Supporting Information

Polynorbornenes with Pendant Perylene Diimides for Organic Electronic Applications

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Figure S1. Kinetics of the polymerisation of C11PDI

Figure S2. TGA traces and DSC traces

Figure S3. UV-Vis spectra of polymer films

Figure S4. Cyclic voltammograms of monomers

Figure S5. OFET device characteristics for C11PDI HP

Figure S6. UV-Vis spectra of polymer / P3HT blend films

Figure S7. Surface potential images for polymer / P3HT blend films

Figure S8. GPC traces for the diblock homopolymer

Additional Experimental Details
Figure S1. Kinetics of the polymerisation of C11PDI (M) in NMR tube under nitrogen initiated by the 1st generation Grubbs initiator in CD₂Cl₂ as determined using §H NMR spectroscopy. The dotted line is a fit to a first order expression in M.

Figure S2. TGA traces (left) and DSC traces (second heating, right) for N-PDI HP, C7 PDI HP, and C11 PDI HP, both recorded at a heating rate of 5 °C min⁻¹ under N₂.
**Figure S3.** The UV-Vis absorption spectra films of PDI polymers on glass, spin-coated using 10 mg mL$^{-1}$ solutions in toluene at 1000 rpm for 1 min.

**Figure S4.** The cyclic voltammograms of N-PDI, C7PDI, and C11PDI in CH$_2$Cl$_2$ / 0.1 M [$^n$Bu$_4$N][PF$_6$] recorded with a scan rate of 50 mV s$^{-1}$, with ferrocene as an internal reference.
Figure S5. OFET device characteristics for **C11PDI HP** after annealing at 200 °C.

Figure S6. Absorption spectra of **C11PDI HP/P3HT** and **C7PDI HP/P3HT** films on PEDOT:PSS-coated ITO. These films were prepared in similar fashion to those used as active layers of OPV cells.
Figure S7. Surface potential (top two) images for P3HT:C11PDI HP (left two) and P3HT:C7PDI HP (right two) obtained by KPFM. Here, major topographical hills lead to dark areas and thus low surface potential in the images, especially for the P3HT:C7PDI HP blend. The bottom two panels represent the surface potential along the red line in the two upper images.
Figure S8. GPC traces of “diblock” homopolymer based on C11PDI after synthesis of first and second blocks.

Additional Experimental Details

*N,N'-Bis(1-undecyl-dodecyl)perylene-3,4,9,10-tetracarboxylic diimide.*1 A mixture of perylene-3,4,9,10-tetracarboxydianhydride (6.0 g, 15 mmol), 1-undecyl-dodecylamine (12 g, 35 mmol), zinc acetate (1.6 g, 8.7 mmol), and imidazole (70 g) were heated at 180 °C for 5 h before it was allowed to cool to room temperature and treated with 2 N aqueous HCl (400 mL). The mixture was then extracted with chloroform (2 × 200 mL). The organic phase was washed with water (3 × 100 mL) and dried over MgSO₄. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel, using CHCl₃ / hexane (1:1 and then 2:1) as eluent to give the desired product as a red solid (12 g, 77%). $^1$H NMR (500 MHz, CDCl₃): δ
8.64 (m, 8H), 5.18 (m, 2H), 2.22 (m, 4H), 1.86 (m, 4H), 1.4–1.1 (m, 72H), 0.80 (t, \( J = 6.6 \) Hz, 12H). The \(^1\)H NMR spectrum is consistent with the literature.\(^1\)

\( N,N'\)-Bis(1-heptyloctyl)perylene-3,4,9,10-tetracarboxylic diimide.\(^2\) A mixture of perylene-3,4,9,10-tetracarboxyldianhydride (6.6 g, 17 mmol), 8-aminopentadecane (10 g, 43 mmol), zinc acetate (1.6 g, 8.7 mmol) and imidazole (70 g) were heated at 180 °C for 5 h before it was allowed to cool to room temperature and treated with 2 N aqueous HCl (400 mL). The mixture was then extracted with chloroform (2 × 200 mL). The organic phase was washed with water (3 × 100 mL) and dried over MgSO\(_4\). The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel, using CHCl\(_3\) / hexane (1:1 and then 2:1) as eluent to give the desired product as a red solid (10 g, 73%). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 8.59–8.63 (m, 4H), 8.50–8.52 (d, \( J = 8.0 \) Hz, 4H), 5.18–5.23 (m, 2H), 2.22–2.29 (m, 4H), 1.88–1.92 (m, 4H), 1.25–1.38 (m, 40H), 0.82 (t, \( J = 6.6 \) Hz, 12H). The \(^1\)H NMR spectrum is consistent with the literature.\(^2\)

**Compound A1.** \( N,N'\)-Bis(1-undecyl-dodecyl)-perylene-3,4,9,10-tetracarboxylic diimide (1.0 g, 1.0 mmol) and potassium hydroxide (powder, 0.19 g, 3.4 mmol) in tert-butanol (18 mL) were heated to 120 °C for 50 min under nitrogen. After the solution was cooled to \( ca. \) 100°C, it was treated with acetic acid (17 mL) and 2 N aqueous HCl (10 mL). The resultant mixture was stirred at room temperature overnight and then extracted with chloroform (100 mL). The organic layer was washed sequentially with water (2 × 20 mL), 0.5 N aqueous NaHCO\(_3\) (20 mL), and water (20 mL). The mixture was dried over MgSO\(_4\), and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with CHCl\(_3\) to give A1 as a red solid (0.33...
$\delta$ : 8.72–8.66 (m, 8H), 5.18 (m, 1H), 2.25 (m, 2H), 1.88 (m, 2H), 1.35–1.29 (m, 36H), 0.82 (t, $J$ = 6.3 Hz, 6H). Anal. Calcd for C$_{47}$H$_{55}$NO$_5$: C, 79.07; H, 7.76; N, 1.96. Found: C, 78.86; H, 7.79; N, 1.94. The $^1$H NMR spectrum is consistent with the literature.$^1$

**Compound A2.$^2$** $N,N'$-Bis(1-heptyloctyl)perylene-3,4,9,10-tetracarboxylic diimide (3.2 g, 4.0 mmol), potassium hydroxide (0.55 g, 8.4 mmol) in tert-butanol (90 mL) were heated to 120 °C and maintained at this temperature for 50 min under nitrogen. After the solution was cooled to ca. 80 °C, it was treated with acetic acid (72 mL) and 2 N aqueous HCl (50 mL). The resultant mixture was stirred at room temperature overnight and then extracted with chloroform (100 mL). The organic layer was washed sequentially with water (2 x 40 mL), 0.5 N aqueous NaHCO$_3$ (40 mL), and water (2 x 40 mL). The mixture was dried over MgSO$_4$ and filtered, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel eluted with CHCl$_3$. A2 was obtained as a red solid (1.4 g, 59%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.69–8.50 (m, 8H), 5.18 (m, 1H), 2.24 (m, 2H), 1.86 (m, 2H), 1.34–1.20 (m, 20H), 0.81(t, $J$ = 6.5 Hz, 6H). The $^1$H NMR spectrum is consistent with that reported in the literature.$^2$

$N,N'$-Bis(2-decyl-tetradecyl)-perylene-3,4:9,10-tetracarboxydimide.$^3$ Perylene-3,4,9,10-tetracarboxyldianhydride (4.0 g, 10 mmol), 2-decyl-tetradecylamine (17.0 g, 48.0 mmol) and imidazole (31 g) were combined in a round-bottomed flask with an air condenser, and the reaction flask was immersed in an oil bath at 160 °C for 3 h after which the reaction flask was removed from the oil bath. After it was cooled to room temperature, 2 N HCl aqueous (400 mL) was added. The reaction mixture was extracted with CHCl$_3$, dried over MgSO$_4$, and filtered. The solvent was removed by rotary
evaporation, and the residue was purified by column chromatography, eluting with CHCl₃, to give a red solid (10.4 g, 98%). ¹H NMR (500 MHz, CDCl₃): δ 8.52 (d, J = 8.0 Hz, 4H), 8.38 (d, J = 8.0, 4H), 4.09 (d, J = 7.5 Hz, 4H), 1.97 (m, 2H), 1.5–1.0 (m, 80H), 0.83 (m, 12H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 163.5, 134.2, 131.2, 129.2, 126.1, 123.2, 122.8, 44.7, 36.6, 31.9, 31.7, 30.1, 29.69, 29.66, 29.65, 29.4, 26.5, 22.7, 14.1 (12 alkyl carbons missing, presumably due to overlap).³

“Diblock”-type C11PDI HP synthesis. C11PDI (100 mg, 0.112 mmol) was dissolved in anhydrous dichloromethane (4.0 mL) under N₂ and “first generation” Grubbs initiator (1.5 mg, 0.0018 mmol) in dichloromethane (1.0 mL) was added. The reaction mixture was stirred for 5 h until all, and then part of the solution (1.3 mL) was taken out for GPC analysis (Polymer 1 Mₙ = 22.8 kDa, Mₘ/Mₙ = 1.9 in THF, [monomer]/[initiator] = 62). To the remaining solution, C11PDI monomer (60 mg, 0.067 mmol) in anhydrous dichloromethane (1.0 mL) was added and the reaction mixture was stirred for overnight before it was added to methanol (200 mL) dropwise; the resulting red precipitate was filtered for GPC analysis. (Polymer 2 Mₙ = 42.7 kDa, Mₘ/Mₙ = 2.3 in THF, [monomer]/[initiator] = 111).

References