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Supporting information for

Fluorenone Imide /Cyanated Fluorenone Imide and Diketopyrrolopyrrole Based Dual-Acceptor Polymers for n-Type Organic Thin-Film Transistors

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1. Materials characterization

¹H spectra was recorded on Bruker Ascend-400 spectrometers. Thermogravimetric analysis (TGA) was conducted on a Mettler and STARe TA Instrument at a heating rate of 10 °C min⁻¹ under a N₂ flow rate of 90 mL min⁻¹. UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. Two-dimensional grazing incidence wide angle X-ray scattering (2D-GIWAXS) measurements were performed at the Beamline PLS-II 9A SAXS of Pohang Accelerator Laboratory, Republic of Korea.

2. Materials synthesis

The synthetic procedures of the intermediates and target products were illustrated in



Scheme S1, 2. Compound 1 was prepared according to the previous literature with high vields.^{1, 2}

Scheme S1. Synthetic route to four dibrominated monomers. Reagents and conditions: *i*) Br₂, Ag₂SO₄/H₂SO₄, 100 °C; *ii*) Ac₂O, 130 °C; *iii*) 2-decyltetradecan-1-amine DMAP/1, 4-dioxane, 90 °C, then Ac₂O, 130 °C; *iv*) malononitrile, TiCl₄, pyridine/DCM, rt.

2, 7-Dibromo-9-oxo-9H-fluorene-4, 5-dicarboxylic acid (compound 2):

A mixture of compound **1** (1.34 g, 5 mmol), Ag₂SO₄ (1.86 g, 6 mmol) and Br₂ (3 mL) in 20 mL concentrated sulphuric acid was stirred at 100 °C for 48 h. After cooling to room temperature, Na₂SO₃ aqueous solution was added to the mixture slowly to quench the excess of Br₂. The solids, i.e. AgBr and the product, were added into a NaHCO₃ solution, and then the mixture was filtrated to remove AgBr. The resulting solution was acidified by 2M H₂SO₄ solution to afford compound **2** as a precipitate. After filtered again, the product was washed with deionized water three times and dried in vacuo to give 2.01 g (95%) of light yellow solid. ¹H NMR (400 MHz, DMSO): δ ppm 13.68 (s, 2H), 8.00 (d, *J* = 2.0 Hz, 2H), 7.98 (d, *J* = 2.0 Hz, 2H). ¹³C NMR (100 MHz, DMSO): δ ppm 188.83, 166.91, 141.43, 137.75, 137.30, 133.17, 129.14, 123.26. HRMS (m/z): Calcd. for C₁₅H₅Br₂O₅ [M-H]⁻, Exact Mass: 422.8509; Found: 422.8515.

2, 6-Dibromo-4H-fluoreno[4,5-cde]oxepine-4,8,10-trione (compound 3):

Compound 2 (824 mg, 1 mmol) was stirred in 10 mL acetic anhydride under reflux for

12 h. After cooling to room temperature, the solid was collected by filtration, washed with methanol, and dried under vacuum overnight to afford a light-brown solid as the compound **3**, which was used for the following reaction without further purification (377 mg, 93%).

2, 6-Dibromo-9-(2-decyltetradecyl)fluoreno[4,5-cde]azepine-4,8,10(9H)-trione (compound FOI-Br):

Compound **3** (405 mg, 1.0 mmol), 2-decyltetradecan-1-amine (530 mg, 1.5 mmol) and DMAP (146 mg, 1.2 mmol) were added into a flask with 20 mL anhydrous 1, 4-dioxane. The resulting mixture was heated to 90 °C and stirred overnight, and the reaction turned into a clear solution, and 5 mL acetic anhydride was then added in one portion. The mixture was heated to 130 °C and stirred for another 6 h. After cooling to room temperature, the mixture was extracted with dichloromethane (DCM) three times, and the combined organic layer was dried over Na₂SO₄. The solvent was removed under a reduced pressure to afford a residue, which was purified by column chromatography over silica gel using petroleum ether (PE):DCM (3:1) as the eluent to afford the target compound as a white solid (370 mg, 50%). ¹H NMR (400 MHz, CDCl₃): δ ppm 8.59 (d, *J* = 1.8 Hz, 2H), 8.04 (d, *J* = 1.8 Hz, 2H), 4.35 (d, *J* = 7.2 Hz, 2H), 1.92 – 1.78 (m, 1H), 1.45 – 1.12 (m, 40H), 0.87 (t, 6H). ¹³C NMR (125 MHz, CDCl₃): δ ppm 188.08, 163.72, 140.79, 137.94, 134.91, 132.10, 128.64, 125.34, 51.06, 36.59, 31.93, 31.69, 30.03, 29.70, 29.66, 29.62, 29.37, 29.36, 26.44, 22.70, 14.14. HRMS (m/z): Calcd. for C₃₉H₅₃Br₂NO₃ [M]⁻, Exact Mass: 741.2392; Found: 741.2397.

2-(2,6-Dibromo-9-(2-decyltetradecyl)-8,10-dioxo-9,10-dihydrofluoreno[4,5cde]azepin-4(8H)-ylidene)malononitrile (compound FCNI-Br):

Compound **FOI-Br** (370 mg, 0.5 mmol), malononitrile (100 mg, 1.5 mmol) and 3 mL pyridine in 30 mL DCM were stirred at 0 °C. Then 0.5 mL TiCl₄ was added slowly to the mixture and the reaction system was stirred at room temperature overnight. The mixture was extracted with dichloromethane (DCM) three times and the combined organic layer was dried over Na₂SO₄. The solvent was removed under a reduced pressure to afford a residue, which was further purified by column chromatography over silica gel using PE:DCM = 3:1 as the eluent to afford the target compound as a

light yellow solid (158 mg, 40%). ¹H NMR (400 MHz, CDCl₃): δ ppm 8.77 (d, J = 1.6 Hz, 2H), 8.63 (d, J = 1.6 Hz, 2H), 4.33 (d, J = 7.2 Hz, 2H), 1.92 – 1.78 (m, 1H), 1.29 (m, 40H), 0.88 (t, 6H). ¹³C NMR (100 MHz, CDCl₃): δ ppm 163.30, 156.21, 140.94, 135.79, 135.13, 133.73, 128.83, 125.14, 112.02, 80.53, 51.25, 36.54, 31.93, 31.69, 30.01, 29.70, 29.67, 29.66, 29.60, 29.37, 29.36, 26.40, 22.70, 14.13. HRMS (m/z): Calcd. for C₄₂H₅₃Br₂N₃O₂ [M]⁻, Exact Mass: 789.2505; Found: 789.2510.



Scheme S2. Synthesis of polymers PFOI-DPP and PFCNI-DPP.

General procedure for polymerizations via Stille coupling for the synthesis of polymers

PFOI-DPP and **PFCNI-DPP**.

A glass tube was charged with two monomers (1.0 eq), Pd₂(dba)₃ (0.015 eq), and P(*o*-tolyl)₃ (0.12 eq). The tube and its contents were subjected to 3 pump/purge cycles with argon, followed by the addition of anhydrous toluene (2-3 mL) via syringe. The tube was sealed under argon flow and then stirred at 100 °C for 3 minutes, 120 °C for 2 minutes, and 140 °C for 3 h under microwave irradiation.¹ After cooling to room temperature, the reaction mixture was slowly dripped into 50 mL methanol under vigorous stirring. After stirring for 10 minutes, the solid precipitate was transferred to a Soxhlet thimble. After drying, the crude product was subjected to sequential Soxhlet extraction with solvent sequence depending on the solubility of the particular polymer.¹ After final extraction, the polymer solution was concentrated to ~20 mL, and then dripped into 50 mL methanol under vigorous stirring. The polymer was collected by filtration and dried under reduced pressure to afford a deep colored solid as the product.

PFOI-DPP: The solvent sequence for Soxhlet extraction was methanol, acetone, hexane, dichloromethane, and chloroform. **PFOI-DPP** was obtained as a blue solid with a yield of 75%. $M_n = 63.1$ kg/mol, dispersity = 1.8. ¹H NMR (400 MHz, C₂D₂Cl₄) δ : ppm 8.79-8.49 (dd, 8H), 4.37-3.58 (br, 6H) 1.39-0.74 (m, 125H).

PFCNI-DPP: The solvent sequence for Soxhlet extraction was methanol, acetone, hexane, dichloromethane, and chloroform. **PFCNI-DPP** was obtained as a dark green solid with a yield of 70%. $M_n = 51.1$ kg/mol, dispersity = 2.5. ¹H NMR (400 MHz, C₂D₂Cl₄) δ : ppm 8.58-7.53 (br, 8H), 4.43-3.97 (br, 6H) 1.38-0.70 (m, 124H).



Figure S1. ¹H NMR spectrum of polymer PFOI-DPP in C₂D₂Cl₄.



Figure S2. ¹H NMR spectrum of polymer PFCNI-DPP in C₂D₂Cl₄.

3. Thermal properties

Thermogravimetric analysis (TGA) was conducted on a Mettler, STARe TA Instrument at a heating rate of 10 $^{\circ}$ C min⁻¹ under a N₂ flow rate of 90 mL min⁻¹.



Figure S3. TGA curves of polymers PFOI-DPP and PFCNI-DPP.

4. Computational studies

Density functional theory (DFT) calculations were performed with the Gaussian 09 program. The widely used the Becke three-parameter hybrid functional combined with Becke-Lee-Yang-Parr correlation functional (B3LYP) with 6-31G(d) basis sets was employed to get theoretical predictions on the single molecular geometries, the frontier orbital energy levels, and isosurfaces of the imide-functionalized fluorenone derivatives.

5. Electrochemical properties

Cyclic voltammetry (CV) measurements of polymer films were carried out on a CHI660 potentiostat/galvanostat electrochemical workstation at a scan rate of 50 mV s⁻¹ with 0.1 M tetra-(n-butyl ammonium hexafluorophosphate in acetonitrile as the supporting electrolyte, a platinum disk as working electrode, a platinum wire as counter electrode, and the Ag/Ag⁺ as a reference electrode, and the ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as the reference for all measurements.



Figure S4. Cyclic voltammogram of Fc/Fc⁺.

6. Device Fabrication and Characterization

Top-gate/bottom-contact (TG/BC) organic thin-film transistors (OTFTs) were fabricated to investigate charge transport properties of the polymers.¹ Source-drain electrodes of 3 nm Cr/30 nm Au were patterned on borosilicate glass by photolithography, with a channel length (*L*) of 10, 20, 50, or 100 μ m and a channel width (*W*) of 5 mm. Next, the polymer active layer was spin-coated from its hot chlorobenzene (CB) solution (5 mg mL⁻¹), using on-center spin-coating method. The

polymer active layer was thermally annealed at 80-160 °C for 10 min followed by a cooling-down process. Then, ~400 nm CYTOP was coated on top and annealed at 100 °C for 15 min. Finally, 50 nm Al was evaporated on top as the gate electrode to complete the device fabrication. The OTFT characterization was done inside a N₂-filled glove box using Keithley S4200 semiconductor analyzer. To calculate the linear mobility, the standard equation $I_{sd} = \mu_{lin}C_i(W/L)(V_g-V_{th})V_{sd}$ was used, where I_{sd} is the source to drain current, μ_{lin} is the linear mobility, W is the channel width, L is the channel length, V_g is the gate voltage, V_{th} is the threshold voltage, and V_{sd} is the source to drain voltage ($V_{sd} = 10$ V curve used for linear mobility extraction).¹ Similarly, $I_{sd} = \mu_{sat}C_i(W/2L)(V_g-V_{th})^2$ was used for the saturation field-effect mobility calculation at $V_{sd} = 70$ V for the saturation regime, wherein μ_{sat} is the saturation mobility.

7. Morphology studies

GIWAXS measurements were conducted on a Xenocs-SAXS/WAXS system with Xray wavelength of 1.5418 Å. The film samples were irradiated at a fixed angle of 0.2°, and all film samples were prepared from with chlorobenzene (CB).

Table	S1 .	2D-	GIWA	XS	packing	parameters	of p	olymer	films.
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Polymer	Crystallog	Number	
		$q_{xy,(100)}$ (Å ⁻¹)	2.60E-01
	a profile(100)	d _{xy, (100)} (Å)	2.42E+01
	q _{xy} prome(100)	FWHM (Å ⁻¹)	7.22E-02
ρεωι-υδδ		CCL _{xy, (100)} (Å)	7.83E+01
1101-011	qz profile(010)	$q_{z,(010)}({ m \AA})$	1.66E+00
		$d_{z,(010)}(A)$	3.79E+00
		FWHM (Å ⁻¹)	2.48E-01
		CCL _{z, (010)} (Å)	2.28E+01
		$q_{xy,(100)}$ (Å ⁻¹)	2.74E-01
	a profile(100)	$d_{xy,(100)}(A)$	2.29E+01
	q _{xy} prome(100)	FWHM (Å-1)	1.04E-01
PFCNI-DPP		CCL _{xy, (100)} (Å)	5.45E+01
	q _z profile(010)	$q_{z,(010)}$ (Å)	1.61E+00
		d _{z, (010)} (Å)	3.91E+00
		FWHM (Å ⁻¹)	3.04E-01

			$CCL_{z,(010)}(\text{\AA})$	1.86E+01
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8. References

Z. Chen, Y. Zhang, P. Wang, J. Yang, K. Yang, J. Li, J. Yang, Y. Li, H. Dong, X. Guo, *Chem. Commun.* 2022, **58**, 12467-12470.

2. Z. Chen, J. Li, J. Wang, K. Yang, J. Zhang, Y. Wang, K. Feng, B. Li, Z. Wei, X. Guo, *Angew. Chem. Int. Ed.* **2022**, e202205315.