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Branched alkyl ester side chains rendering large polycyclic (3*E*,7*E*)-3,7-bis(2-oxoindolin-3-ylidene)benzo[1,2-b:4,5-b']difuran-2,6(3*H*,7*H*)dione (IBDF) based donor-acceptor polymers solution-processability for organic thin film transistors

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-7.2600.069 Ч 3.45 -48.41-5.78 8 .96 86 66. 5.0 4.5 4.0 f1 (ppm) 3.5 2.5 2.0 1.5 1.0 5.5 3.0 0.5 Э.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 0.0 -0.5 -1

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Fig. S1 300 MHz ¹H NMR spectrum for nonacosan-15-yl 4-bromobutanoate (1a) in CDCl₃.



Fig. S3 300 MHz ¹H NMR spectrum for heptatriacontan-19-yl 4-bromobutanoate (1c) in CDCl₃.



Fig. S4 300 MHz ¹H NMR spectrum for nonacosan-15-yl 4-(6-bromo-2,3-dioxoindolin-1-yl)butanoate (**2a**) in CDCl₃.



Fig. S5 300 MHz ¹H NMR spectrum for tritriacontan-17-yl 4-(6-bromo-2,3-dioxoindolin-1-yl)butanoate (**2b**) in CDCl₃.



Fig. S6 300 MHz ¹H NMR spectrum for heptatriacontan-19-yl 4-(6-bromo-2,3-dioxoindolin-1-yl)butanoate (**2b**) in CDCl₃.



Fig. S7 300 MHz ¹H NMR spectrum for di(nonacosan-15-yl) 4,4'-((3E,3'E)-(2,6-dioxobenzo[1,2-b:4,5-b']difuran-3,7(2H,6H)-diylidene)bis(6-bromo-2-oxoindoline-1-yl-3-ylidene))dibutyrate (**3a**) in CDCl₃.



Fig. S9 300 MHz ¹H NMR spectrum for di(heptatriacontan-19-yl) 4,4'-((3E,3'E)-(2,6-dioxobenzo[1,2-*b*:4,5-*b*']difuran-3,7(2H,6*H*)-diylidene)bis(6-bromo-2-oxoindoline-1-yl-3-ylidene))dibutyrate (**3c**) in CDCl₃.



Fig. S11 75 MHz ¹³C NMR spectrum for di(tritriacontan-17-yl) 4,4'-((3E,3'E)-(2,6-dioxobenzo[1,2-*b*:4,5-*b*']difuran-3,7(2*H*,6*H*)-diylidene)bis(6-bromo-2-oxoindoline-1-yl-3-ylidene))dibutyrate **(3b)** in CDCl₃.



Fig. S12 75 MHz ¹³C NMR spectrum for di(heptatriacontan-19-yl) 4,4'-((3E,3'E)-(2,6-dioxobenzo[1,2-b:4,5-b']difuran-3,7(2H,6H)-diylidene)bis(6-bromo-2-oxoindoline-1-yl-3-ylidene))dibutyrate (**3c**) in CDCl₃.



Fig. S13 300 MHz ¹H NMR spectrum for **P-33** in $C_2D_2Cl_4$.



10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 **Fig. S15** 300 MHz ¹H NMR spectrum for **P-41** in $C_2D_2Cl_4$.



Fig. S17 HT-GPC curve of **P-37**: $M_n = 40$ kDa; PDI = 3.4.



Fig. S18 HT-GPC curve of **P-41**: $M_n = 39$ kDa; PDI = 4.8.



Fig. S19 TGA curve of P-33.



Fig. S21 TGA curve of P-41.



Fig. S22 Chemical structure of PIBDFBT-40.



Fig. S23 HT-GPC curve of PIBDFBT-40: $M_n = 40$ kDa; PDI = 8.4.



Fig. S24 TGA curve of PIBDFBT-40.



Fig. S25 UV-Vis absorption of PIBDFBT-40.



Fig. S26 Cyclic voltammetry diagram of **PIBDFBT-40**: $E_{HOMO} = -5.72 \text{ eV}$; $E_{LUMO} = -3.88 \text{ eV}$.



Fig. S27 The transfer curves of a BGBC OTFT device with 200 °C-annealed **PIBDFBT-40**. Device dimensions: channel length (L) = 30 µm; channel width (W) = 1000 µm.



40. Device dimensions: channel length (L) = 30 µm; channel width (W) = 1000 µm.