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ADVANCED MATERIALS

Supporting Information

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Power Factor Enhancement in Solution-Processed Organic
n-Type Thermoelectrics Through Molecular Design

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Power factor enhancement in solution-processed organic n-type thermoelectric molecules through side chain design

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Materials

All reagents from commercial sources were used without further purification. Perylene-3,4,9,10-tetracarboxylic dianhydride, imidazole, iodomethane, and 2-(dimethylamino)ethylamine were purchased from Aldrich. 4-(dimethylamino)butylamine and 6-(dimethylamino)hexylamine were purchased from Matrix Scientific. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc.

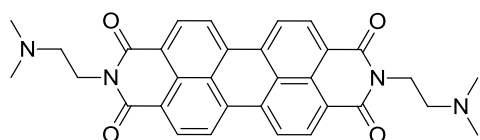
Instrumentation

¹H and ¹³C NMR spectra were recorded using a Varian 500 or 600 MHz spectrometer with the solvent signal as internal reference. Mass spectrometry was performed on a Micromass QTOF2 quadrupole/time-of-flight tandem mass spectrometer (ESI) or a Waters GCT Premier time-of-flight mass spectrometer (FD).

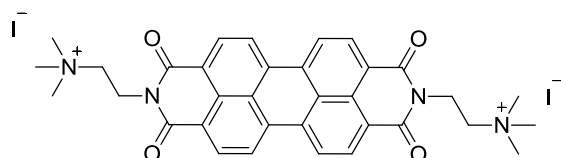
General procedure for the synthesis of dimethylamino perylene diimides. Perylene-3,4,9,10-tetracarboxylic dianhydride and the alkyl amine (4 eq.) were combined with imidazole in a round bottom flask equipped with a stir bar and sealed with a septum. The reaction vessel was purged with argon and subsequently heated with stirring at 130 °C for the indicated amount of time. At the conclusion of the reaction, the vessel was allowed to cool to room temperature, the contents were suspended in methanol, and the solid was collected

by filtration using a 0.8 μm nylon membrane. The solid was washed with methanol and dried under vacuum to afford the pure product.

General procedure for the quaternization of dimethylamino perylene diimides. The dimethylamino substituted perylene diimide and iodomethane (4 eq.) were dissolved in chloroform in a round bottom flask equipped with a stir bar and condenser and refluxed for the indicated amount of time. At the conclusion of the reaction, the mixture was cooled to room temperature and filtered through a 0.8 μm nylon membrane. The solid was washed consecutively with chloroform, diethyl ether, hexane, and ethanol and dried under vacuum to afford the pure product.

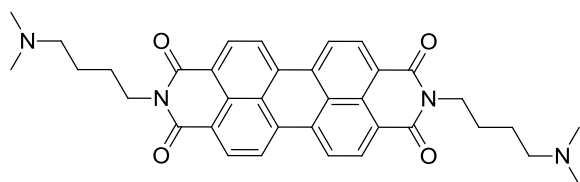


Bis(2-(dimethylamino)ethyl)perylene diimide. The general procedure was employed using perylene-3,4,9,10-tetracarboxylic dianhydride (1.082 g, 2.757 mmol), 2-(dimethylamino)ethylamine (0.9869 g, 11.20 mmol), and imidazole (14.1 g, 207 mmol) in a 50 mL round bottom flask. After 2 h at 130 $^{\circ}\text{C}$ and workup, 1.46 g (99%) of the desired product was obtained. ^1H NMR (600 MHz, CDCl_3): δ 2.37 (s, 12H), 2.70 (t, $J = 7.0$ Hz, 4H), 4.37 (t, $J = 7.0$ Hz, 4H), 8.62 (d, $J = 8.0$ Hz, 4H), 8.69 (d, $J = 7.9$ Hz, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ 38.31, 45.69, 56.97, 123.28, 123.46, 126.63, 129.61, 131.66, 134.83, and 163.64. MS (FD): m/z $[\text{M}]^+$ calcd for $[\text{C}_{32}\text{H}_{28}\text{N}_4\text{O}_4]^+$, 532.2; found, 532.2.

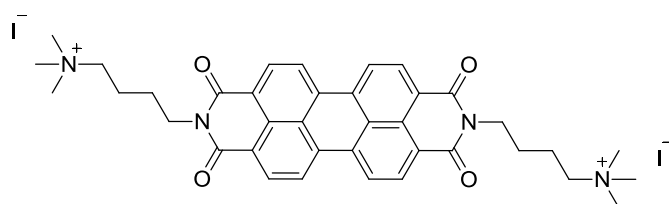


Bis(2-(trimethylammonium)ethyl)perylene diimide diiodide. The general procedure was

employed using bis(2-dimethylamino)ethyl-erylene diimide (0.9048 g, 1.699mmol), iodomethane (0.42 mL, 6.8 mmol), and chloroform (50 mL). After refluxing for 3 h and workup, 1.36 g (98%) of the desired product was obtained. ^1H NMR (600 MHz, DMSO- d_6): δ 3.25 (s, 18H), 3.67 (t, $J = 7.4$ Hz, 4H), 4.51 (t, $J = 7.0$ Hz, 4H), 8.61 (d, $J = 8.1$ Hz, 4H), 8.96 (d, $J = 8.1$ Hz, 4H). ^{13}C NMR (150 MHz, DMSO- d_6): δ 33.70, 52.48, 61.78, 122.41, 124.79, 125.33, 128.35, 131.00, 133.92, and 162.68. MS (ESI): m/z $[\text{M} + \text{Na}]^+$ calculated for $[\text{C}_{34}\text{H}_{34}\text{I}_2\text{N}_4\text{O}_4 + \text{Na}]^+$, 839.0567; found, 839.0552.

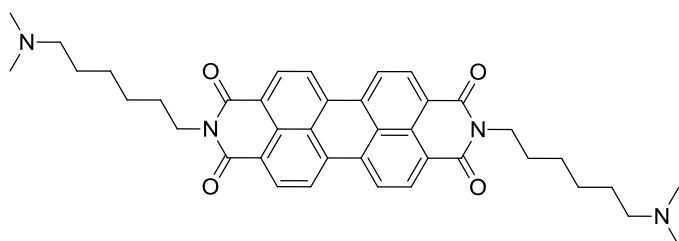


Bis(4-(dimethylamino)butyl)erylene diimide. The general procedure was employed using perylene-3,4,9,10-tetracarboxylic dianhydride (1.008 g, 2.569 mmol), 4-(dimethylamino)butylamine (1.203 g, 10.35 mmol), and imidazole (14.4 g, 211 mmol) in a 50 mL round bottom flask. After 1.25 h at 130 °C and workup, 1.44 g (95%) of the desired product was obtained. ^1H NMR (600 MHz, CDCl_3): δ 1.59 – 1.68 (m, 4H), 1.75 – 1.84 (m, 4H), 2.24 (s, 12H), 2.35 (t, $J = 7.6$ Hz, 4H), 4.23 (t, $J = 7.7$ Hz, 4H), 8.49 (d, $J = 8.0$ Hz, 4H), 8.59 (d, $J = 7.9$ Hz, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ 25.28, 26.19, 40.57, 45.53, 59.49, 123.17, 123.36, 126.43, 129.38, 131.45, 134.62, and 163.42. MS (FD): m/z $[\text{M}]^+$ calcd for $[\text{C}_{36}\text{H}_{36}\text{N}_4\text{O}_4]^+$, 588.3; found, 588.3.

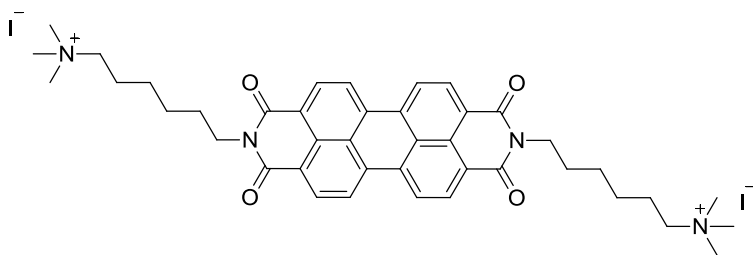


Bis(4-(trimethylammonium)butyl)erylene diimide diiodide. The general procedure was

employed using bis(4-dimethylamino)butyl-perylene diimide (0.7813 g, 1.327 mmol), iodomethane (0.35 mL, 5.6 mmol), and chloroform (40 mL). After refluxing for 2 h and workup, 1.14 g (98%) of the desired product was obtained. ^1H NMR (600 MHz, DMSO- d_6): δ 1.71 (p, $J = 7.3$ Hz, 4H), 1.79 – 1.88 (m, 4H), 3.08 (s, 18H), 3.36 – 3.42 (m, 4H), 4.12 (t, $J = 7.4$ Hz, 4H), 8.43 (d, $J = 8.0$ Hz, 4H), 8.74 (d, $J = 7.9$ Hz, 4H). ^{13}C NMR (150 MHz, DMSO- d_6): δ 19.87, 24.44, 52.35, 64.98, 122.73, 124.21, 125.42, 128.30, 130.95, 133.76, and 162.77. MS (ESI): m/z $[\text{M} + \text{Na}]^+$ calcd for $[\text{C}_{38}\text{H}_{42}\text{I}_2\text{N}_4\text{O}_4 + \text{Na}]^+$, 895.1193; found, 895.1182.



Bis(6-(dimethylamino)hexyl)perylene diimide. The general procedure was employed using perylene-3,4,9,10-tetracarboxylic dianhydride (1.042 g, 2.656 mmol), 6-(dimethylamino)hexylamine (1.522 g, 10.55 mmol), and imidazole (17.1 g, 251 mmol) in a 50 mL round bottom flask. After 1.5 h at 130 °C and workup, 1.64 g (96%) of the desired product was obtained. ^1H NMR (600 MHz, CDCl_3): δ 1.37 – 1.55 (m, 12H), 1.77 (p, $J = 7.8$ Hz, 4H), 2.21 (s, 12H), 2.26 (t, $J = 7.5$ Hz, 4H), 4.18 (t, $J = 7.4$ Hz, 4H), 8.41 (d, $J = 8.0$ Hz, 4H), 8.54 (d, $J = 7.9$ Hz, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ 27.30, 27.40, 27.83, 28.12, 40.71, 45.62, 59.97, 122.48, 122.96, 125.40, 128.64, 130.64, 133.52, and 162.76. MS (FD): m/z $[\text{M}]^+$ calcd for $[\text{C}_{40}\text{H}_{44}\text{N}_4\text{O}_4]^+$, 644.3; found, 644.3.



Bis(6-(trimethylammonium)hexyl)perylene diimide diiodide. The general procedure was employed using bis(6-dimethylamino)hexyl-perylene diimide (0.9086 g, 1.409 mmol), iodomethane (0.35 mL, 5.6 mmol), and chloroform (50 mL). After refluxing for 2 h and workup, 1.28 g (98%) of the desired product was obtained. ^1H NMR (600 MHz, $\text{DMSO-}d_6$): δ 1.36 (p, $J = 7.2$ Hz, 4H), 1.45 (p, $J = 7.2$ Hz, 4H), 1.67-1.75 (m, 8H), 3.04 (s, 18H), 3.26-3.31 (m, 4H), 4.08 (t, $J = 7.5$ Hz, 4H), 8.50 (d, $J = 7.9$ Hz, 4H), 8.83 (d, $J = 7.9$ Hz, 4H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): δ 22.08, 25.68, 26.18, 27.32, 52.14, 65.28, 121.75, 123.62, 124.46, 127.54, 130.19, 133.04, and 162.23. MS (ESI): m/z $[\text{M} - \text{I}]^+$ calcd for $[\text{C}_{42}\text{H}_{50}\text{IN}_4\text{O}_4]^+$, 801.2871; found, 801.2861.

Electron paramagnetic resonance (EPR) analysis

EPR samples of ethyl, butyl, and hexyl PDI were prepared by dropcasting solutions of each onto 2 cm by 2 cm quartz microscope cover slides. Each solution was approximately 1 mg/mL solution of PDI/deionized water. These samples were dried at 75 °C for 45 minutes. Upon drying, they were transferred into a dry glovebox with a nitrogen atmosphere. Inside the glovebox, the samples were cleaved into approximately 3 mm-wide pieces; the most uniform and rectangular pieces were saved as the final samples. Before measurement, samples were baked for 20 minutes at 120 °C inside the glovebox and then inserted into 4 mm-diameter quartz EPR tubes. These tubes were sealed with plastic caps and Teflon tape inside the glovebox. They were then transferred outside of the glovebox and their EPR spectra were measured within two hours.

Spin concentrations were determined by comparing the integrated signal intensity of a sample with the integrated signal intensity of a standard of known concentration. In this experiment, the spin concentration calculations were complicated by the variation in film thickness that resulted from the dropcasting. The thickness of each sample was measured using profilometry. The film was scraped off in three locations down to the substrate and the average difference in thickness across these sites was quoted as the average thickness of the dropcasted film. To calculate the spin concentrations, we measured the samples after a 20 minute, 120 C bake and compared the normalized, integrated intensity of the samples to the normalized, integrated intensity of a standard material. 2,2-diphenyl-1-picrylhydrazyl (DPPH) was used as the standard sample and a calibrator for determining the g-factor of each material. Error in comparing the spin concentration stemmed from uncertainty with regards to the concentration of the standard and the error in measuring the length, width, and thickness of each sample. Raw EPR signatures are shown in **Figure S1**.

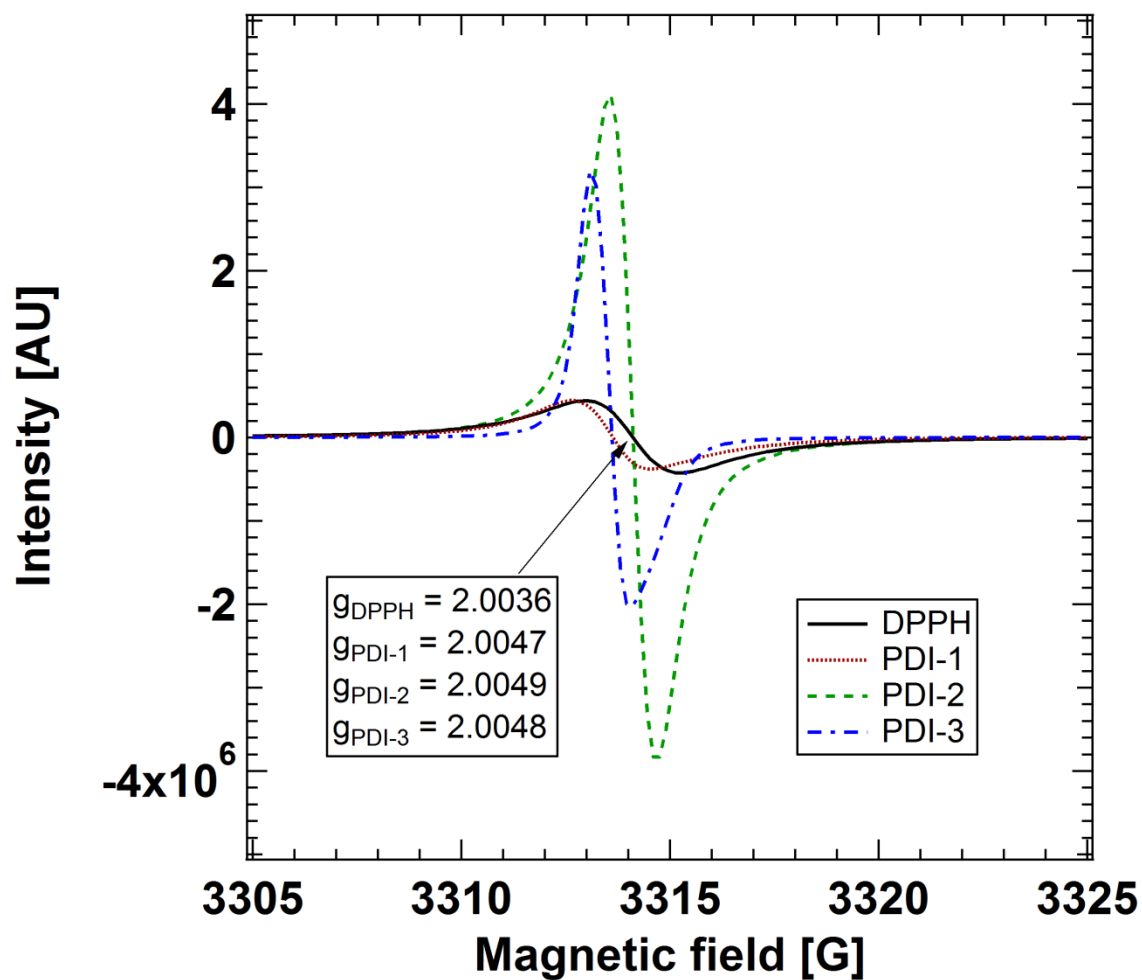


Figure S1: EPR signatures for PDI-1, PDI-2, and PDI-3 in comparison to a reference sample of DPPH.

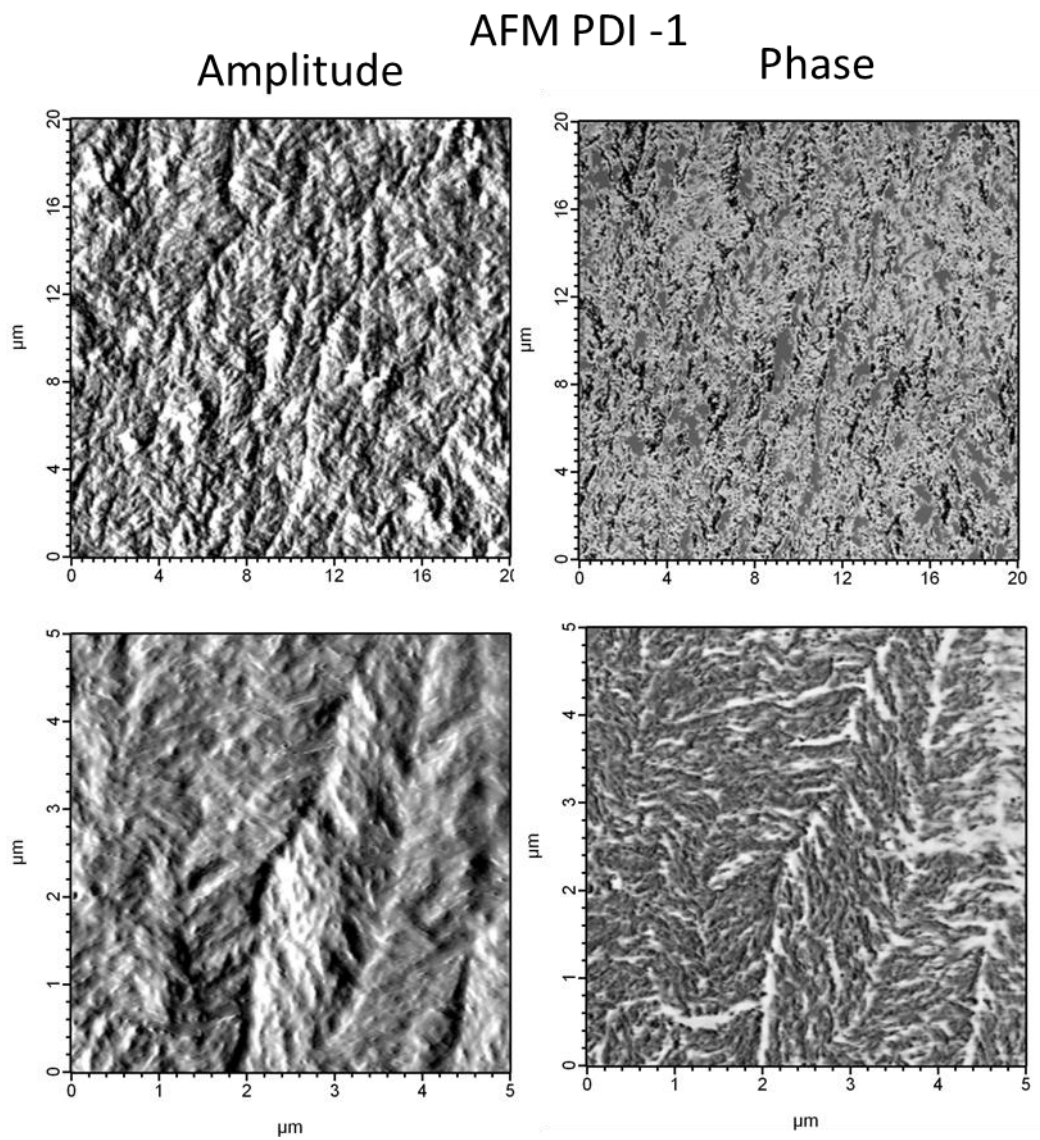


Figure S2: AFM images of thin films of PDI-1. Both the amplitude and the phase images are shown. Domains in these thin films appear to be hundreds of nanometers to microns in size.