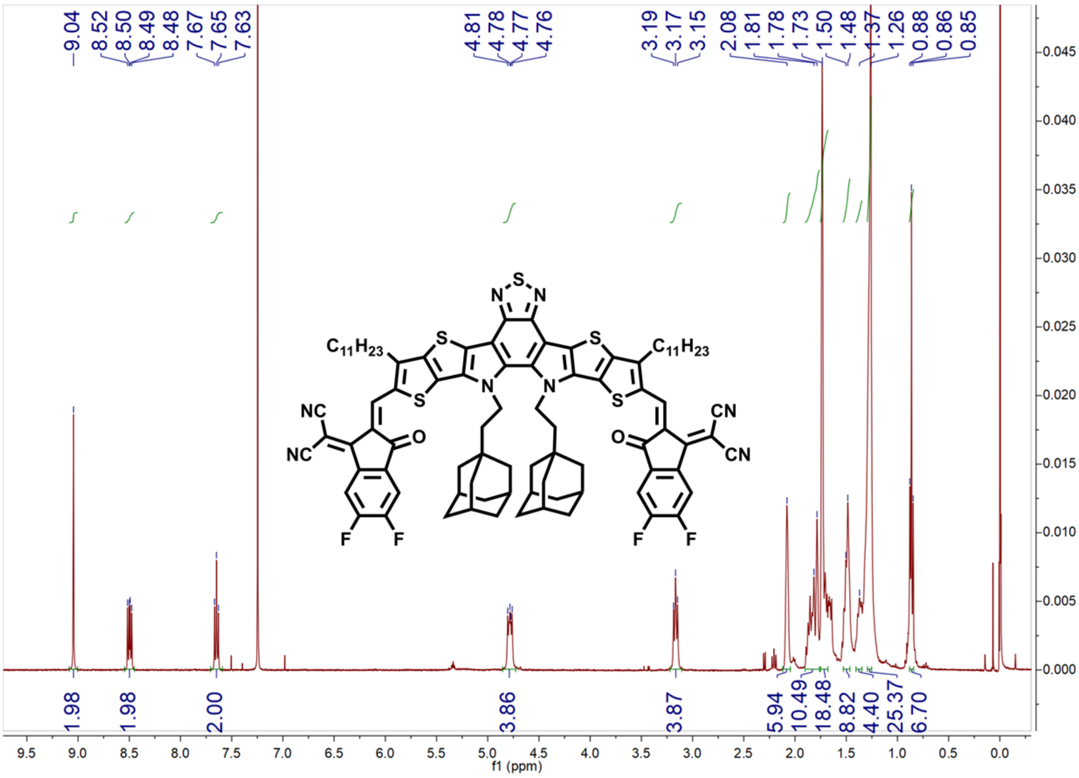


Fig. S1 ^{1}H-NMR spectrum of compound ADAD.

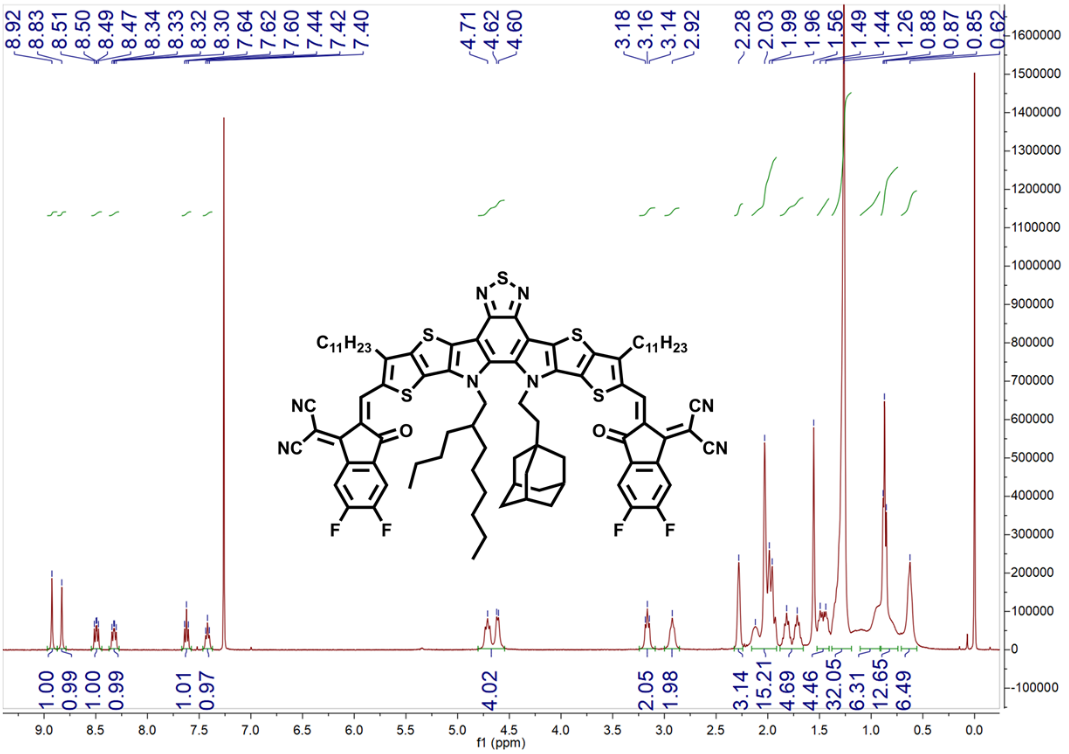


Fig. S2 ^{1}H-NMR spectrum of compound BOAD.

Supplementary MALDI-TOF Figures

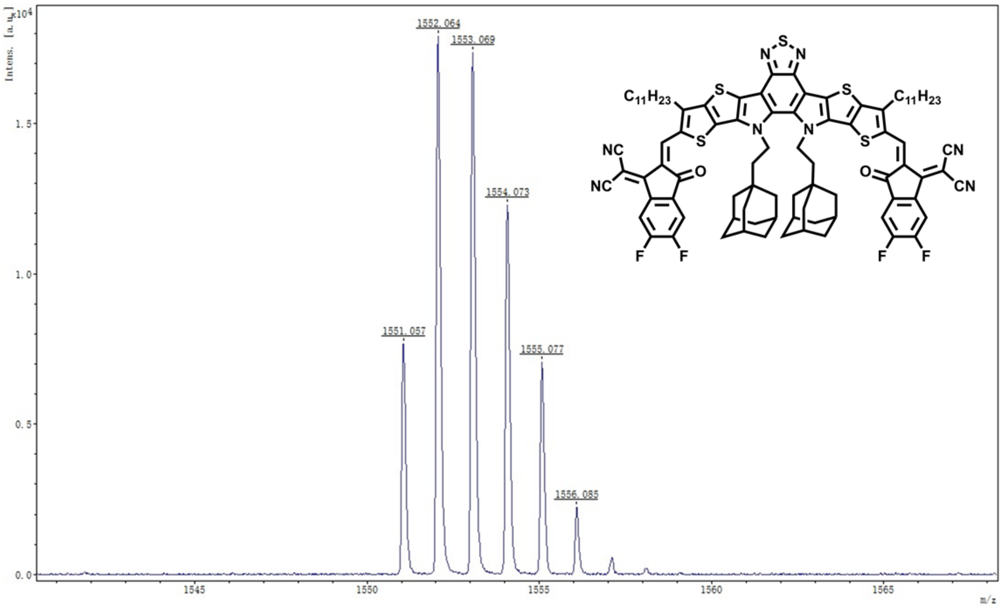


Fig. S3 MALDI-TOF mass spectrum of ADAD.

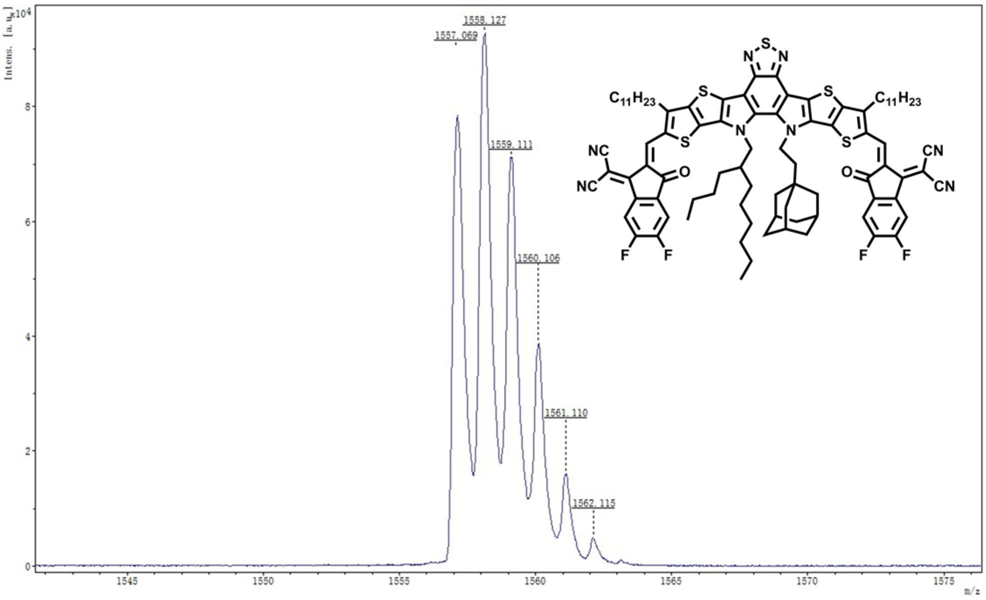


Fig. S4 MALDI-TOF mass spectrum of BOAD.

Supplementary Figures and tables

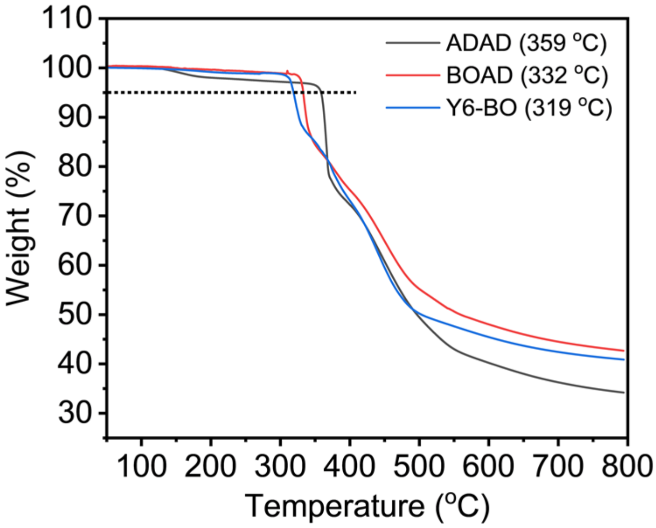


Fig. S5 TGA curves of ADAD, BOAD and Y6-BO.

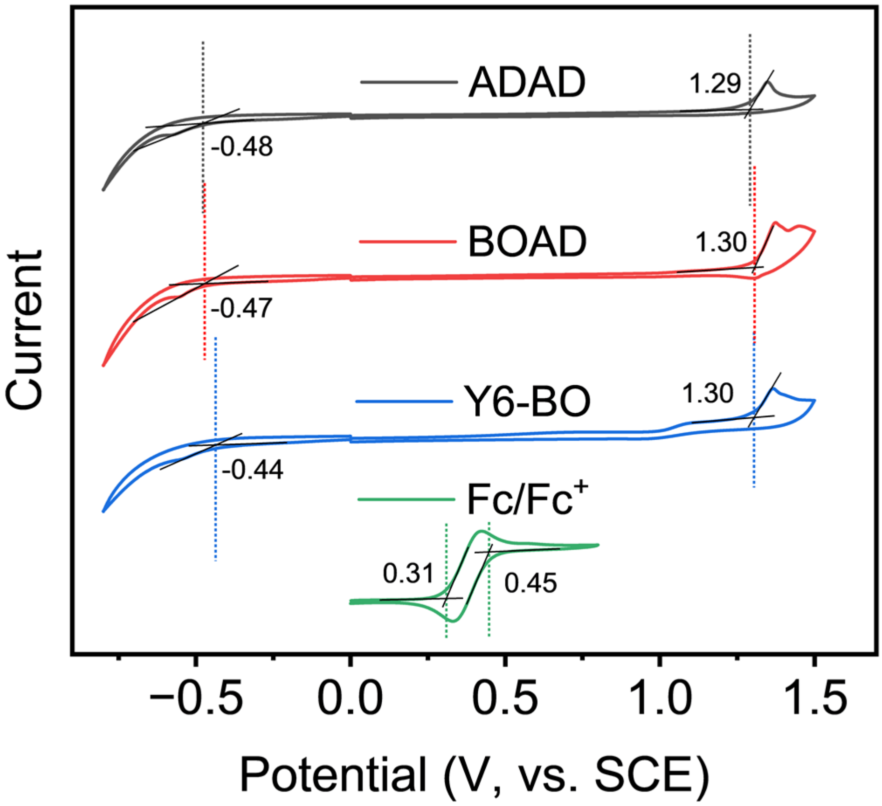


Fig. S6 Cyclic voltammograms of ADAD, BOAD, Y6-BO, and Fc/Fc$^+$ in acetonitrile solutions.

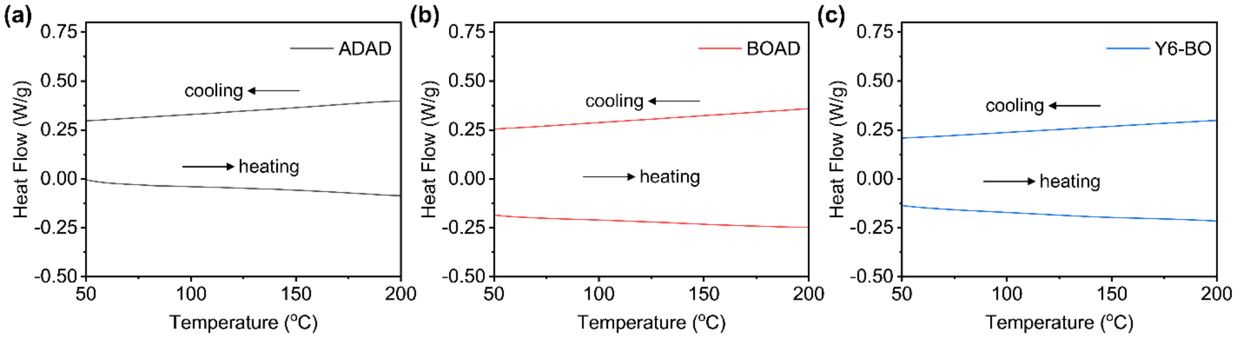


Fig. S7 DSC curves of (a) ADAD, (b) BOAD, and (c) Y6-BO.

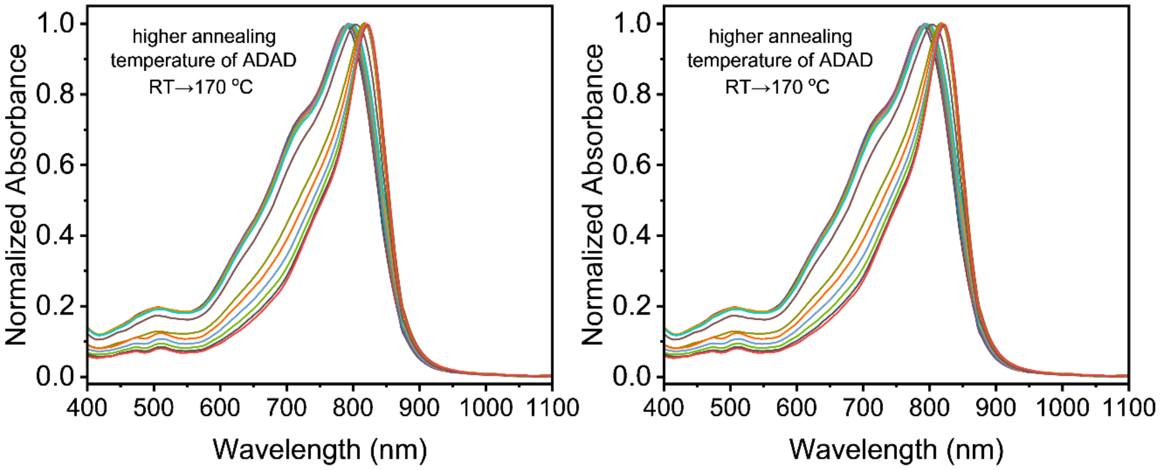


Fig. S8 UV-Vis absorption curves of ADAD and BOAD upon thermal annealing at varied temperatures.

Table S1 Crystal data and structure refinement for BOAD and Y6-BO[a]

Compound	BOAD	Y6-BO
CCDC Deposition Number	2415114	2415115
chemical formula	$C_{85}H_{86}F_4N_8O_2S_5$, $C_{87}H_{90}F_4N_8O_2S_5$	$C_{80}H_{82}F_4N_8O_2S_5$
formula weight	3003.88	1423.83
crystal size (mm)	0.25	0.12
temperature (K)	297(2)	220(2)
radiation	1.54178	1.54178
crystal system	triclinic	monoclinic
space group	P -1	C 1 2/c 1
a (Å)	19.2965(12)	23.663(3)
b (Å)	20.7153(15)	59.004(6)
c (Å)	24.3334(15)	14.0873(13)
α (°)	77.257(5)	90
β (°)	81.479(4)	113.590(6)
γ (°)	63.137(5)	90
V (Å^3)	8450.3(10)	18025(3)
Z	2	8
ρ_{calc} (g/cm^3)	1.181	1.049
F (000)	3168	6000
absorpt coefficient (mm^{-1})	1.734	1.601
θ range (°)	1.864 to 46.495[b]	2.996 to 50.000[c]
reflections collected	48463 (R_{int} = 0.1095)	84911 (R_{int} = 0.1677)
independent reflections	14681	9244
refns obs. [I>2σ (I)]	8679	5785
data/restraints/parameters	14681/512/1897	9244/463/881
goodness-of-fit on F^2	1.074	1.022
R_1, wR_2 [I>2σ (I)]	0.1215/0.3012	0.1460/0.3743
R_1, wR_2 (all data)	0.1690/0.3464	0.1816/0.4150
Largest diff. peak/hole (e Å^{-3})	0.938/-0.369	0.877/-0.539

[a] Due to long and branched alkyl chains on the molecules and very small size of single crystals, there may be some structural uncertainty.

[b] Due to low resolution, the data with the 2θ range above 93 degrees are cut off.

[c] Due to low resolution, the data with the 2θ range above 100 degrees are cut off.

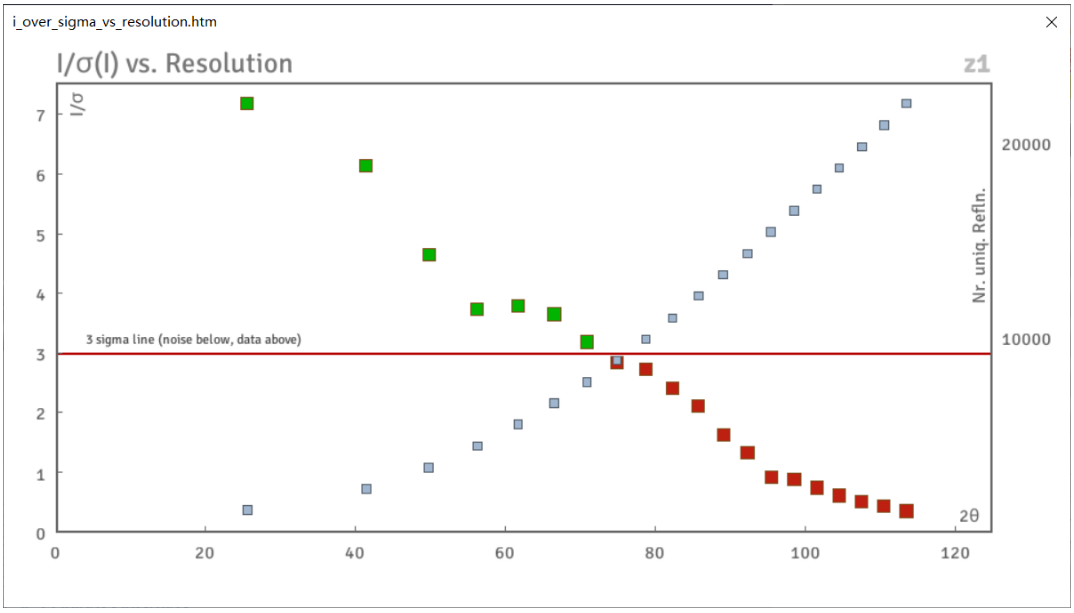


Fig. S9 I/σ(I) vs. resolution plots of BOAD single crystal.

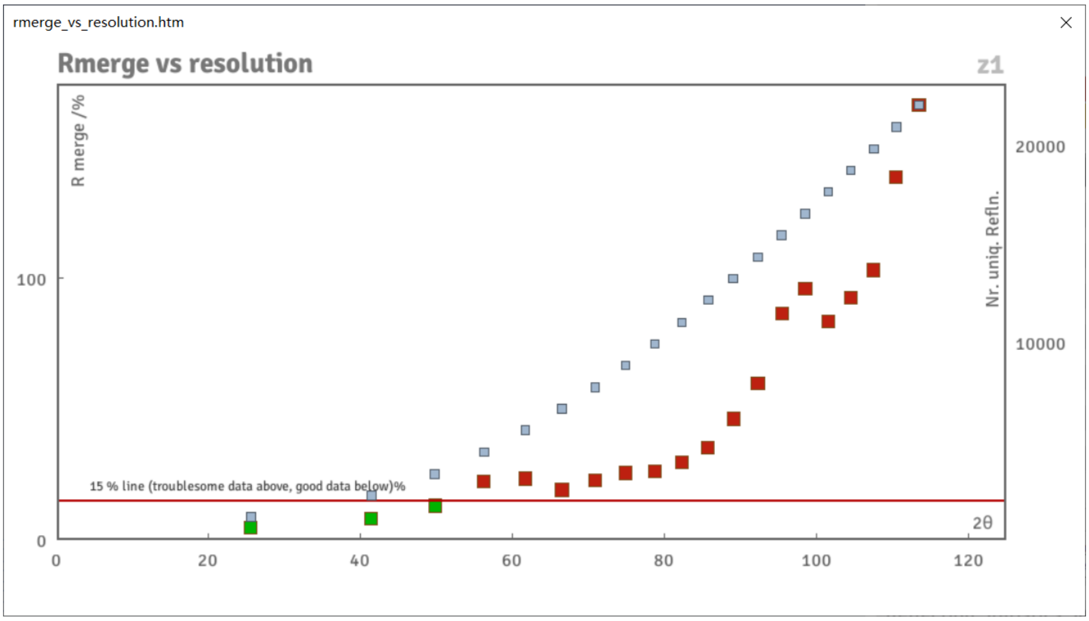


Fig. S10 Rmerge vs. resolution plots of BOAD single crystal.

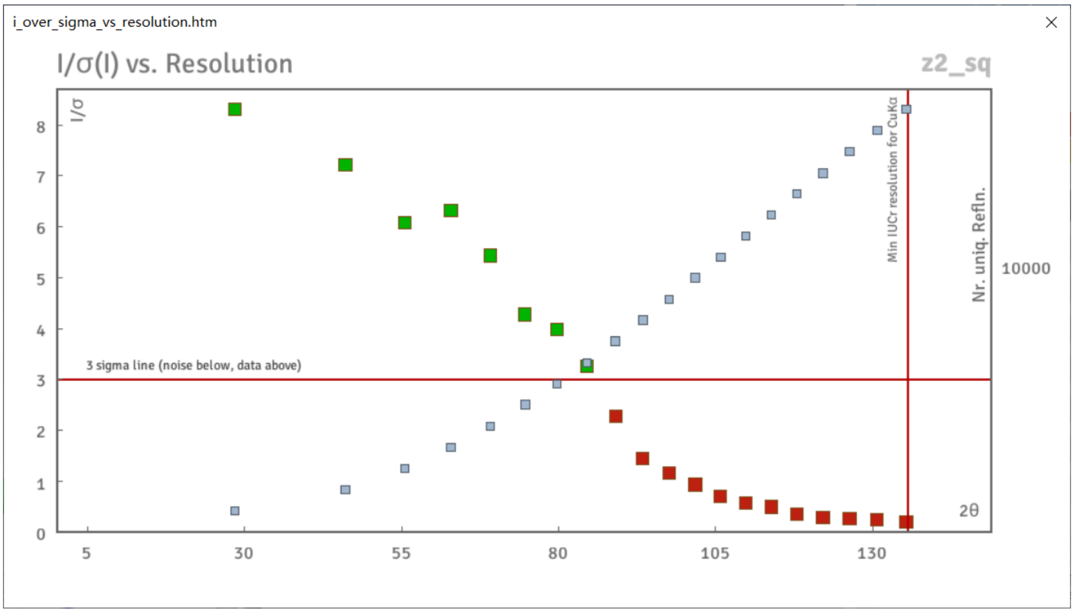


Fig. S11 I/σ(I) vs. resolution plots of Y6-BO single crystal.

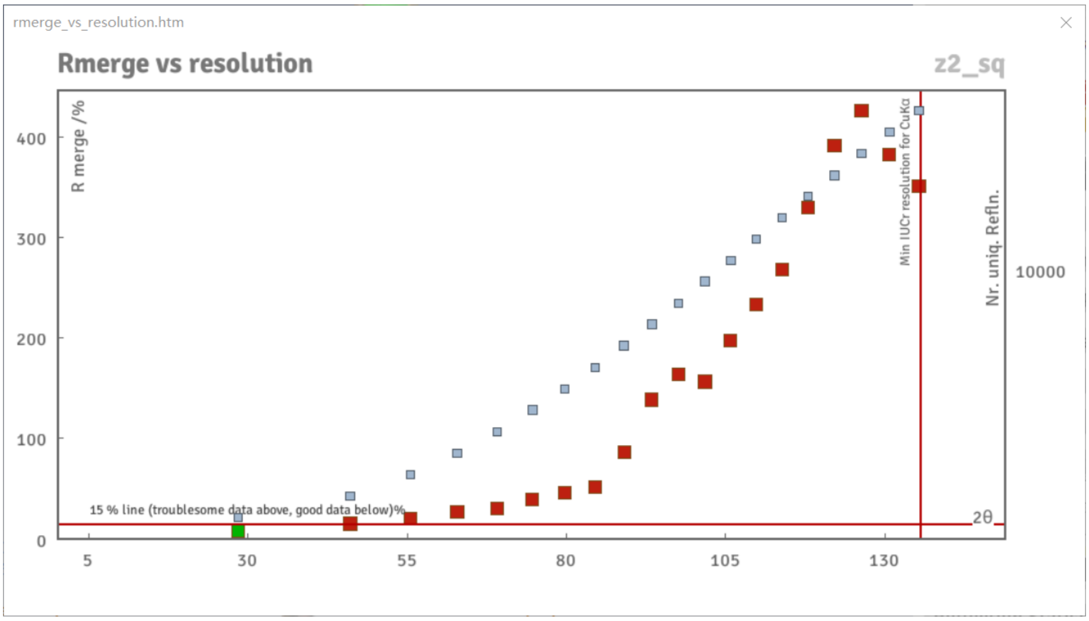


Fig. S12 Rmerge vs. resolution plots of Y6-BO single crystal.

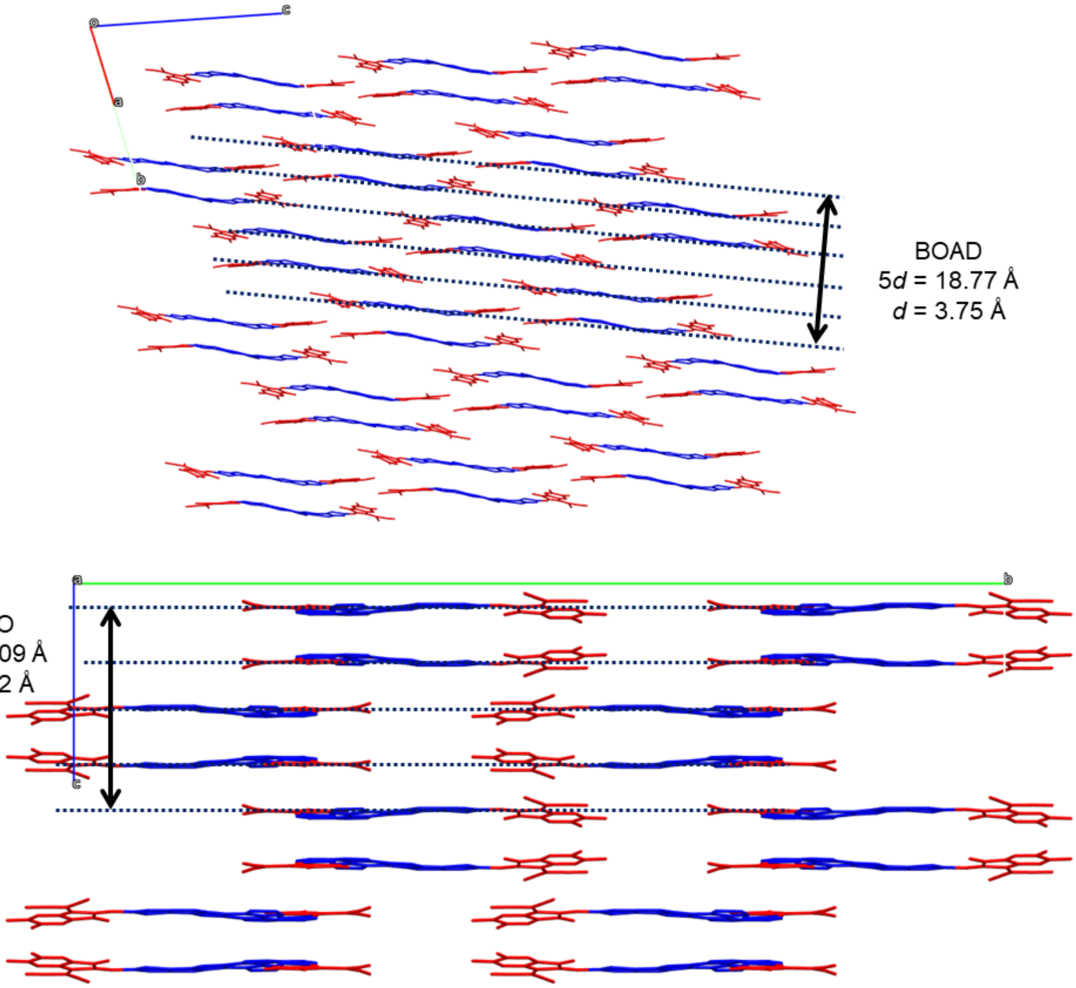


Fig. S13 π-π stacking distances of BOAD and Y6-BO in the single crystals.

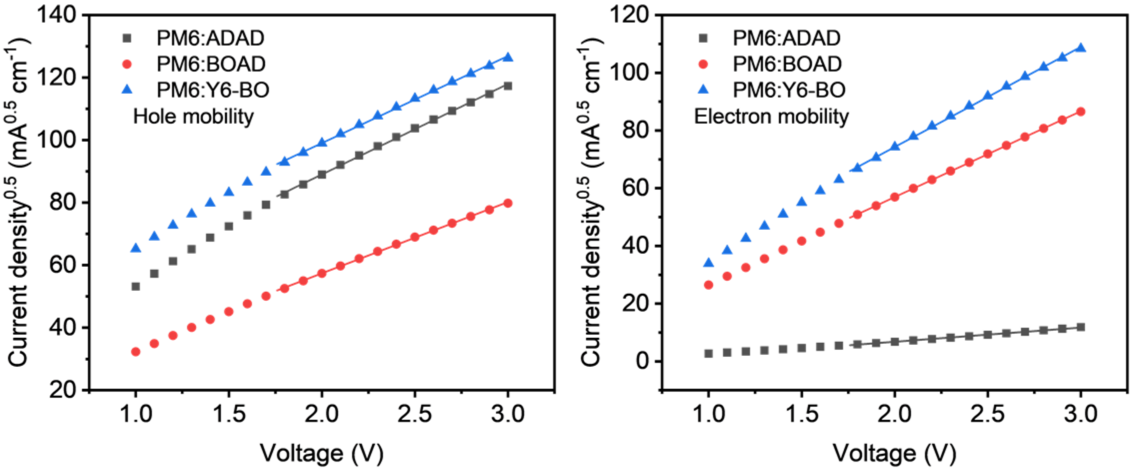


Fig. S14 $J^{0.5}$-V curves of (a) hole-only devices and (b) electron-only devices.

Table S2 Hole and electron mobilities of different devices

Active layer	**$\mu_h\times10^{-4}$ (cm^2 V^{-1} s $^{-1}$)**	**$\mu_e\times10^{-4}$ (cm^2 V^{-1} s $^{-1}$)**	**μ_h/μ_e**
PM6:ADAD	3.02±1.27	0.073±0.006	41.62
PM6:BOAD	2.13±0.59	3.07±0.93	0.69
PM6:Y6-BO	2.79±0.87	4.58±1.90	0.61

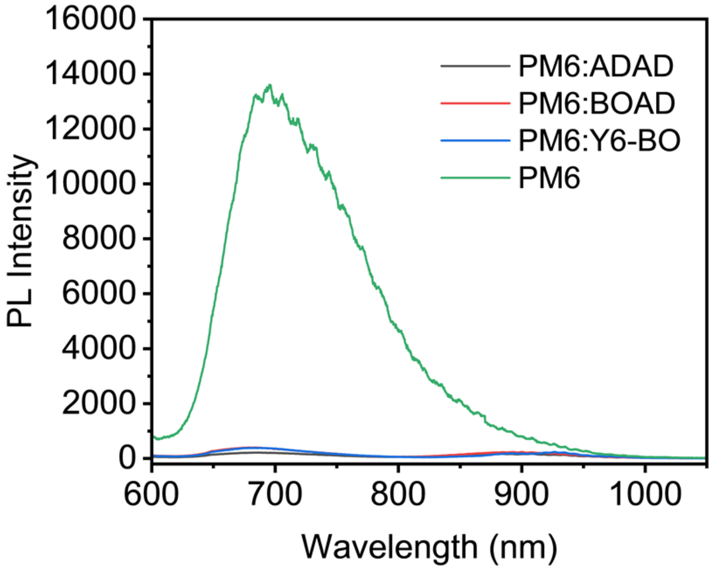


Fig. S15 PL spectra of PM6, PM6:ADAD,PM6:BOAD, and PM6:Y6-BO films.

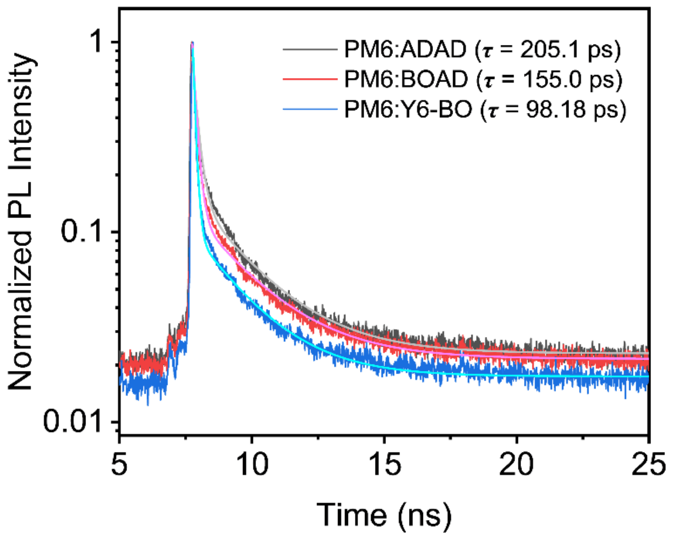


Fig. S16 TRPL spectra of the PM6:ADAD, PM6:BOAD and PM6:Y6-BO blend films.

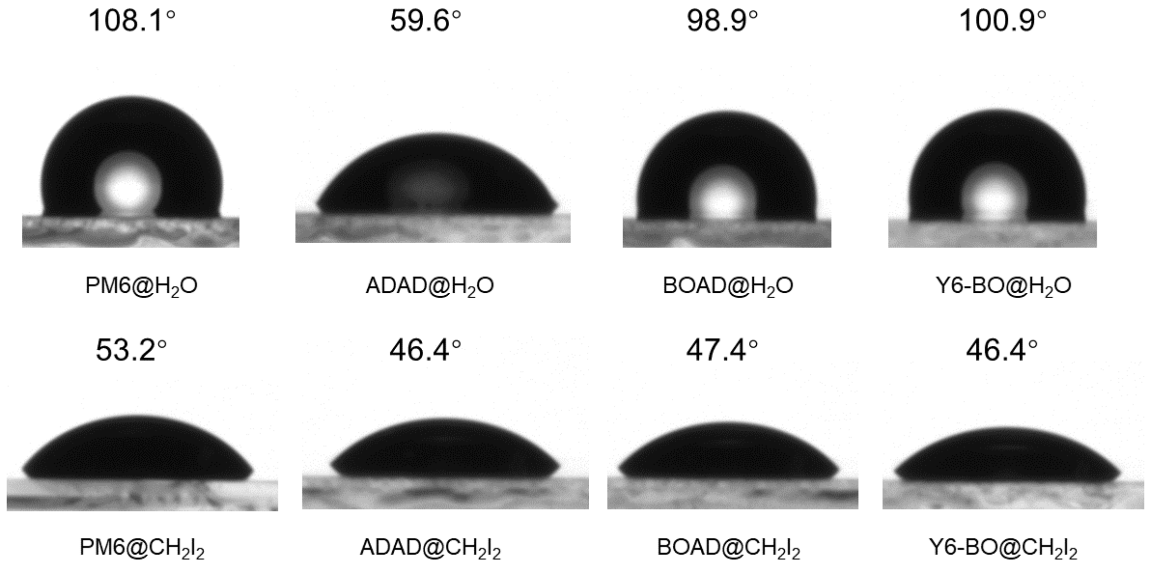


Fig. S17 Contact angle images of thin films with water and diiodomethane droplets.

Table S3 The contact angle and the calculated surface energy of different films

Surface	θ_{water} (°)	$\theta_{\text{diiodomethane}}$ (°)	$\gamma^{p\ a}$ (mN m^{-1})	$\gamma^{d\ b}$ (mN m^{-1})	γ^{c} (mN m^{-1})	$\chi^{\text{D-A}\ d}$
PM6	108.1	53.2	0.12	23.42	23.54	/
ADAD	59.6	46.4	18.09	27.42	45.51	3.59 K
BOAD	98.9	47.4	0.13	36.45	36.58	1.43 K
Y6-BO	100.9	46.4	0.01	37.65	37.66	1.65 K

[a] Surface tension from polarity component. [b] Surface tension from dispersion component. [c] The total surface tension is calculated through the equation of $\gamma = \gamma^{p} + \gamma^{d}$. [d] The Flory-Huggins interaction parameter between the donor (D) and acceptor (A) is calculated with the equation of $\chi^{D-A} = K(\sqrt{\gamma_D} - \sqrt{\gamma_A})^2$.

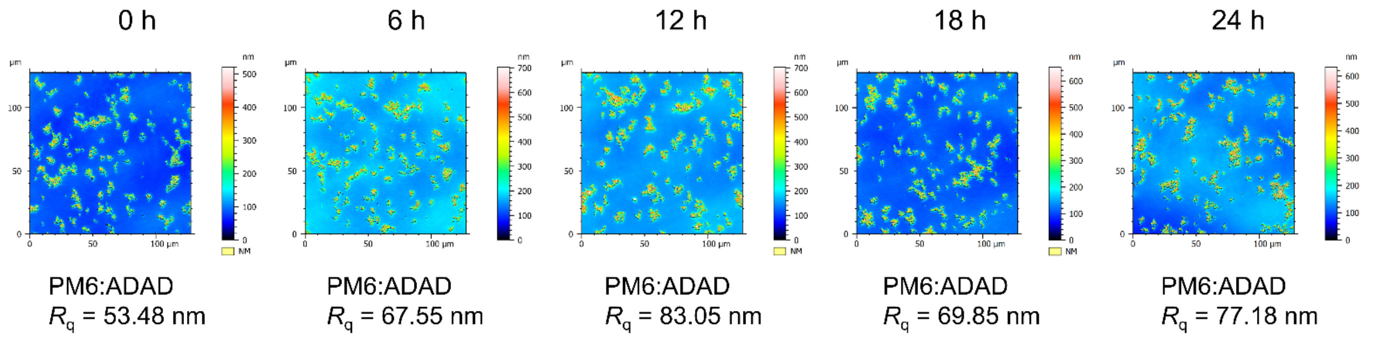


Fig. S18 CLSM height images of PM6:ADAD blend films after thermal treatment at 80 °C for various time.

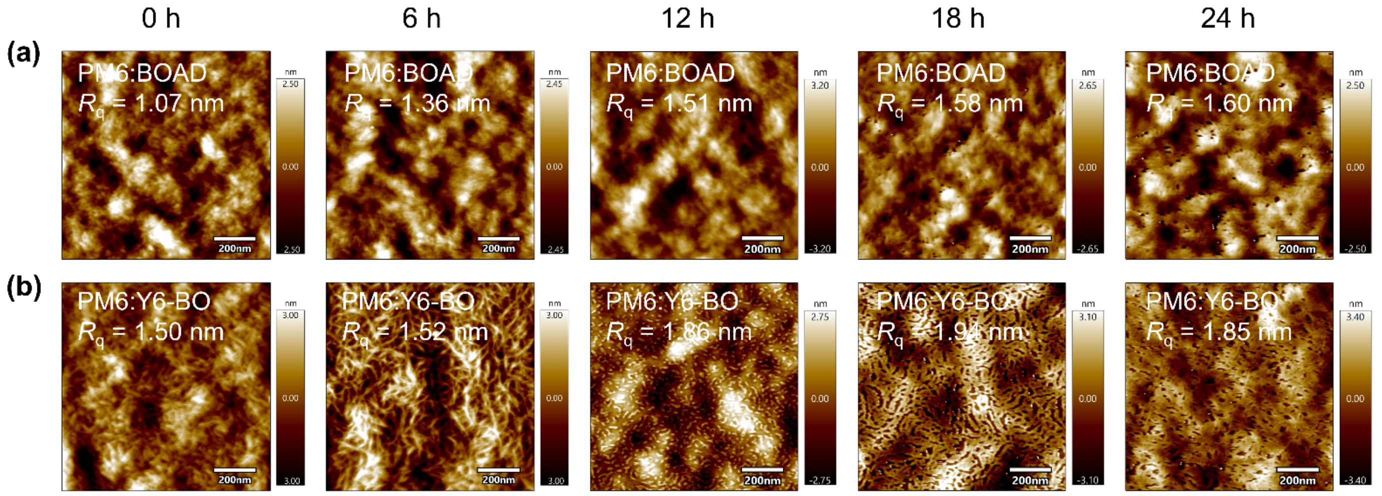


Fig. S19 AFM height images of (a) PM6:BOAD and (b) PM6:Y6-BO blend films after thermal treatment at 80 °C for various time.