Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

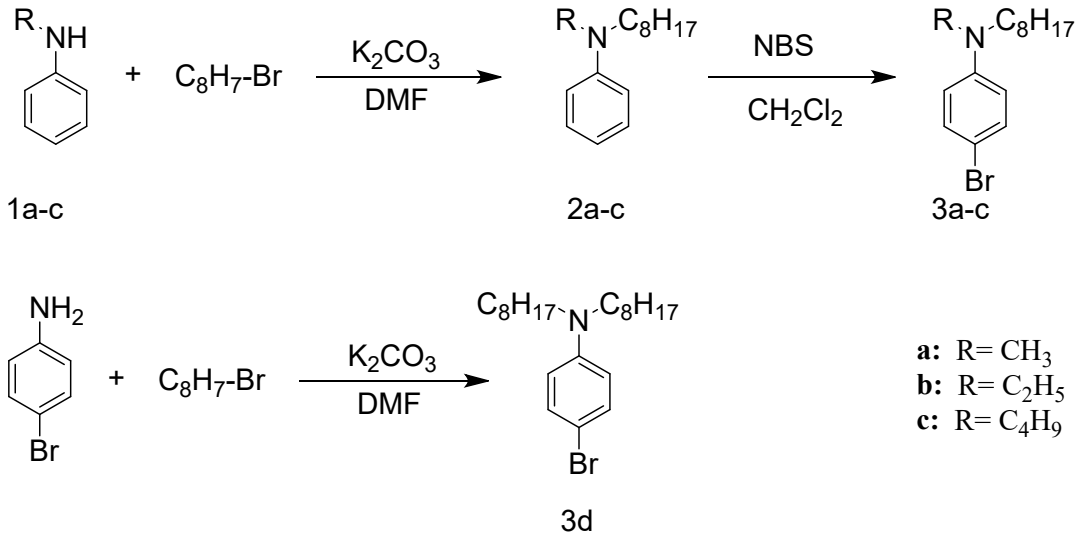
Constructing two-dimensional crossed molecular packing through branching chain engineering of amino-indenofluorene derivatives

Zhi-Ping, Fan*, [a, b] Xiang-Yang. Li, [a] Bing. Sun, [a] Chun-Lin Sun, [a] Zi-Fa Shi, [a] Xiang-Feng Shao [a] and Hao-Li Zhang* [a, c]

Materials

The chemical reagents and solvents were purchased and used as received without further purification except noting.

Synthesis



Scheme 1. The synthetic route of the 4-boromo-dialkylaniline derivatives

General Procedure for 2a-c: A mixture of Monoalkyl aniline (0.1 mol), K_2CO_3 (0.12 mol), n-Octyl Bromide (0.1 mol), and DMF (300 ml) was stirred under argon at 80 °C for about 12h. The mixture was then poured into water and extracted with dichloromethane for three times. The organic layer was dried (Na2SO4), filtered, and the solvent was evaporated to obtain colourless oil. The crude product was purified by column chromatography (hexane as eluent).

N-methyl-N-octylaniline (2a) : Colourless oil, 92% yield. **1H NMR (400 MHz, CDCl3)** δ 7.25-7.21(t, 2H), 6.71-6.69 (d, 2H), 6.67-6.65 (d, 1H), 3.32-3.28 (t, 2H), 2.93 (s, 3H), 1.59-1.53(m, 2H), 1.33-1.27(m, 10H), 0.91-0.87 (t, 3H). **^{13}C NMR (101 MHz, CDCl3)** δ 149.50, 129.23, 115.92, 112.21, 52.96, 38.36, 31.99, 29.67, 29.48, 27.35, 26.81, 22.80, 14.23.

N-ethyl-N-octylaniline (2b) : Colourless oil, 94% yield.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.24-7.20 (t, 2H), 6.68-6.66(d, 2H), 6.64-6.62(d, 1H), 3.40-3.34(m, 2H), 3.27-3.23 (t, 2H), 1.63-1.56 (m, 2H), 1.33-1.25 (m 10H), 1.18-1.14 (t, 3H), 0.92-0.89(t, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.99, 129.36, 115.22, 111.71, 50.56, 44.99, 32.04, 29.72, 29.55, 27.64, 27.39, 22.86, 14.31, 12.42.

C4C8Ph:

N-ethyl-N-octylaniline (2c) : Colourless oil, 91% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.20-7.16 (t, 2H), 6.69-6.67(d, 1H), 6.62-6.60(d, 2H), 3.26-3.22(t, 2H), 3.12-3.08 (t, 2H), 1.65-1.54 (m, 4H), 1.42-1.25 (m, 12H), 0.97-0.93 (t, 3H), 0.90-0.87(t, 3H). **^{13}C NMR (101 MHz, CDCl3)** δ 148.54, 129.25, 117.06, 112.68, 44.01, 31.91, 29.59, 29.49, 29.43, 29.35, 27.25, 27.21, 22.74, 20.42, 14.21, 14.12.

General Procedure for 3a-c. The reagents 2 (50 mmol) were dissolved in dry dichloromethane (100 ml), and cooled to 0 °C. N-Bromobutanimide (NBS, 50 mmol) was added. The mixture was stirred for 30 min at 0 °C, and then it was stirred for 12 h at room temperature. The mixture was extracted with 5% NaOH solution (30 ml), and the organic layer was dried (Na_2SO_4), filtered, and evaporated to dryness. The crude product was purified by column chromatography (silica gel, hexane as eluent), to give the product as colourless oil.

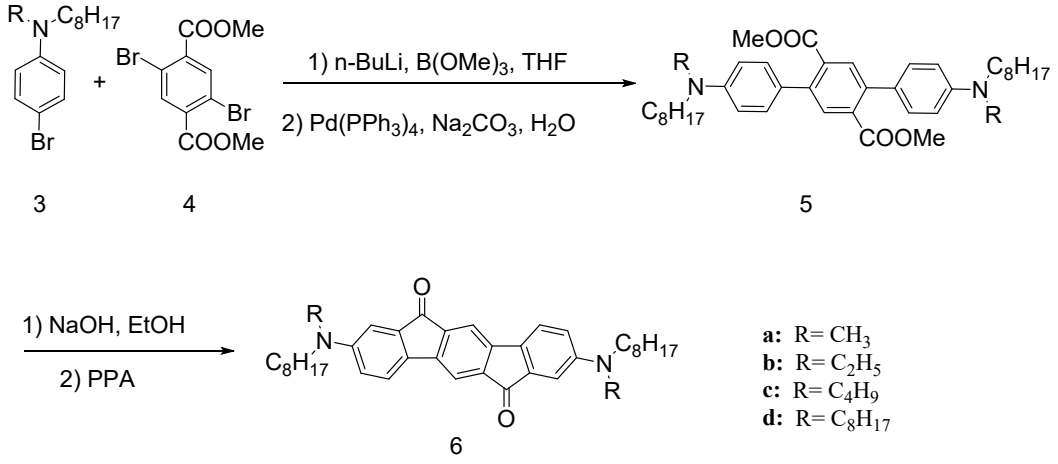
4-bromo-N-methyl-N-octylaniline (3a): 92% yield. **^{1}H NMR (400 MHz, CDCl3)** δ 7.29-7.27 (d, 2H), 6.56-6.54 (d, 2H), 3.29-3.25(t, 2H), 2.90 (s, 3H), 1.58-1.53(m, 2H), 1.33-1.23(m, 10H), 0.90-0.88 (t, 3H). **^{13}C NMR (101 MHz, CDCl3)** δ 148.41, 131.87, 113.76, 107.69, 52.96, 38.51, 31.97, 29.64, 29.45, 27.29, 26.65, 22.80, 14.25.

4-bromo-N-ethyl-N-octylaniline (3b): 91% yield. **^{1}H NMR (400 MHz, CDCl3):** δ 7.29-7.27 (d, 2H), 6.53-6.51 (d, 2H), 3.35-3.30 (m, 2H), 3.22-3.17 (t, 2H), 1.59-1.52

(m, 2H), 1.32-1.25 (m, 10H), 1.15-1.11 (t, 3H), 0.91-0.88 (t, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.05, 131.94, 113.47, 106.96, 50.68, 45.16, 31.97, 29.63, 29.46, 27.49, 27.31, 22.80, 14.25, 12.27.

4-bromo-N-buthyl-N-octylaniline (3c): 91% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.25-7.23 (t, 2H), 6.50-6.48 (d, 2H), 3.24-3.19(m, 4H), 1.57-1.49 (m, 4H), 1.38-1.27 (m, 12H), 0.96-0.92 (t, 3H), 0.90-0.87(t, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 147.03, 131.78, 113.21, 106.62, 51.16, 50.87, 31.89, 29.55, 29.40, 29.23, 27.18, 27.06, 22.73, 20.37, 14.20, 14.09.

4-bromo-N,N-dioctylaniline (3d): 95% yield. A mixture of 4-bromoaniline (0.1 mol), K_2CO_3 (0.25 mol), n-Octyl Bromide (0.2 mol), and DMF (500 ml) was stirred under argon at 80 °C for about 12h. The mixture was then poured into water and extracted with dichloromethane for three times. The organic layer was dried (Na2SO4), filtered, and the solvent was evaporated to obtain colourless oil. The crude product was purified by column chromatography (hexane as eluent). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.25-7.23 (t, 2H), 6.47-6.47 (d, 2H), 3.22-3.19(t, 4H), 1.58-1.49 (m, 4H), 1.34-1.22(m, 20H), 0.90-0.87(t, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 147.05, 131.77, 113.23, 106.63, 51.14, 31.85, 29.51, 29.35, 27.15, 27.05, 22.69, 14.15.



3 4 5 6

Scheme 1. The synthetic route of the IFD derivatives

General Procedure for 5a-d. The reagents **3a-d** (10 mmol) were dissolved in dry tetrahydrofuran (50 ml) under argon, and cooled to -78 °C. A solution of n-BuLi (2.5 M, 4 ml) was added dropwise to the mixture for 30 min. Then the mixture was stirred

at -78 °C for 1h. $B(OBu)_3$ (4 ml,15 mmol) was added. The solution was stirred for 30min at -78 °C, and then it was stirred for 8h at room temperature.

The dimethyl 2,5-dibromoterephthalate (0.7 g, 2 mmol), $Pd(PPh_3)_4$ (116 mg, 0.1 mmol) and Na_2CO_3 (2M, 10 ml) were added into the mixture, and the solution was degassed with argon. The mixture was reflux under argon for 8 h and then was cooled to room temperature. The reaction was quenched with water (30 ml) and extracted whit ethyl acetate (30 ml) for three times. The organic layer was dried (Na_2SO_4), filtered, and evaporated to dryness. The crude product was purified by column chromatography to give the product as yellow solid.

compound 5a: 74% yield. **^{1}H NMR (400 MHz, $CDCl_3$, ppm)** δ 7.73 (s, 2H), 7.23-7.21(d, 4H), 6.73-6.69 (d, 4H), 3.71 (s, 6H), 3.36-3.32 (t, 4H), 2.96 (s, 6H), 1.64-1.58 (m, 4H), 1.33-1.29 (m, 20H), 0.91-0.88 (t, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.58, 148.90, 139.88, 132.89, 131.63, 129.34, 126.98, 111.73, 52.91, 52.31, 38.44, 31.99, 29.68, 29.49, 27.35, 26.92, 22.81, 14.27.

compound 5b: 74% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72(s, 2H), 7.23-7.21(d, 4H), 6.68-6.66 (d, 4H), 3.73(s,6H), 3.42-3.37(t, 4H), 3.29-3.24 (t,4H), 1.65-1.57 (m,4H), 1.33-1.29(m,24H), 1.19-1.16 (t, 6H), 0.91-0.87(t, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.59, 147.49, 139.67, 132.72, 131.52, 129.36, 126.23, 111.26, 52.26, 50.50, 44.97, 31.94, 29.63, 29.46, 27.62, 27.31, 22.77, 14.24, 12.45.

compound 5c: 83% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 (s, 2H), 7.22-7.20(d,4H), 6.66-6.64 (d,4H), 3.74 (s, 6H), 3.31-3.26 (m,8H), 1.63-1.55 (m,8H), 1.39-1.24 (m,24H), 0.98-0.95 (t,6H), 0.91-0.87 (t,6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.65, 147.71, 139.70, 132.73, 131.58, 129.37, 126.15, 111.27, 52.31, 51.15, 50.86, 31.98, 29.66, 29.54, 29.50, 27.37, 27.33, 22.81, 20.50, 14.28, 14.20.

compound 5a: 81% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (s, 2H), 7.22-7.20 (d,4H), 6.66-6.64 (d,4H), 3.72 (s, 6H), 3.30-3.26 (t, 8H), 1.62-1.58 (m,8H), 1.34-1.26 (m,40H), 0.91-0.88 (t,12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.64, 147.81, 139.76, 132.82, 131.58, 129.40, 126.31, 111.38, 52.31, 51.15, 50.86, 31.98, 29.66, 29.54, 29.50, 27.37, 27.33, 22.81, 20.50, 14.28, 14.20.

General Procedure for 6a-d. The compounds **5a-d** (1 mmol) and KOH (5.6 g, 10 mmol, dissolved in 10 ml H_2O) were dissolved in ethanol (20 ml) and heated to reflux for 24 h. After cooling, the EtOH was evaporated to dryness. Hydrochloric acid (6%) was added to neutral, and then saturated ammonium chloride solution was added until no more precipitation occurred. The precipitate was collected and then heated to dryness at 120 °C.

After dryness, the precipitate was mixed with polyphosphoric acid (PPA, 30 g) and heated to 160 °C, keeping vigorous stirring for 3 h. The mixture was poured into ice. The precipitate was collected, washed with water and heated to dryness to afford crude product. The crude product was recrystallized with dimethylformamide (DMF) to give pure product.

MOA-IFD (6a): 57% yield, black needles. **^{1}H NMR (400 MHz, $CDCl_3$, ppm)** δ 7.47 (s, 2H), 7.28-7.26 (d, 2H), 6.99 (d, 2H), 6.69-6.67 (dd, 2H), 3.36-3.32 (t, 4H), 2.99 (s, 6H), 1.62-1.54 (m, 4H), 1.36-1.25 (m, 20H), 0.90-0.86 (t, 6H).**^{13}C NMR (101 MHz, $CDCl_3$, ppm)** δ194.6, 150.0, 145.4, 139.3, 135.6, 130.8, 121.2, 116.4, 114.4, 108.1, 52.9, 38.7, 31.8, 29.5, 29.3, 27.1, 26.7, 22.6, 14.1. **ESI-HRMS** calculated for $C_{38}H_{48}N_2O_2$ ($[M+H]^+$):565.3794; Found: 565.3789.

EOA-IFD (6b): 57% yield, black flacks. **^{1}H NMR (400 MHz, $CDCl_3$, ppm)** δ 7.46 (s, 2H), 7.27-7.25 (d, 2H), 6.96 (d, 2H), 6.66-6.64 (dd, 2H), 3.43-3.38 (t, 4H), 3.30-3.26 (t, 4H), 1.61-1.59 (m, 4H), 1.34-1.25 (m, 20H), 1.19-1.16 (t, 6H), 0.90-0.87 (t, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ = 194.71, 149.02, 145.52, 139.48, 135.96, 130.57, 121.46, 116.32, 114.43, 108.14, 50.91, 45.45, 31.97, 29.63, 29.46, 27.78, 27.31, 22.80, 14.22, 12.56. **ESI-HRMS** calculated for $C_{38}H_{48}N_2O_2$ ($[M+H]^+$):593.411; Found: 593.4106.

BOA-IFD (6c): 62% yield, black flacks. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47(s,2H), 7.28-7.26(d,2H), 6.97-6.96(d,2H), 6.67-6.64(dd, 2H), 3.34-3.29 (m, 8H), 1.64,-1.56 (m, 8H), 1.38-1.31 (m, 24H), 1.00-0.97(s, 6H), 0.93-0.89(s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 194.81, 149.13, 145.49, 139.44, 135.88, 130.43, 121.41, 116.27, 114.38, 108.10, 51.47, 51.19, 31.97, 29.67, 29.63, 29.47, 27.51, 27.28, 22.80, 20.47, 14.25, 14.14. **ESI-HRMS** calculated for $C_{38}H_{48}N_2O_2$ ($[M+H]^+$):649.473; Found:

649.4731.

DOA-IFD (6d): 57% yield, black powders. **^{1}H NMR (400 MHz, $CDCl_3$, ppm)** δ 7.46 (s, 2H), 7.26-7.24 (d, 2H), 6.95 (s, 2H), 6.64-6.62 (d, 2H), 3.31-3.27 (t, 8H), 1.60-1.56 (m, 8H), 1.32-1.28 (m, 40H), 0.90-0.87 (t, 12H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ = 194.67, 149.20, 145.50, 139.50, 135.94, 130.50, 121.43, 116.35, 114.41, 108.19, 51.51, 31.98, 29.62, 29.46, 27.53, 27.29, 22.80, 14.22. **ESI-HRMS** calculated for $C_{38}H_{48}N_2O_2$ ($[M+H]^+$):761.599; Found: 761.5981.

Intermolecular interactions

Table S1. Intermolecular interactions including electrostatic interactions, dispersion, repulsion, and polarization energy components. The dimer 1 (D1), dimer 2 (D2) and dimer 3 (D3) are the edge-to-edge, face-to-face and edge-to-face stacked molecules (Figure 3), respectively.

		E_ele (kJ/mol)	E_pol (kJ/mol)	E_dis (kJ/mol)	E_rep (kJ/mol)	E_tot (kJ/mol)
MOA-IFD	D1	-15	-7.38	-27.46	19.79	-33.01
	D2	-3.31	-4.72	-152.62	69.67	-96.86
	D3	-12.4	-2.63	-38.34	20.78	-35.6
aEOA-IFD	D1	-27.58	-10.52	-88.35	73.23	-68.65
	D2	-22.81	-4.33	-102.72	69.3	-73.95
	D3	-21.53	-4.67	-106.34	58.82	-82.49
bEOAIFD	D1	-26.43	-10.47	-82.49	59.41	-70.84
	D2	-8.18	-4.17	-96.72	45.84	-67.64
	D3	-16.06	-4.97	-91.98	36.03	-78.5
BOAIFD	D1	-25.89	-11.64	-63.94	49.17	-61.29
	D2	-11.67	-3.61	-97.24	47.63	-70.25
	D3	-11.67	-3.61	-97.24	47.63	-70.25

The 2D-GIXRD patterns of the films annealed at different temperature

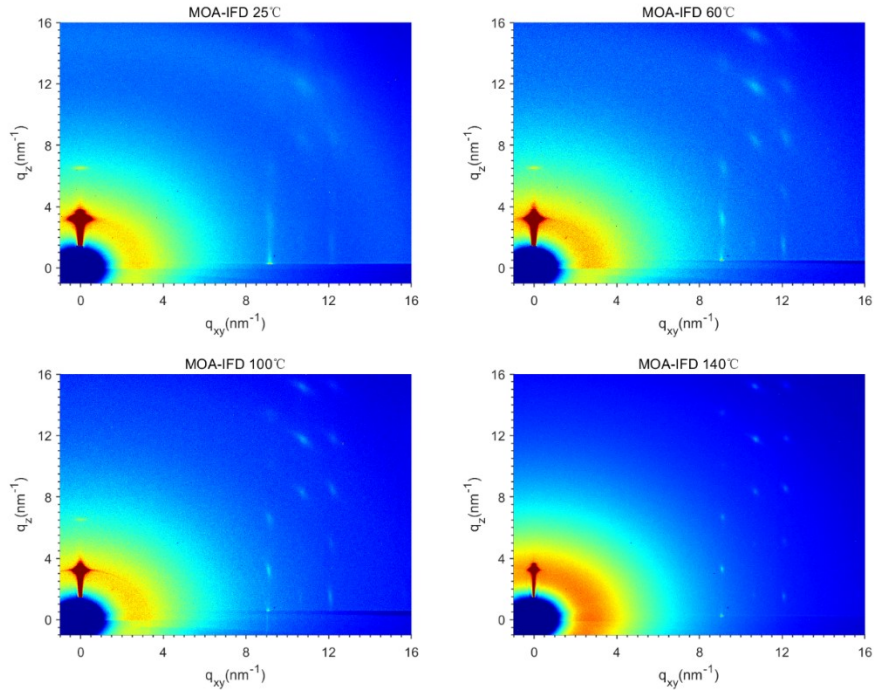


Figure S1. The 2D-GIXDs of the MOA-IFD films annealed at different temperature.

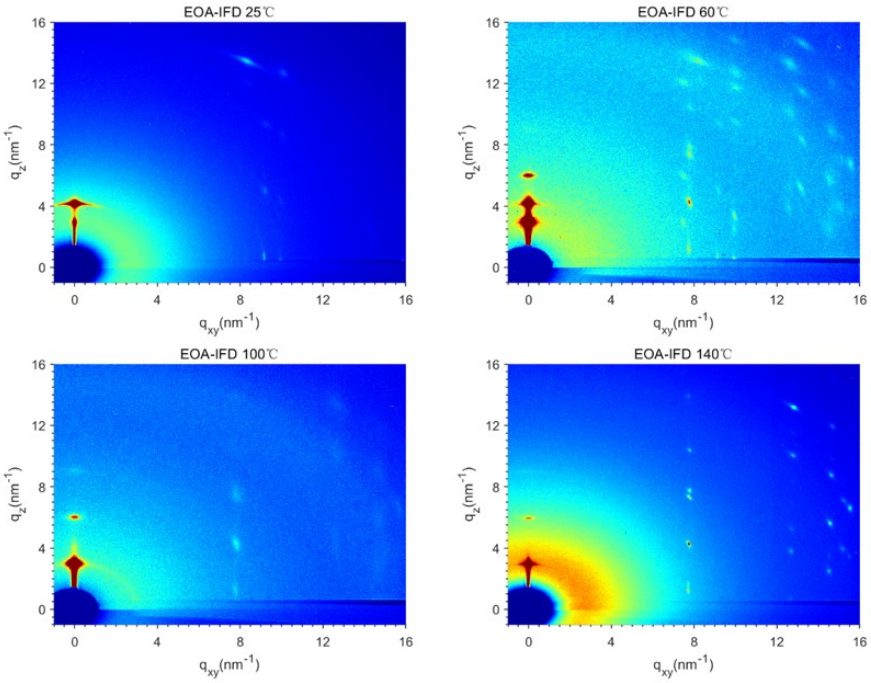


Figure S2. The 2D-GIXDs of the EOA-IFD films annealed at different temperature.

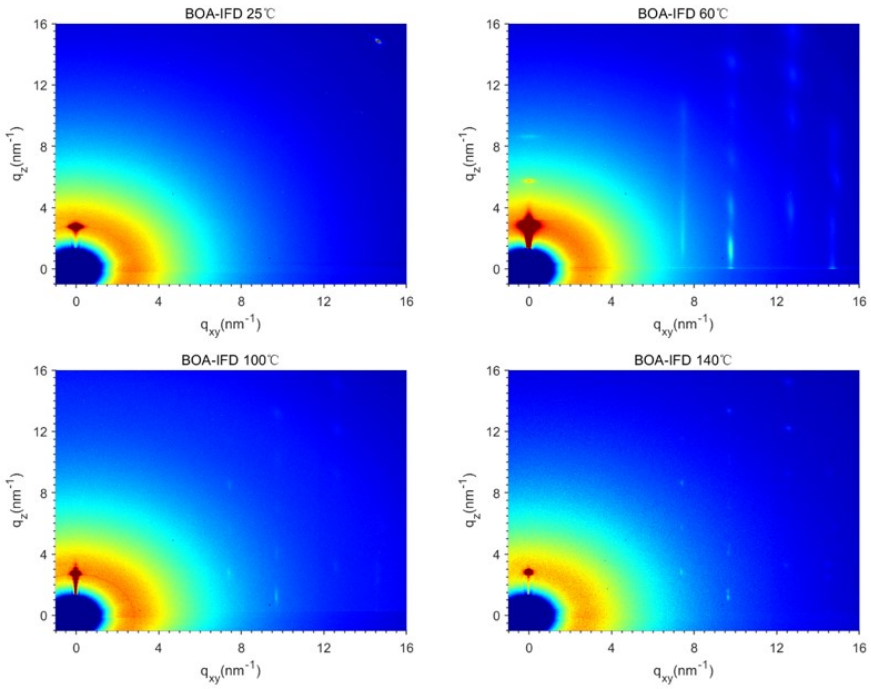


Figure S3. The 2D-GIXDs of the BOA-IFD films annealed at different temperature.

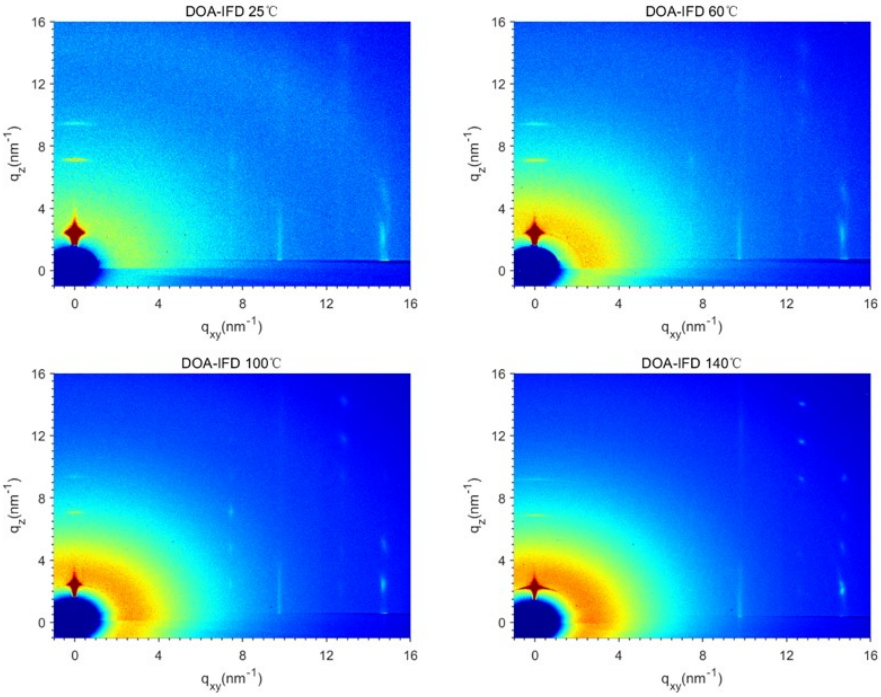


Figure S4. The 2D-GIXDs of the DOA-IFD films annealed at different temperature.

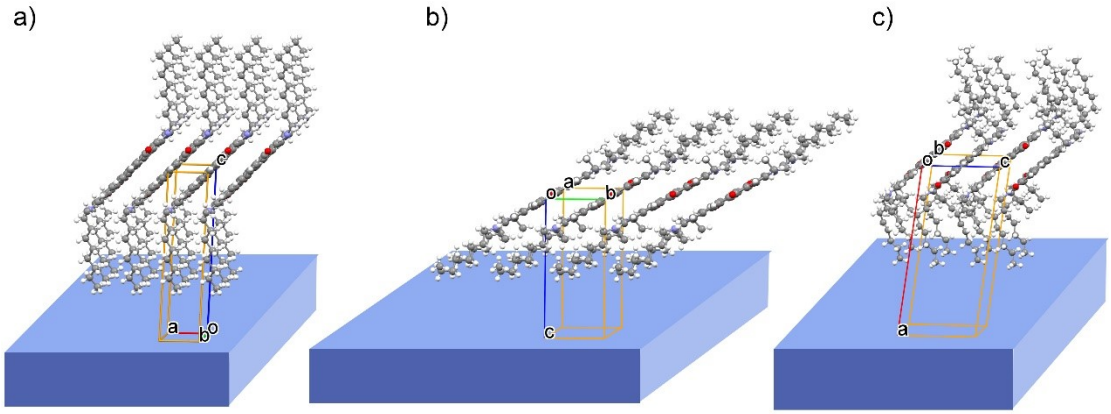


Figure S5. The molecular orientation in the films of the a) MOA-IFD, b) EOA-IFD and c) BOA-IFD/DOA-IFD on the substrate. The 2D-GIXRD results reveal that the (001) plane is parallel with the surface of the substrate for the triclinic crystals including MOA-IFD and EOA-IFD, while the (100) plane is parallel with the surface of the substrate for the monoclinic crystals including the BOA-IFD and DOA-IFD.