

1 Supplementary Information

2 **Deuteration-enhanced neutron contrasts to probe amorphous domain**
3 **sizes in organic photovoltaic bulk heterojunction films**

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41 **Supplementary Notes**

42

43 **Supplementary Note 1.** Synthesis and characterizations of *d*-Y6 and *d*-Y7.

44 **Compound S2.** To the round bottom flask (25 mL) charged with dodecanoic-D23 acid

45 (2.0 g, 9.0 mmol) under nitrogen atmosphere, thionyl chloride (SOCl₂) (1.3 mL, 18.0

46 mmol) was added. The reaction mixture was placed into preheated oil bath at 60 °C.

47 After 5 minutes the nitrogen balloon was changed, due to hydrogen chloride gas

48 released in the reaction, this process was continued until there is no more hydrogen

49 chloride gas evolved from the reaction. Excess thionyl chloride was removed under

50 reduced pressure and dried over high vacuum for overnight. The residue Compound S1

51 is used in next step without further purification. To a stirring mixture solution of 3-

52 bromothiophene (1.3 g, 8.0 mmol) and Compound 1 (2.0 g, 8.0 mmol) in CH₂Cl₂ (30

53 mL), AlCl₃ (1.0 g, 8.0 mmol) was added in portions over 15 min. The resulting solution

54 was stirred for 3 h at room temperature. Cold water (20 mL) was then slowly added to

55 quench the reaction. The crude product was extracted from the mixture solution with

56 CH₂Cl₂ (3 × 20 mL). The combined organic layers were washed with brine and dried

57 over anhydrous MgSO₄. Removal of the organic solvent gives the colorless liquid

58 product of Compound S2 (3.8g, 84%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.5 (d, *J*

59 = 5.2 Hz, 1H), 7.1 (d, *J* = 5.2 Hz, 1H).

60 **Compound S4.** To a stirring mixture solution of Compound S2 (2.0 g, 5.0 mmol) and

61 K₂CO₃ (1.6 g, 11.0 mmol) in DMF (30 mL), ethyl thioglycolate (0.58 mL, 5.3 mmol)

62 was added. The resulting mixture solution was stirred for 24 h at ambient temperature.

63 A solution of NaOH (0.05 g, 1.3 mmol) in ethanol (3 mL) was added, and the reaction

64 was continued for another 24 h. The reaction mixture was poured into water (50 mL)

65 and extracted with ethyl acetate (3×20 mL). The organic layer was washed with water

66 (3×20 mL) and dried over anhydrous MgSO_4 . The crude product of Compound S3

67 was obtained by removing organic solvents and used directly for the next step without

68 further purification. To a mixture solution of Compound S3 (1.5 g, 1.5 mmol) in ethanol

69 (30 mL), NaOH (0.16 g, 4.0 mmol) was added. The resulting solution was heated to

70 reflux for ca. 3 h. After starting materials was completely consumed by TLC indication,

71 the solvent was removed in vacuo. 30 mL of water was added to the residue. The pH

72 was adjusted to 1 with 10 M HCl to precipitate the titled product. Recrystallization from

73 hexane gave the product Compound S4 (1.1 g, 80%). $^1\text{H NMR}$ (400 MHz, Chloroform-

74 *d*) δ 7.5 (d, $J = 5.2$ Hz, 1H), 7.1 (d, $J = 5.2$ Hz, 1H), 2.8 (s, 2H).

75 **Compound S5.** A mixture of Compound S4 (1.0 g, 2.8 mmol), copper (0.09 g, 1.46

76 mmol), and quinoline (5 mL) was heated to reflux for 3 h. The resultant solution was

77 concentrated by vacuum distillation. Ethyl acetate (20 mL) was added, and the collected

78 organic layer was washed with 1 M HCl (3×15 mL) and dried over anhydrous MgSO_4 .

79 The solvent was removed in vacuo, and the residue was passed through a silica gel

80 column eluting with hexane to yield Compound S5 (550 mg, 63%). $^1\text{H NMR}$ (400 MHz,

81 Chloroform-*d*) δ 7.4 (dd, $J = 5.2, 1.6$ Hz, 1H), 7.2 (d, $J = 5.2$ Hz, 1H), 7.0 (d, $J = 1.3$

82 Hz, 1H), 2.7 (s, 2H).

83 **Compound 1.** Compound S5 (500 mg, 1.6 mmol) was dissolved in anhydrous
84 tetrahydrofuran (THF, 20 mL) in an argon atmosphere, and stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min.
85 *n*-butyllithium (1.6 mmol, 2.5 mol/L, 0.64 mL) was added into the solution by dropwise
86 at $-78\text{ }^{\circ}\text{C}$ and continued to stir for 2 h. Tributyltin chloride (220 mg, 0.67 mmol) was
87 dripped in the mixture. After stirring for 30 min, the mixture was moved to room
88 temperature and reacted overnight. Then, the mixture was extracted with
89 dichloromethane, concentrated in vacuo, and dried to produce crude product. Then,
90 redissolve the crude product in hexanes and filter, and condense the filtrate to obtain
91 the Compound 1 (820 mg, 85%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.2 (s, 1H), 6.9
92 (s, 1H), 2.7 (s, 2H), 1.7 – 1.5 (m, 6H), 1.4 – 1.3 (m, 6H), 1.2 – 1.0 (m, 6H), 0.9 (t, $J =$
93 7.3 Hz, 9H).

94 **Compound S7.** To a solution of Compound S6 (1.5 g, 10 mmol) in acetic anhydride
95 (10 mL) and triethylamine (5.0 mL) was added ethyl acetoacetate (1.4 mL, 11.0 mmol)
96 under argon. The mixture was stirred at room temperature for 12 h, and then the mixture
97 was poured into the mixture of concentrated HCl (10 g) and ice-water (10 g). After that,
98 the mixture was stirred for half an hour at room temperature, additional HCl (18.0 mL,
99 5M) was added into the mixture, and then the mixture was refluxed for 2 h. After the
100 crude product was cooled to room temperature, add water (100 mL) and then the
101 mixture was extracted with CHCl_3 ($3 \times 50\text{ mL}$). The organic phase was dried over
102 anhydrous MgSO_4 . After removing the solvent, the residue was purified using column
103 chromatography on silica gel employing CHCl_3 as an eluent, yielding a pale yellow

104 solid (755 mg, 51%). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 3.25 (s, 2H).

105 ***d*-IC.** To a solution of Compound 6 (150 mg, 1.0 mmol) and malononitrile (130 mg,
106 2.0 mmol) in ethanol (20 mL) was added sodium acetate (107 mg, 1.3 mmol). The
107 mixture was stirred for 2 h at room temperature. A volume of 30 mL of H₂O was added,
108 and the mixture was stirred at room temperature for half an hour, and then a drop of
109 concentrated HCl was added to acidify the mixture with PH = 2. After that, the brown
110 solid was filtered off and washed with water (4 \times 100 mL). The residue was purified
111 using column chromatography on silica gel employing CH₃OH/CHCl₃ (1:1, v/v) as an
112 eluent, yielding a brown solid (118 mg, 46.6%). $^1\text{H NMR}$ (400 MHz, Acetone-*d*6) δ
113 3.31 (s, 2H).

114 **Compound S9.** Synthesis of Compound S9 was carried out in a similar manner to that
115 of Compound S7. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 3.26 (s, 2H).

116 ***d*-2FIC.** Synthesis of Compound *d*-2FIC was carried out in a similar manner to that of
117 *d*-IC. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 3.75 (s, 2H).

118 **Compound 3.** Compound 1 (2.7 g, 4.4 mmol), compound 2 (0.8 g, 2.0 mmol) and
119 Pd(PPh₃)₂Cl₂ (62 mg, 0.09 mmol) were dissolved in 30 mL of dry toluene and stirred at
120 80 °C overnight. The reaction mixture was allowed to cool to room temperature. 100
121 mL of water was added, and the mixture was extracted with dichloromethane (2 \times 100
122 mL). The precipitate was filtered and washed with methanol and *n*-hexane. The product
123 of Compound 3 was obtained as a red solid.

124 **Compound 4.** Compound 3 (850 mg, 1.0 mmol) and triphenylphosphine (3.2 g, 10.0

125 mmol) were dissolved in the *o*-dichlorobenzene (15 mL) under nitrogen. After being
126 heated at 180 °C overnight, the aqueous phase was extracted with dichloromethane and
127 the organic layer was dried over Na₂SO₄ and filtered. After removing the solvent, the
128 red residue was added into a three-necked round bottom flask. 1-Bromo-2-ethylhexane-
129 D17 (3.0 g, 1.5 mmol), KI (1.3 g, 7.8 mmol), K₂CO₃ (3.2 g, 23.2 mmol) and DMF (30
130 mL) were added and the mixture was deoxygenated with argon for 15 min. The mixture
131 was refluxed at 80 °C for overnight. After removing the solvent from the filtrate, the
132 residue was extracted with ethyl acetate and H₂O. The organic layers were combined
133 and dried over MgSO₄, filtered and purified with column chromatography on silica gel
134 using *n*-hexane/dichloromethane (10/1, v/v) as the eluent to give a red solid (532 mg,
135 51%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.0 (s, 2H), 2.8 (s, 4H). MS (MALDI-TOF)
136 calcd for C₅₆H₆D₇₆N₄S₅: 1046.9913; found: 1046.5179 (M⁺).

137 **Compound 5.** A Vilsmeier reagent was prepared firstly. 8 mL anhydrous DMF was
138 added to a dry 100 mL two-necked round bottom flask, and the solution was cooled to
139 0 °C and stirred when 0.8 mL phosphorous oxychloride (POCl₃) was added by syringe
140 under argon protection. The mixture kept at 0 °C for 2 h, and then Compound 4 (420
141 mg, 0.4 mmol) in dry 1,2-dichloroethane (25 mL) was added. Then, the mixture
142 solution was allowed to reflux overnight. After cooling to room temperature, 100 mL
143 water was added to quench the reaction. The mixture was extracted with
144 dichloromethane, and the organic layer was collected, washed with water and dried with
145 anhydrous MgSO₄. After removal of the solvent under reduced pressure, the residue

146 was purified by column chromatography on silica gel using a mixture solvent as eluent
147 (petroleum ether/dichloromethane, v/v = 1/1) to give a yellow solid (389 mg, 88%). ¹H
148 NMR (400 MHz, Chloroform-*d*) δ 10.1 (s, 2H), 3.2 (s, 4H). MS (MALDI-TOF) calcd
149 for C₅₈H₆D₇₆N₄O₂S₅: 1102.9811; found: 1102.3838 (M⁺).

150 ***d*-Y6**. To a three-necked round bottom flask were added Compound 5 (220 mg, 0.2
151 mmol), *d*-2FIC (140 mg, 0.6 mmol), pyridine (0.15 mL) and chloroform (25 mL). The
152 mixture was deoxygenated with nitrogen for 20 min and then stirred at reflux for 12 h.
153 After cooling to room temperature, the mixture was poured into methanol (200 mL)
154 and filtered. The residue was purified by column chromatography on silica gel using a
155 mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 1/1) to give a blue
156 solid (255 mg, 83%). ¹H NMR (400 MHz, Chloroform-*d*) δ 9.2 (s, 2H), 3.2 (s, 4H). ¹³C
157 NMR (100 MHz, Chloroform-*d*) δ 186.3, 159.0, 154.1, 147.7, 145.3, 137.9, 136.1,
158 135.4, 134.6, 134.0, 133.3, 130.7, 120.1, 115.1, 114.7, 113.7, 68.9, 29.8. The presence
159 of C-F coupling is evidenced by the doublet at δ 155.64 (d, *J*=16.2 Hz), 153 (dd, *J*=14.8,
160 7.3 Hz). HRMS (MALDI) calculated for C₈₂H₆D₈₀F₄N₈O₂S₅: 1531.0429; found:
161 1531.0424 (M⁺). Elemental analysis calculated for C₈₂H₇D₈₀F₄N₈O₂S₅: C, 64.23; N,
162 7.31. Found: C, 64.12; N, 7.13.

163 ***d*-Y7** The material was synthesized following the same route as *d*-Y6. ¹H NMR (400
164 MHz, Chloroform-*d*) δ 9.17 (s, 1H), 8.79 (s, 1H), 7.97 (s, 1H), 3.21 (s, 2H) ppm; ¹³C
165 NMR (151 MHz, Chloroform-*d*) δ 186.42, 158.89, 154.37, 147.68, 145.46, 139.71,
166 139.31, 138.90, 137.93, 136.38, 136.21, 135.97, 134.04, 133.70, 131.01, 127.06,

167 125.16, 120.08, 115.19, 114.71, 113.81, 68.90, 29.80, 29.47 ppm.

168

169 **Supplementary Note 2.** Synthesis and characterizations of *d*-IDIC.

170 **Compound S11.** To a suspension of Compound S10 (500 mg, 1.9 mmol) in anhydrous

171 DMSO (15 ml) was added potassium tert-butoxide (1.2 g, 11.3 mmol) in portion. The

172 reaction mixture was heated at 80 °C for 1 h, followed by the addition of 1-

173 Bromohexane-D13 (2.0 g, 11.3 mmol) dropwise. After complete addition, the resultant

174 mixture was heated at 90 °C for 5 h, then poured into ice-water. The resulting mixture

175 was extracted with chloroform (3 × 50 mL) and the combined organic extracts were

176 washed with brine. The organic mixture was dried over anhydrous magnesium sulfate.

177 After filtration, the solvent was removed by rotary evaporation to give a brown liquid.

178 The crude product was purified by column chromatography using

179 hexane/dichloromethane (v/v = 4:1) as the eluent to afford pale yellow solid (1.1 g,

180 87%). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.20 (s, 2H), 7.18 (d, *J* = 4.6 Hz, 2H), 6.89

181 (d, *J* = 4.8 Hz, 2H). MS (MALDI-TOF) calcd for C₄₀H₆D₅₂S₂: 654.7244; found:

182 654.7194 (M⁺).

183 **Compound S12.** A Vilsmeier reagent was prepared firstly. 8 mL anhydrous DMF was

184 added to a dry 100 mL two-necked round bottom flask, and the solution was cooled to

185 0 °C and stirred when 0.8 mL phosphorous oxychloride (POCl₃) was added by syringe

186 under argon protection. The mixture kept at 0 °C for 2 h, and then Compound S11 (280

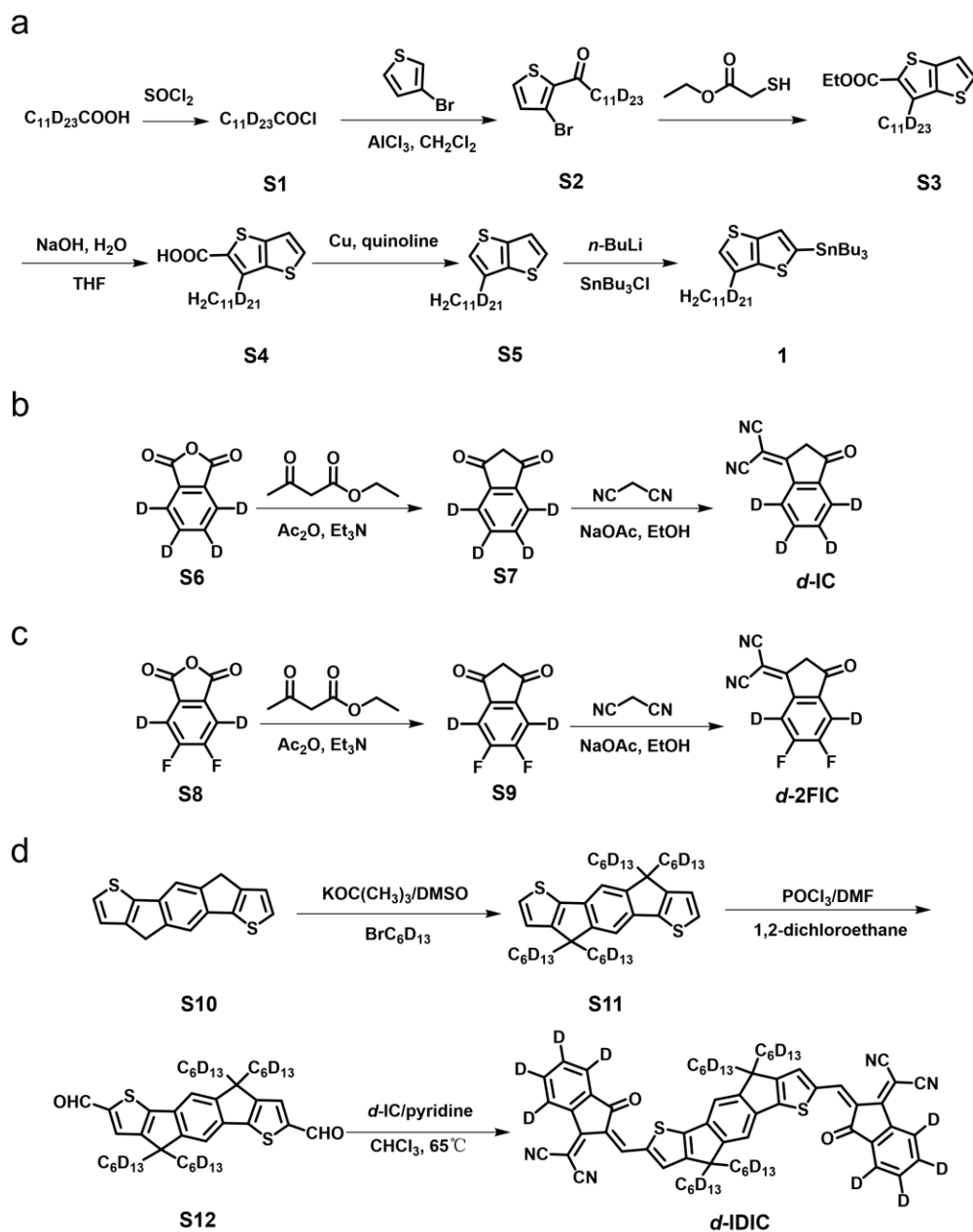
187 mg, 0.4 mmol) in dry 1,2-dichloroethane (25 mL) was added. Then, the mixture

188 solution was allowed to reflux overnight. After cooling to room temperature, 100 mL
189 water was added to quench the reaction. The mixture was extracted with
190 dichloromethane, and the organic layer was collected, washed with water and dried with
191 anhydrous MgSO₄. After removal of the solvent under reduced pressure, the residue
192 was purified by column chromatography on silica gel using a mixture solvent as eluent
193 (petroleum ether/dichloromethane, v/v = 1/1) to give a yellow solid (270 mg, 89%). ¹H
194 NMR (500 MHz, Chloroform-*d*) δ 9.9 (s, 2H), 7.6 (d, *J* = 1.4 Hz, 2H), 7.5 (s, 2H). MS
195 (MALDI-TOF) calcd for C₄₂H₆D₅₂O₂S₂: 710.7142; found: 710.6473 (M⁺).

196 ***d*-IDIC**. To a three-necked round bottom flask were added Compound S12 (142 mg,
197 0.2 mmol), *d*-IC (120 mg, 0.6 mmol), pyridine (0.15 mL) and chloroform (25 mL). The
198 mixture was deoxygenated with nitrogen for 20 min and then stirred at reflux for 12 h.
199 After cooling to room temperature, the mixture was poured into methanol (200 mL)
200 and filtered. The residue was purified by column chromatography on silica gel using a
201 mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 1/1) to give a blue
202 solid (173 mg, 81%). ¹H NMR (400 MHz, Chloroform-*d*) δ 9.0 (s, 2H), 7.7 (s, 2H), 7.6
203 (s, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 188.5, 160.9, 160.4, 157.7, 156.8, 141.3,
204 140.1, 138.7, 138.1, 137.9, 137.1, 122.2, 116.2, 115.0, 114.9, 69.1, 54.2. HRMS
205 (MALDI) calculated for C₆₆H₆D₆₀N₄O₂S₂: 1070.8388; found: 1070.8384 (M⁺).
206 Elemental analysis calculated for C₆₆H₆D₆₀N₄O₂S₂: C, 73.96; N, 5.23. Found: C, 73.56;
207 N, 5.07.

208

209 **Supplementary Figures**

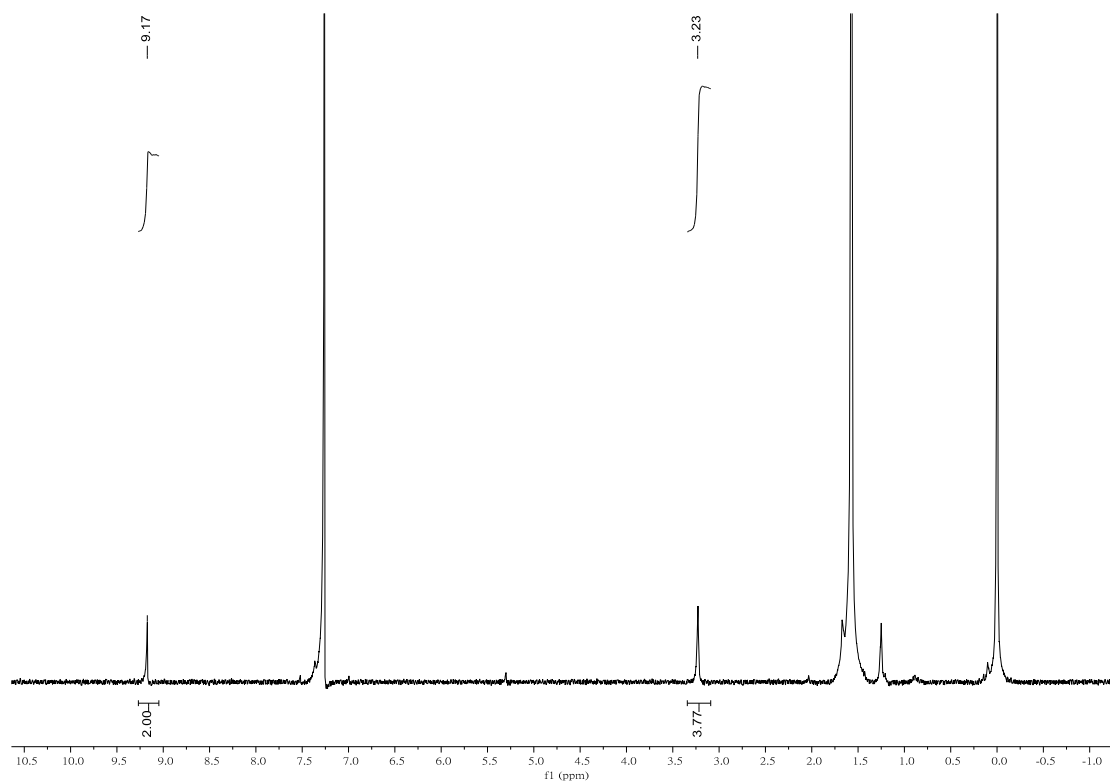


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211 **Supplementary Fig. 1 Synthetic routes.** Synthetic routes of **a** Compound 1, **b** *d*-IC, **c**

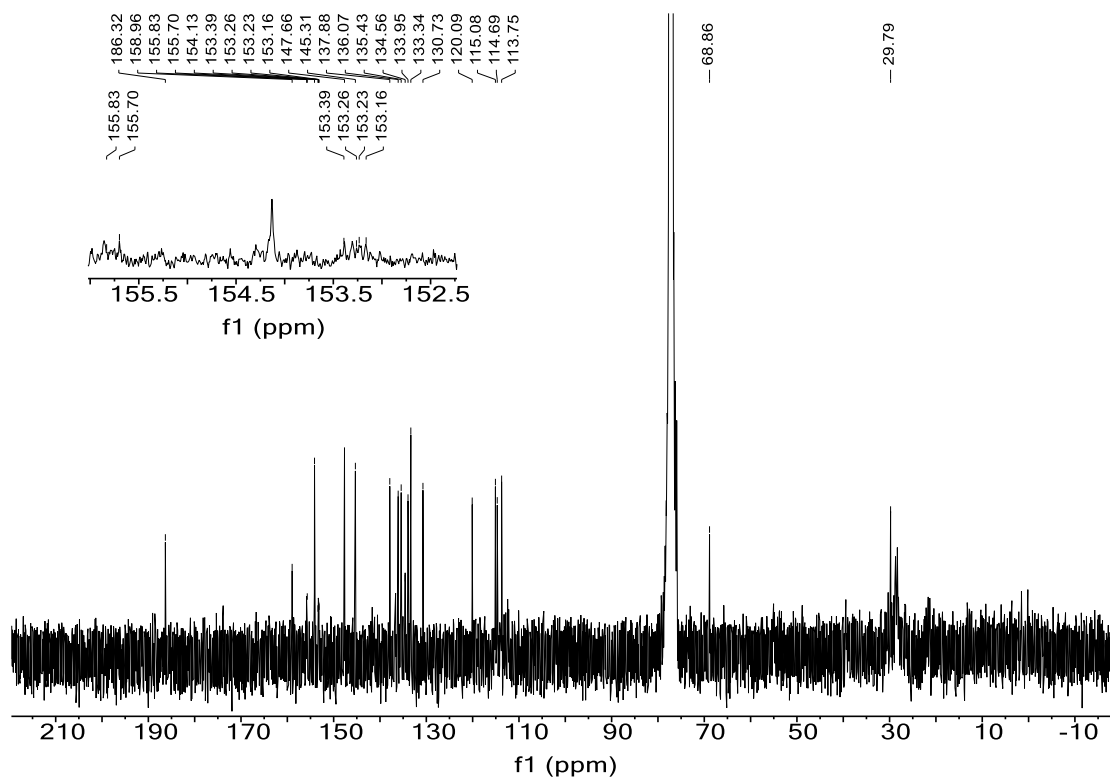
212 *d*-2FIC, and **d** *d*-IDIC.

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214

215 **Supplementary Fig. 2** ^1H NMR spectrum of *d*-Y6.

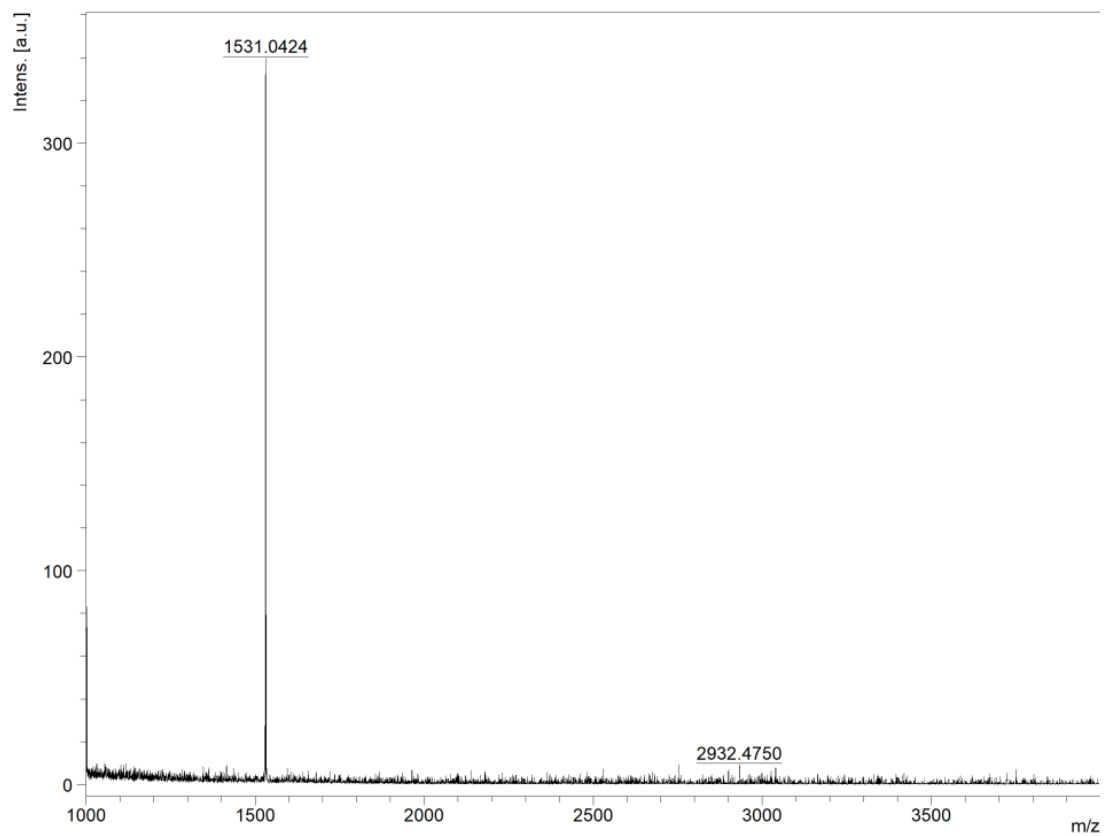


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217 **Supplementary Fig. 3** ^{13}C NMR spectrum of *d*-Y6. The inset is the enlarged spectrum

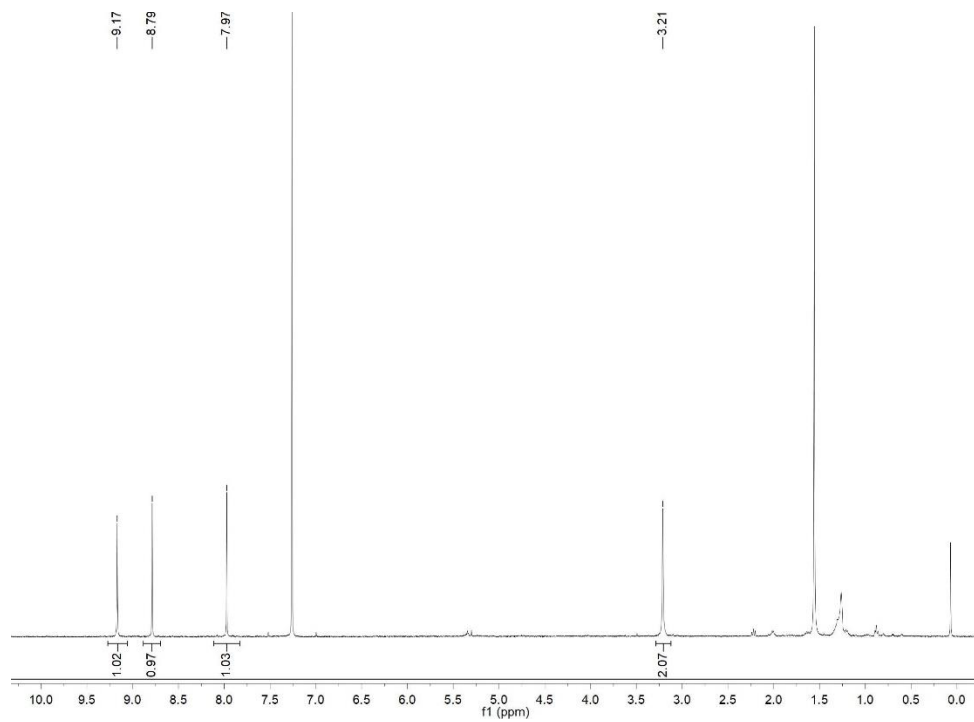
218 between 152 and 156 ppm to highlight the presence of C-F coupling.

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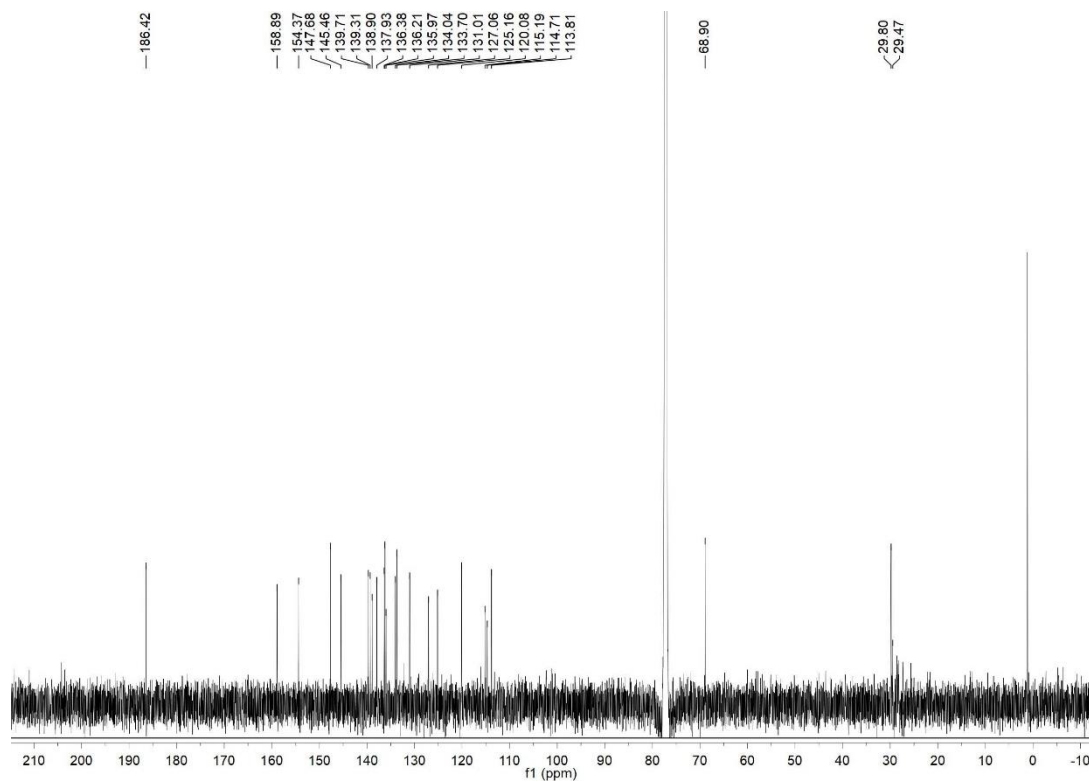
220

221 **Supplementary Fig. 4** HRMS (MALDI) spectrum of *d*-Y6.



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223 **Supplementary Fig. 5** ¹H NMR spectrum of *d*-Y7.

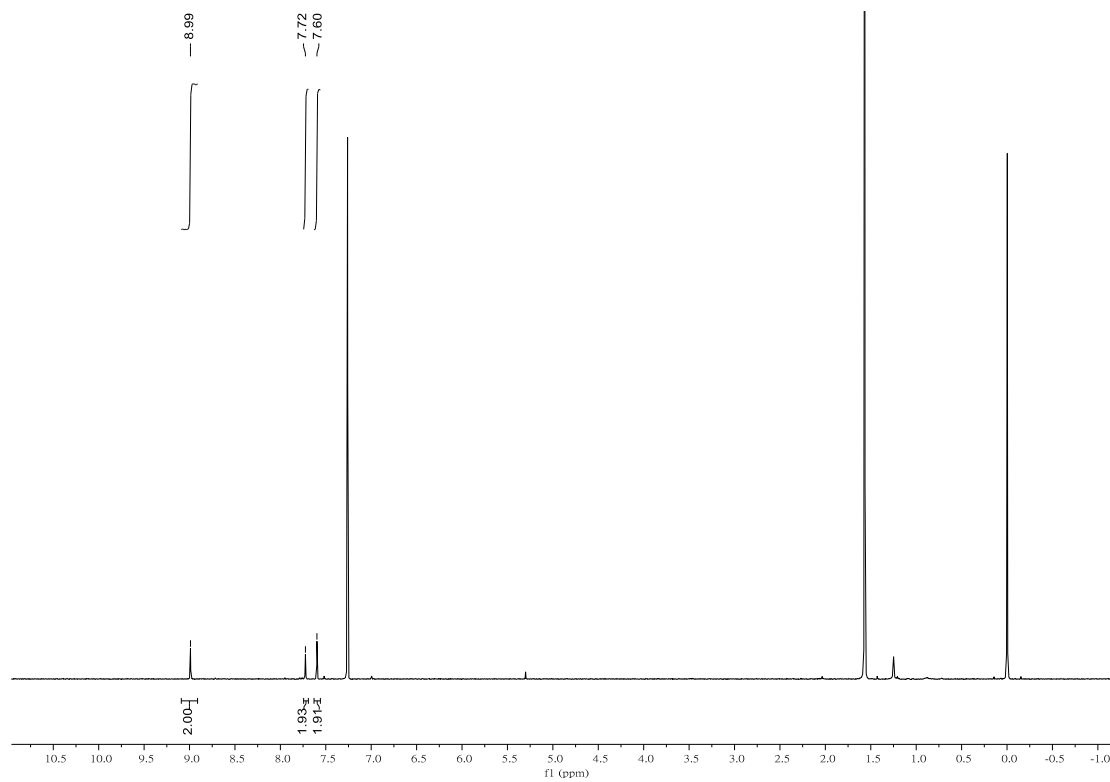


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225 **Supplementary Fig. 6** ^{13}C NMR spectrum of *d*-Y7.

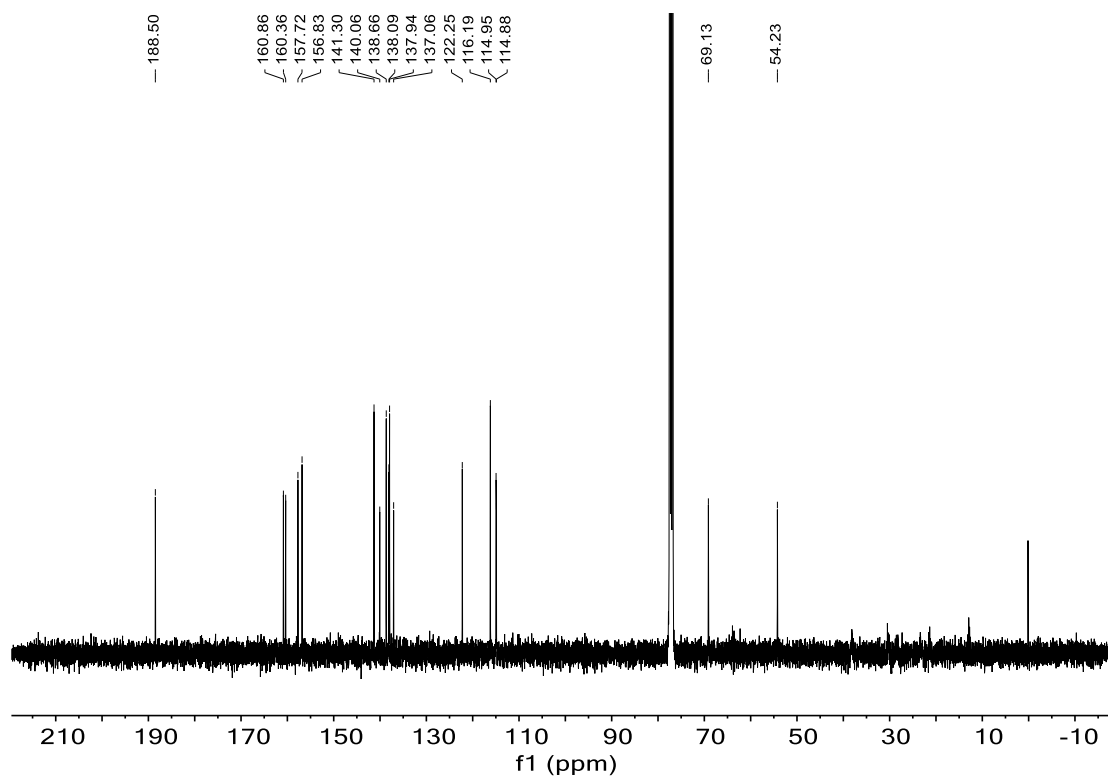
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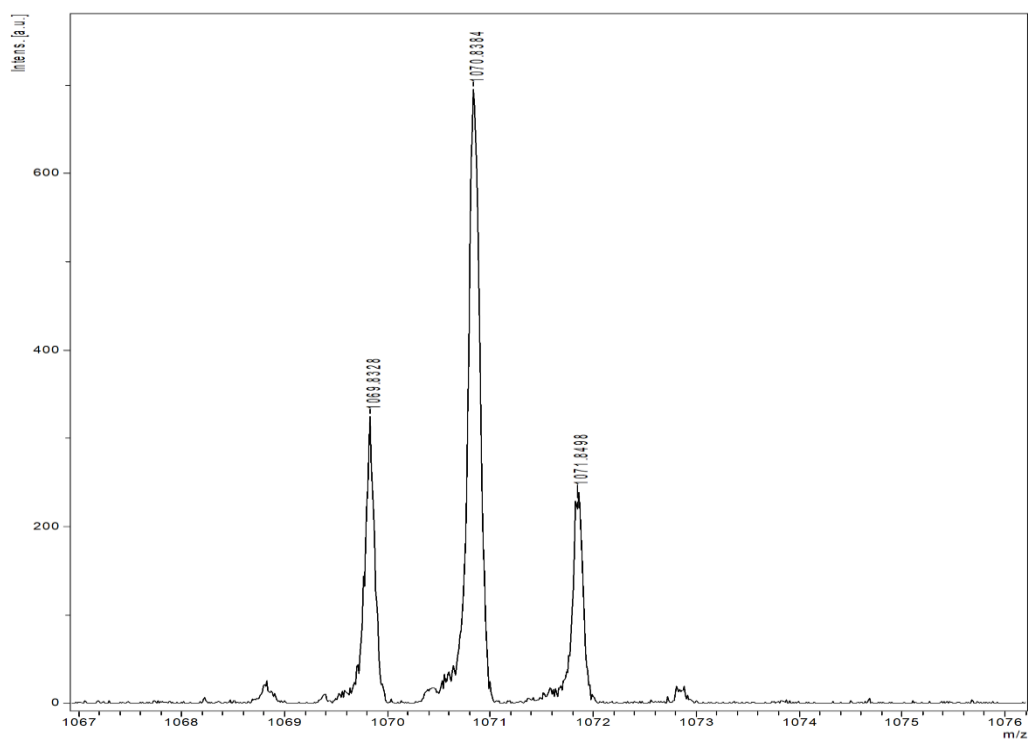
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229 **Supplementary Fig. 7** ^1H NMR spectrum of *d*-IDIC.



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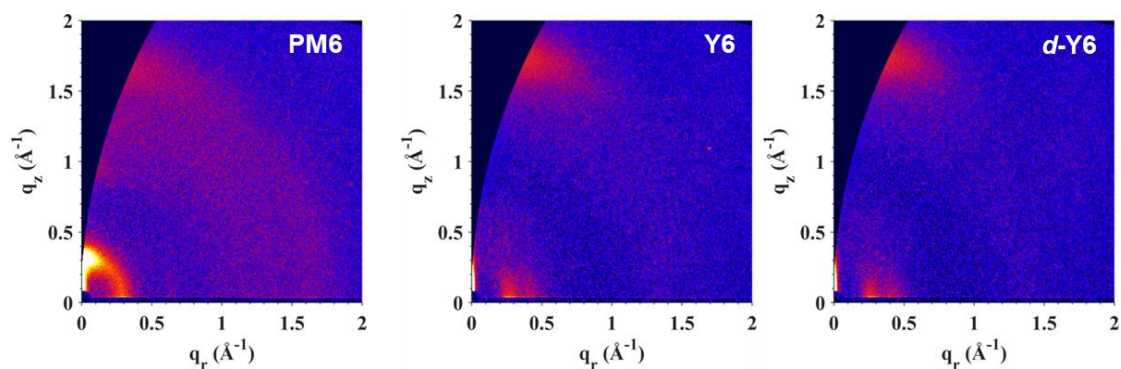
231 **Supplementary Fig. 8** ^{13}C NMR spectrum of *d*-IDIC.



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233 **Supplementary Fig. 9** HRMS (MALDI) spectrum of *d*-IDIC.

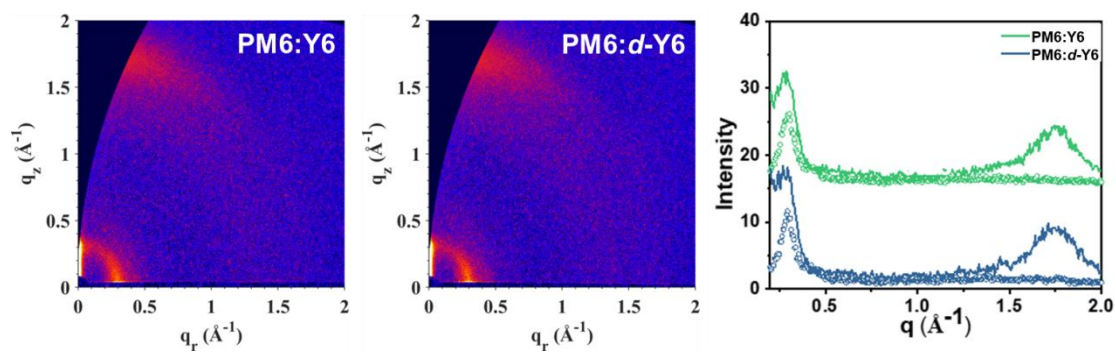
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236 **Supplementary Fig. 10** 2D GIWAXS patterns of pure PM6, Y6, and *d*-Y6 films.

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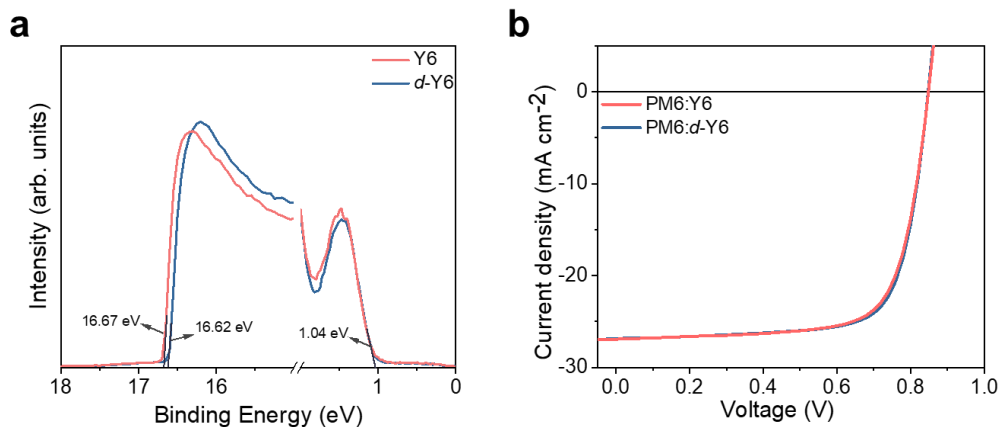
238

239 **Supplementary Fig. 11** 2D GIWAXS patterns and intensity profiles along the in-plane

240 (dashed line) and out-of-plane (solid line) directions of PM6:Y6 and PM6:*d*-Y6.

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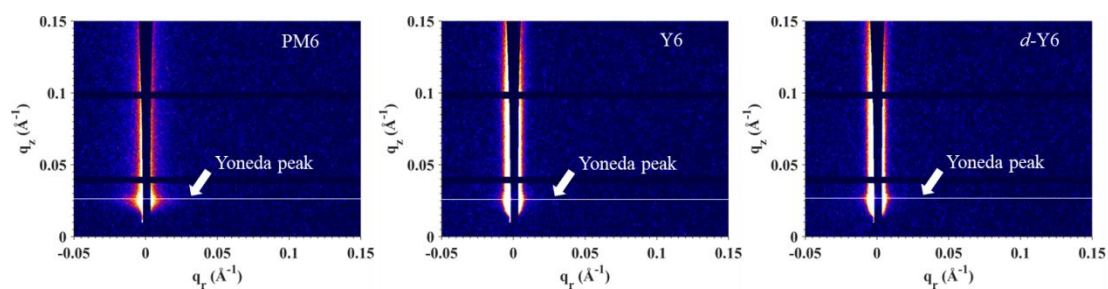


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244 **Supplementary Fig. 12 a** UPS spectra of PM6:Y6 and PM6:*d*-Y6 blend films and **b**

245 *J*-*V* curves of the corresponding devices.

246



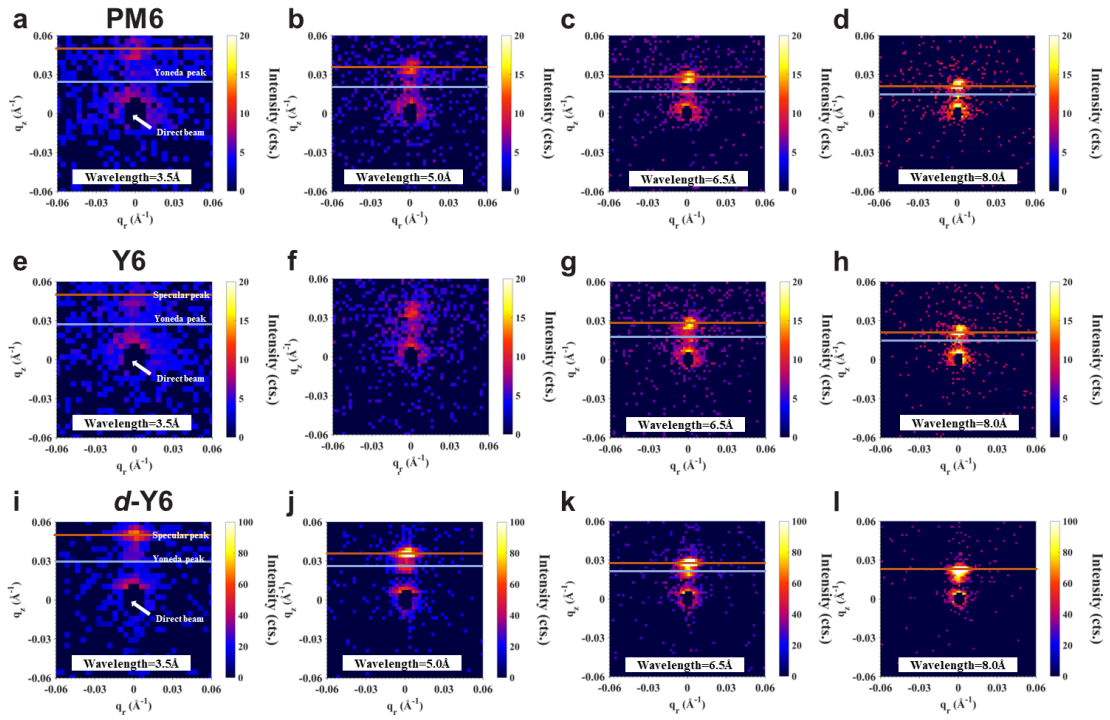
247

248 **Supplementary Fig. 13** 2D GISAXS patterns of pure PM6, Y6, and *d*-Y6 films

249 measured with the vertical beam stop. The Yoneda peak was marked by the white line

250 for each film.

251



252

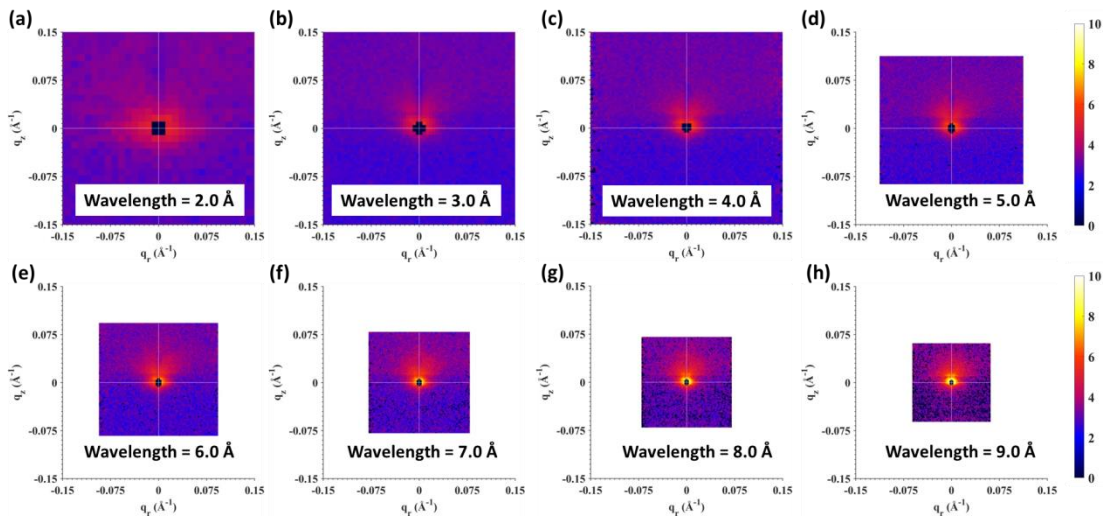
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Supplementary Fig. 14 2D TOF-GISANS data of **a-d** pure PM6, **e-h** Y6 and **i-l** *d*-Y6

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films with different peak neutron wavelengths, taken at the same incident angle of 0.804° .

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256

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Supplementary Fig. 15 2D TOF-GISANS patterns of the PM6:Y6 blend film

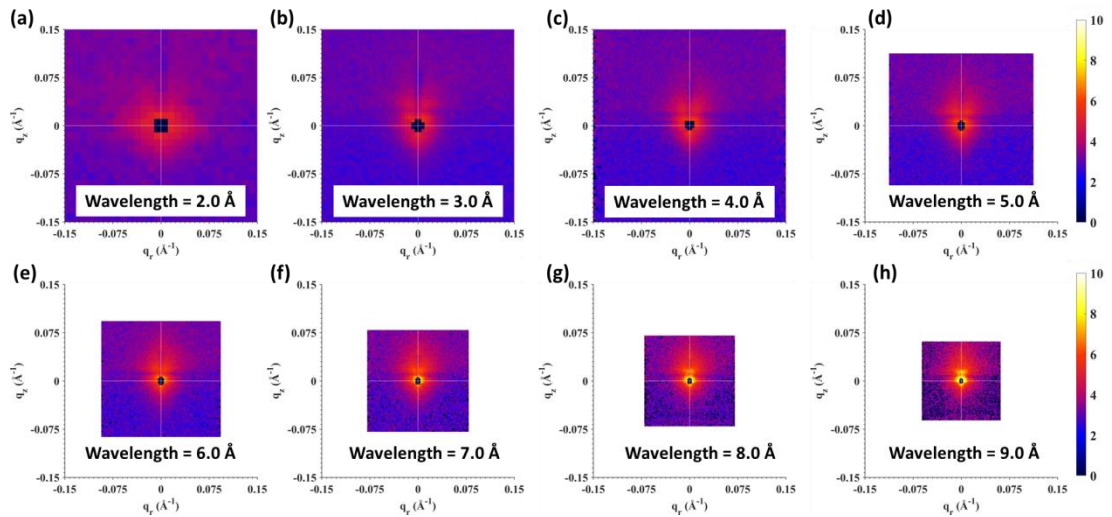
258

measured at wavelengths of **a-h** 2-9 Å. All measurements were taken at the same

259

incident angle of 0.606° .

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261

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Supplementary Fig. 16 2D TOF-GISANS patterns of the PM6:*d*-Y6 blend film

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measured at wavelengths of **a-h** 2-9 Å. All measurements were taken at the same

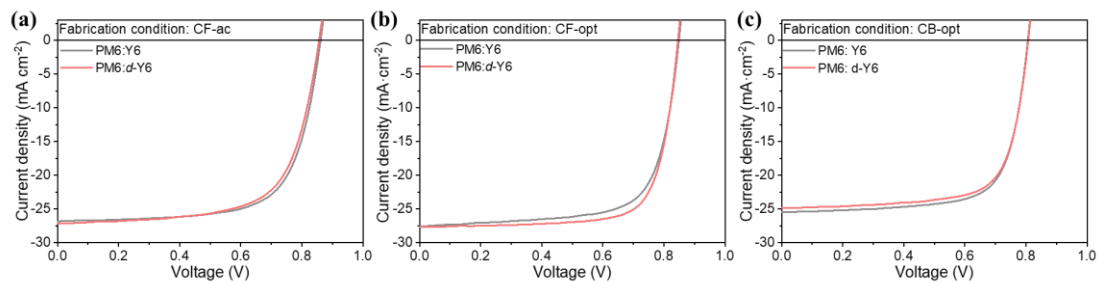
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incident angle of 0.606°.

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Supplementary Fig. 17 Typical J-V curves of the devices based on PM6:Y6 and

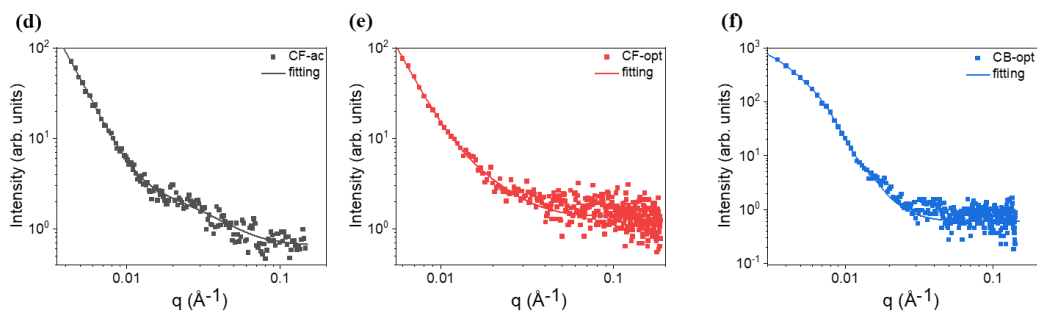
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PM6:*d*-Y6 under three different conditions (**a** CF-ac, **b** CF-opt, **c** CB-opt) mentioned

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in the main text.

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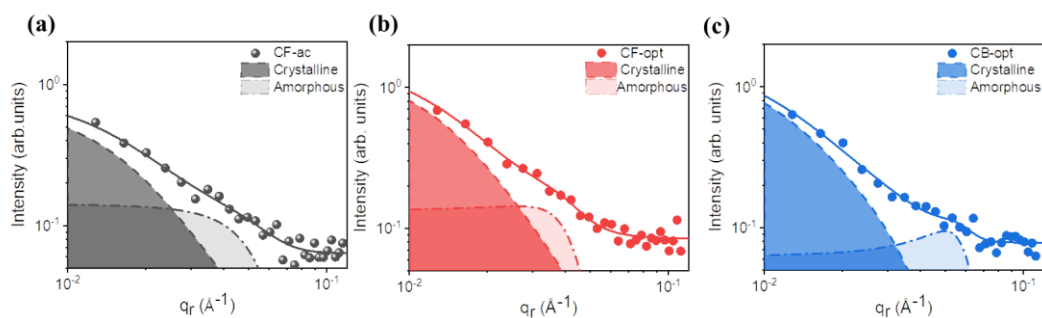
274 **Supplementary Fig. 18** Horizontal linecuts along the in-plane direction (dotted lines)

275 extracted from the 2D GISAXS patterns of **a** PM6: *d*-Y6 as cast, **b** CF-optimized, and

276 **c** CB-optimized blend films with their best fittings (solid lines).

277

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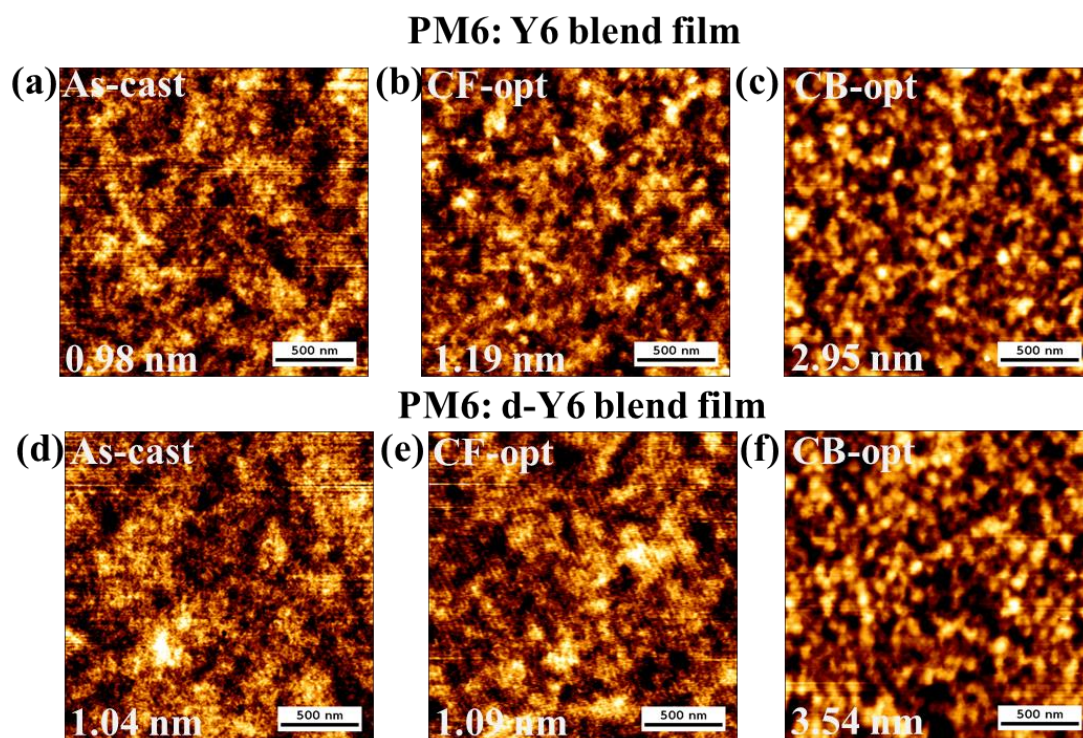
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280 **Supplementary Fig. 19** Horizontal linecuts along the in-plane direction (dotted lines)

281 extracted from the 2D GISANS patterns of **a** PM6: *d*-Y6 as cast, **b** CF-optimized, and

282 **c** CB-optimized blend films with their best fittings (solid lines).

283



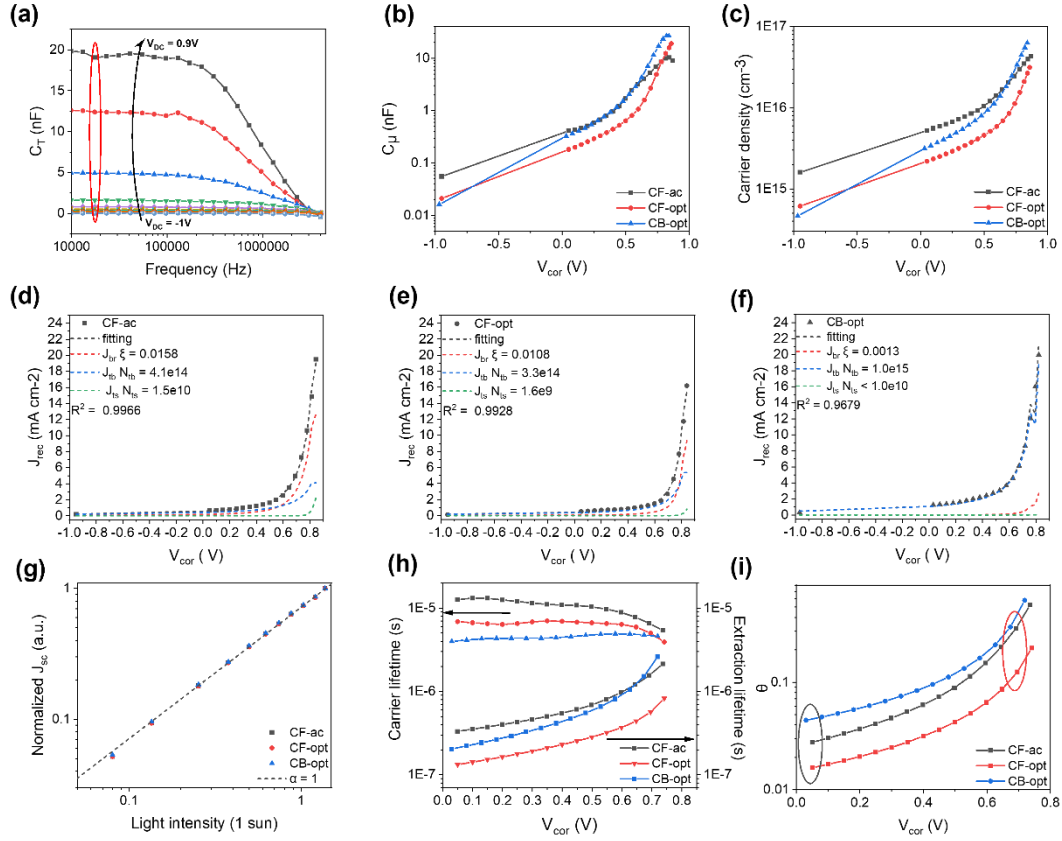
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285 **Supplementary Fig. 20** AFM topography images of PM6:Y6 (**a-c**) and PM6: *d*-Y6 (**d-**

286 **f**) blend films processed under different conditions mentioned in the main text. The

287 root-mean-square (RMS) roughness of heights is labelled at the inset for each image.

288



289

290 **Supplementary Fig. 21 a** The total capacitance associated with the active layer (C_T) of

291 the CF-optimized device as a function of the A.C. frequency applied, corrected for

292 geometric capacitance. V_{DC} is the background bias applied to the device under 1 sun

293 illumination, which increases from -1 V to 0.9 V. Chemical capacitance (C_μ) is taken

294 at a low frequency of 17 kHz where the C_T saturates, as highlighted in red. **b** C_μ , **c**

295 charge carrier density stored within the active layer as a function of applied bias after

296 correcting for series resistance (V_{cor}). The fits of the recombination current of **d** as-cast,

297 **e** CF-optimized, and **f** CB-optimized PM6:Y6 device via superposition of bimolecular,

298 bulk, and surface-trap assisted recombination as discussed in the main text. **g** the

299 intensity-dependent J_{sc} measurements for the three devices. **h** the charge carrier lifetime

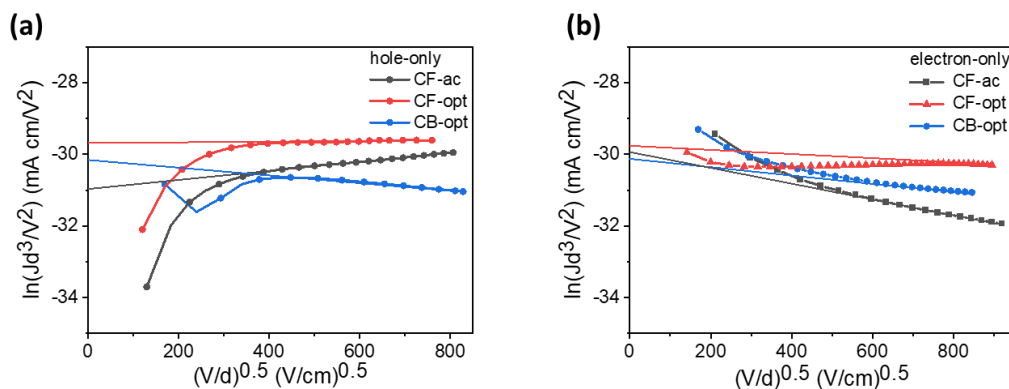
300 $\tau = \frac{qnL}{J_{rec}}$ and charge extraction time $\tau_{ext} = \frac{qnL}{J}$ as a function of V_{cor} , where q is the

301 elementary charge, n is the charge carrier density, L is the active layer thickness and

302 J_{rec} and J are recombination current density and current density under light,

303 respectively. θ the competition factor $\theta = \frac{\tau_{ext}}{\tau}$ derived as a function of V_{cor} with the
 304 short-circuit condition and maximum power output point highlighted in black and red,
 305 respectively.

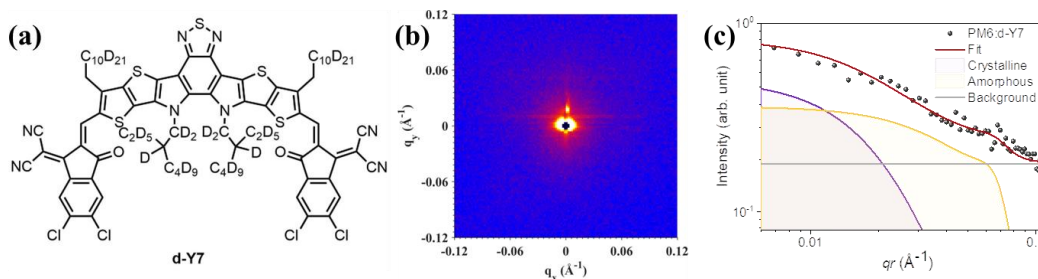
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307

308 **Supplementary Fig. 22** *J-V* characteristics in the dark for **a** hole-only and **b** electron-
 309 only devices based on PM6:Y6 with different processing conditions.

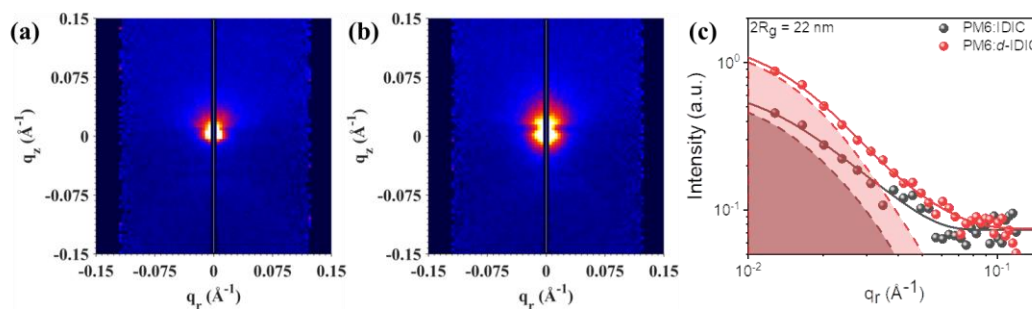
310



311

312 **Supplementary Fig. 23** **a** Molecular structure of *d*-Y7. **b** the 2D GISANS pattern of
 313 PM6:*d*-Y7 blend films and **c** the corresponding horizontal linecut along the in-plane
 314 direction (dots) with its best fit (solid line).

315



316

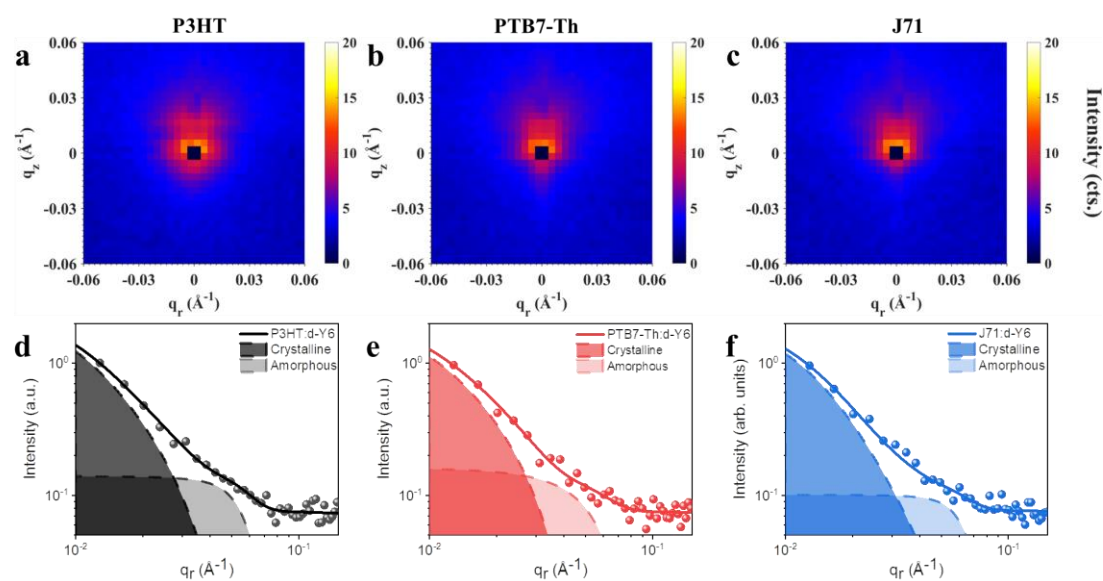
317 **Supplementary Fig. 24** 2D GISANS patterns of **a** PM6:IDIC, **b** PM6:*d*-IDIC blend

318 films and **c** corresponding horizontal linecuts along the in-plane direction (dots) with

319 their best fittings (solid line).

320

321



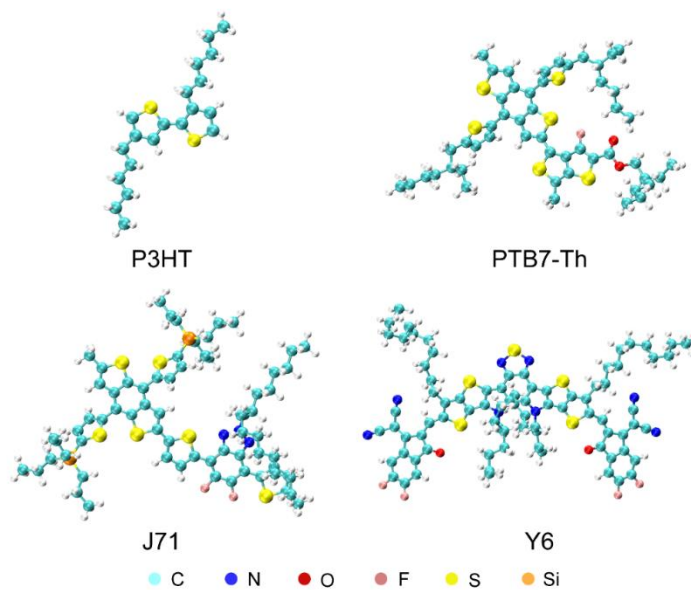
322

323 **Supplementary Fig. 25** 2D GISANS patterns of **a** P3HT: *d*-Y6, **b** PTB7-Th: *d*-Y6,

324 and **c** J71: *d*-Y6, with their corresponding horizontal linecuts (dots) and best fittings

325 (solid line) shown in **d-f**.

326



327

328 **Supplementary Fig. 26** Molecular structures of the P3HT, PTB7-Th, J71 monomers
 329 and Y6 molecule.

330

331 **Supplementary Tables**

332 **Supplementary Table 1** SLD values of pure and blend films under the X-ray.

Sample	Critical angle (°)	SLD (\AA^{-2})
PM6	0.211	1.76×10^{-5}
Y6	0.207	1.74×10^{-5}
<i>d</i> -Y6	0.207	1.69×10^{-5}
PM6:Y6	0.204	1.72×10^{-5}
PM6: <i>d</i> -Y6	0.205	1.75×10^{-5}

333

334 **Supplementary Table 2** SLD values of pure and blend films under the neutron beam.

Sample	SLD (\AA^{-2})
--------	---------------------------

PM6	$(1.2 \pm 0.1) \times 10^{-6}$
Y6	$(2.3 \pm 0.1) \times 10^{-6}$
<i>d</i> -Y6	$(6.4 \pm 0.4) \times 10^{-6}$
PM6:Y6	$(1.7 \pm 0.1) \times 10^{-6}$
PM6: <i>d</i> -Y6	$(3.0 \pm 0.2) \times 10^{-6}$

335

336 **Supplementary Table 3** A summary of device characteristics of PM6:Y6 and PM6:*d*-

337 Y6 systems under three different processing conditions mentioned in the main text.

Blends	V_{oc} (V) ^d	J_{sc} (mA·cm ⁻²) ^d	FF (%) ^d	PCE (%) ^d
PM6: Y6 ^a	0.865 (0.861 ± 0.003)	26.9 (26.7 ± 0.2)	69.7 (69.0 ± 0.5)	16.3 (15.9 ± 0.3)
PM6: <i>d</i> -Y6 ^a	0.856 (0.855 ± 0.003)	27.1 (26.7 ± 0.3)	67.2 (66.8 ± 0.5)	15.6 (15.2 ± 0.2)
PM6: Y6 ^b	0.853 (0.850 ± 0.002)	28.0 (27.7 ± 0.5)	74.4 (74.1 ± 0.4)	17.8 (17.4 ± 0.3)
PM6: <i>d</i> -Y6 ^b	0.846 (0.843 ± 0.002)	27.7 (27.7 ± 0.2)	75.1 (74.7 ± 0.3)	17.6 (17.4 ± 0.2)
PM6: Y6 ^c	0.806 (0.798 ± 0.006)	25.5 (24.7 ± 0.6)	72.2 (71.5 ± 0.5)	14.8 (14.1 ± 0.5)
PM6: <i>d</i> -Y6 ^c	0.807 (0.807 ± 0.003)	24.9 (24.6 ± 0.5)	72.1 (72.0 ± 0.4)	14.5 (14.3 ± 0.2)

338

339 ^a As-cast w/o CN & TA. ^b CF-opt (w/ 0.5% CN & TA 90°C 5min). ^c CB-opt (w/

340 0.5% CN & TA 90°C 5min).^d Average values with their standard deviations (in

341 parentheses) are obtained from 5 independent devices.

342 **Supplementary Table 4** Charge carrier mobilities of PM6:Y6 blend films processed

343 under different conditions measured by the SCLC Method.

Active layer	μ_h ($\times 10^{-4}$ cm ² V ⁻¹ s ⁻¹) ^a	μ_e ($\times 10^{-4}$ cm ² V ⁻¹ s ⁻¹) ^a
CF-ac	2.1 ± 0.3	5.9 ± 0.4
CF-opt	4.7 ± 0.2	4.8 ± 0.3

CB-opt 7.5 ± 0.4 6.8 ± 0.3

344 ^a Average values are obtained from 5 independent devices.

345

346 **Supplementary Table 5** Morphology parameters fitted from the GISANS intensity

347 profiles ($2R_{gc}$ is the crystallized acceptor domain size, $2R_{ga}$ is the amorphous acceptor

348 domain size in the intermixing phase.)

Active layer	$2R_{gc}$ (nm)	$2R_{ga}$ (nm)
PM6: <i>d</i> -Y7	13.8	5.4
PM6: <i>d</i> -IDIC	22	N/A
P3HT: <i>d</i> -Y6	33.7	7.5
PTB7-Th: <i>d</i> -Y6	31.7	6.7
J71: <i>d</i> -Y6	28.7	6.7

349