Synthesis of Two Dihydropyrroloindoledione-Based Copolymers for Organic Electronics

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ABSTRACT: Two novel dihydropyrroloindoledione (DPID)-based copolymers have been synthesized in a two directional approach and characterized (gel permeation chromatography (GPC), ultraviolet-visible (UV–vis), cyclic voltammetry, and computational models). These planar, broad absorption copolymers show promise for use in organic electronics, with deep energy levels and low bandgaps. The two-directional Knoevenagel condensation used demonstrates the versatility of DPID as a useful yet underexploited conjugated unit. © 2012 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 1285–1291

KEYWORDS: conjugated polymer; copolymerization; dihydropyrroloindoledione; Knoevenagel condensation; organic electronics; Pummerer-type cyclization; synthesis

INTRODUCTION Organic electronic materials have potential as thin, lightweight, flexible, large-area, and crucially inexpensive devices, fabricated by printing techniques.[1] π-Conjugated polymers routinely exhibit the required solubility and processability[2] and bulk heterojunction organic photovoltaic devices using organic polymers as light absorbing components are now close to 10% power conversion efficiency.[3] However, the drive for efficiency improvements and long-term stability continues.[4]

Diketopyrrolopyrrole (**DPP**)-based copolymers have recently attracted much attention:[5] the electron-deficient inner-core flanked by electronically coupled electron-rich units renders these excellent donor–acceptor *n*-type materials, with their planarity and ability to hydrogen-bond encouraging π–π stacking. This can lead to ambipolar charge transport[6] and high performing organic solar cells.[7] Likewise, the colorants benzodifuranone[8] (**BDF**) and benzodipyrrolidone[9] (**BDP**)—the "stretched" **DPP**—have also been used to construct low-bandgap polymers. The larger **BDP** core extends the conjugation and delocalization of electrons, as well as altering the backbone aspect ratio, which could further enhance π–π stacking and efficient transport.

Recently, vinyl groups have also been incorporated into donor units, also increasing their aspect ratio and reducing steric hindrance between polymer chains. This has been shown to result in closer packing, reducing interlamellar and π-stacking distances.[10]

Here, we report two novel dihydropyrroloindoledione (**DPID**)-based polymers designed for organic electronic applications.

These are structurally related to **DPP** and **BDP**, containing the bis-lactam molecular architecture (Fig. 1). However, the inclusion of vinyl linkages directly flanking the acceptor core units increases their spacing along the polymer backbone. Additionally, the central six-membered ring in **DPID** is aromatic in character, which may further enhance π–π stacking, unlike the quinoidal nature of **BDP** and **BDF**. The synthesis, optical and electrochemical properties, and computation models are presented.

EXPERIMENTAL

Instrumental

"NMR spectra" were recorded on a Bruker DPX0 400 MHz spectrometer using an internal deuterium lock at ambient probe temperatures unless stated otherwise. Chemical shifts (δ) are quoted in ppm relative to the solvent residual peak, with peak multiplicity (bs, broad singlet; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), integration, and coupling constants (*J*) quoted in Hz (uncorrected) as appropriate. $CDCl_3$ was used as the solvent for all spectra unless stated otherwise. Proton solvent residual peaks are taken as: 7.26 for $CDCl_3$, 7.15 for C_6D_6, 3.34 for methanol-d_4, and 2.52 for DMSO-d_6; and carbon solvent residual peaks as: 77.16 for $CDCl_3$, 128.6 for C_6D_6, 49.9 for methanol-d_4, and 39.7 for DMSO-d_6. "Mass spectra" were recorded by the Imperial College London Department of Chemistry Mass Spectrometry Service on a Micromass Platform II or AutoSpec-Q spectrometer. "ultraviolet-visible (UV–vis) detection" was performed using a UV-1601 Shimadzu UV–vis spectrometer. "Molecular

Additional Supporting Information may be found in the online version of this article.
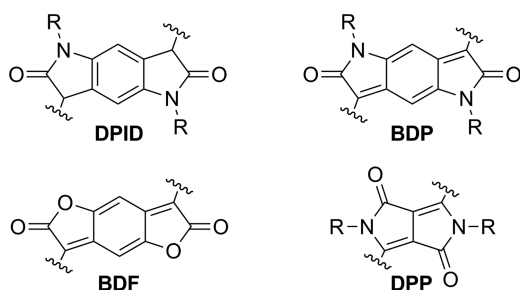
FIGURE 1 A structural comparison of various organic colorant cores with chromophores useful for electronic applications (R is an alkyl group).

weights" (number-average [M_n] and weight-average [M_w]) were recorded on an Agilent Technologies 1200 series gel permeation chromatography (GPC) in chlorobenzene at 80 °C, using two PL mixed B columns in series, calibrated against narrow polydispersity polystyrene standards. "Cyclic voltammetry" (CV) was performed under an argon atmosphere in a three-electrode electrochemical cell at a potential scan rate of 50 mVs^{-1}. Thin-films of the polymers were spin-coated (from chlorobenzene solution, 5 mg mL^{-1}) on conducting indium tin oxide (ITO) glass substrates and used with a platinum mesh counter electrode, Ag/Ag$^+$ reference calibrated against ferrocene and ^{n}Bu$_4$NPF$_6$ as the electrolyte in anhydrous acetonitrile solution (0.1 M). "Microwave chemistry" was performed in a Biotage initiator v.2.3. "Infrared spectra" were recorded using an FTIR spectrometer as evaporated films or neat using sodium chloride windows. Melting points are uncorrected.

Experimental Procedures and Reagents

Detailed experimental procedures are described below. All solvents, reagents, and other chemicals were used as received from commercial sources, or purified using standard procedures unless stated otherwise. The use of anhydrous chemicals, intuitive from the reaction, infers anhydrous conditions under an argon or nitrogen atmosphere. Glassware for inert atmosphere reactions was oven dried and cooled under a flow of nitrogen. All temperatures—other than room temperature—are recorded as bath temperatures of the reaction, unless stated otherwise. Merck aluminum-backed precoated silica gel (50 F254) plates were used for thin-layer chromatography. Visualization was by ultraviolet light (254 nm) and/or either potassium permanganate (VII), vanillin, iodine, or molybdate staining with heating as appropriate. Column chromatography was performed on Merck silia gel (Merck 9385 Kieselgel 60, 230-400 mesh) under a positive air pressure using reagent or guaranteed reagent (GR) grade solvent as received. petroleum ether (PE) refers to petroleum spirit 60–80 °C; Hex refers to hexane. THF was freshly distilled from sodium/benzophenone. For SmI$_2$-mediated reactions, freshly distilled THF was further deoxygenated before use by bubbling with nitrogen gas for 30 min. CH$_2$Cl$_2$ and Et$_3$N were freshly distilled from CaH$_2$. All other solvents and reagents were purchased from commercial sources and used as supplied.

Samarium diiodide was prepared by a modification of the procedure of Imamoto and Ono.[11] Samarium powder (2.00g,

13.8 mmol, 1.2 equiv.) was added to an oven-dried round-bottomed flask, and the flask was sealed and flushed with nitrogen gas for 20 min. THF (110 mL) was added, and the resulting suspension was bubbled with nitrogen gas for 15 min. Finally, iodine (2.80 g, 10.8 mmol, 1.0 equiv.) was added, and the flask flushed again with nitrogen gas for 10 min. The flask was covered in aluminum foil and heated at 60 °C for 18 h. The ~0.1 M solution was allowed to cool to room temperature and then used directly.

2-Octyldodecanoic Acid

To MeCN (850 mL), H$_5$IO$_6$ was added (53.5 g, 0.235 mol), and the mixture was stirred vigorously at room temperature for 15 min. 2-Octyldodecan-1-ol (31.8 g, 0.107 mol) was then added at 0 °C followed by addition of pyridinium chlorochromate (PCC) (460 mg, 2 mol %) in MeCN (2 × 50 mL), and the reaction mixture was stirred for overnight. The reaction mixture was then diluted with ethyl acetate (EtOAc) and washed with aq. NaHCO$_3$ solution and brine, respectively, dried (MgSO$_4$), and concentrated *in vacuo* to give the clean carboxylic acid (33.3 g, 99%).

^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 0.89 (t, J = 6.8 Hz, CH_3, 6H), 1.26–1.32 (m, CH_2, 28H), 1.49 (m, CHCH_2, 2H), 1.62 (m, CHCH_2, 2H), 2.35 (m, CH, 1H). ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 14.1 (2 × CH$_3$), 22.68, 22.70, 27.4, 29.28, 29.36, 29.44, 29.59, 29.63, 31.88, 31.93, 32.18 (16 × CH$_2$), 45.6 (CH), 183.2 (C=O). IR (ATR): ν_{max} (cm^{-1}): 2954, 2913, 2850, 1696, 1471, 1229, 1220, 953, 716. MS (ES$^+$): m/z (%): 335 (100, [M+Na]$^+$), 349 (80), 392 (40); HRMS (ES$^+$): C$_{20}$H$_{40}$O$_2$Na requires 335.2921, found 335.2917.

N,N'-(1,4-Phenylene)bis(2-octyldodecanamide) (2)

To a solution of 2-octyldodecanoic acid (33.3 g, 0.108 mol) in CH$_2$Cl$_2$ (200 mL) was added SOCl$_2$ (14.0 g, 0.117 mol) slowly at 0 °C and the mixture was stirred at room temperature overnight. The mixture was concentrated *in vacuo* to afford 2-octyldodecanoyl chloride which was used without further purification (crude = 35.3 g).

To a stirring solution of *p*-phenylenediamine (5.24 g, 48.5 mmol) and triethylamine (11.7 g, 0.116 mol) in CH$_2$Cl$_2$ (600 mL) was added 2-octyldodecanoyl chloride (35.3 g, 106.7 mmol) dropwise at 0 °C. The resulting mixture was then allowed to warm to room temperature and was stirred for 16 h. After this time the reaction mixture was filtered and washed with water, followed by ethanol, and dried *in vacuo* to yield the product as a poorly soluble yellow solid, which was used without further purification (crude = 35.5 g), m.p. 120–124° C (THF).

^{1}H NMR (400 MHz, CDCl$_3$) δ 0.79–1.01 (m, 12 H, 4 × CH$_3$), 1.19–1.43 (m, 56 H, 28 × CH$_2$), 1.44–1.58 (m, 4 H, 2 × CH$_2$), 1.63–1.79 (m, 4 H, 2 × CH$_2$), 2.10–2.25 (m, 2 H, 2 × CH), 7.15 (s, 2 H, 2 × NH), 7.45 (s, 4 H, 4 × ArCH). ^{13}C NMR (101 MHz, CDCl$_3$) δ 13.98 (2 × CH$_3$), 14.0 (2 × CH$_3$), 22.62 (2 × CH$_2$), 22.64 (2 × CH$_2$), 27.7 (4 × CH$_2$), 29.25 (2 × CH$_2$), 29.30 (2 × CH$_2$), 29.47 (2 × CH$_2$) 29.52 (2 × CH$_2$), 29.59 (2 × CH$_2$), 29.62 (2 × CH$_2$), 29.8 (4 × CH$_2$), 31.86 (2 × CH$_2$), 31.91 (2 × CH$_2$), 33.2 (4 × CH$_2$), 49.1 (2 × CH), 120.8 (4 ×

ArCH), 134.3 (2 × ArC), 174.4 (C=O). IR (ATR): ν_{max} cm^{-1}: 3282 (NH), 2953, 2918, 2849, 1650 (C=O), 1536, 1518. MS (EI$^+$): m/z (%): 697 (100, [M]$^+$), 402 (70); HRMS (ES$^+$): $C_{46}H_{84}O_2N_2$ requires 696.6527, found 696.6506.

N^1,N^4-Bis(2-octyldodecyl)benzene-1,4-diamine (3)

To a stirring solution of 2 (35.5 g, 51.0 mmol) in THF (500 mL) was added LiAlH$_4$ (7.74 g, 0.204 mol). The mixture was reflux for 72 h before quenched by 15-N NaOH solution at 0 °C. The salt was filtered from the mixture and the mixture was washed by ether for two times. The combined organic fractions were dried (MgSO$_4$) and concentrated *in vacuo* afford the unstable product as brown oil (32.3 g, 99% for three steps).

^{1}H NMR (500 MHz, C$_6$D$_6$), δ (ppm): 0.93 (t, J = 6.9 Hz, CH_3, 12H), 1.30–1.36 (m, CH_2, 64H), 1.57 (m, CH, 2H), 2.98 (d, J = 6.3 Hz, NCH_2, 4H), 6.62 (s, ArH, 4H). ^{13}C NMR (125 MHz, C$_6$D$_6$), δ (ppm): 14.8 (4 × CH$_3$), 23.5, 27.6, 30.22, 30.57, 32.73, 32.99, 38.7 (32 × CH), 49.6 (2 × NCH$_2$), 115.3 (4 × ArCH), 141.9 (2 × ArC). IR (ATR): ν_{max} (cm^{-1}): 2920, 2851, 1516, 1464, 1239. MS m/z (ES$^+$): 669 ([M$^+$]100%). HRMS (ES$^+$): $C_{46}H_{89}N_2$ requires 669.7021, found 669.7032.

N,N'-(1,4-Phenylene)bis(2-hydroxy-N-(2-octyldodecyl)acetamide) (4)

To a stirring solution of **3** (32.3 g, 48.3 mmol) and triethylamine (10.8 g, 0.106 mol) in CH$_2$Cl$_2$ (480 mL) was added acetoxyacetyl chloride (14.5 g, 0.106 mol) dropwise at 0 °C. The resulting mixture was then allowed to warm to room temperature and was stirred for 16 h. After this time, a saturated aqueous solution of NaHCO$_3$ was added, and the aqueous layer was washed with 2 × CH$_2$Cl$_2$, and the combined organic fractions were dried (MgSO$_4$) and concentrated *in vacuo* to yield intermediate acetoxy amide as a pale yellow solid (crude = 47.1 g), which was used without further purification.

To a solution of intermediate acetoxy amide (47.1 g, 48.3 mmol) and K$_2$CO$_3$ (65.0 g, 0.48 mol) in MeOH/H$_2$O (9:1, 300 mL) and THF (300 mL) was stirred for 18 h at room temperature. K$_2$CO$_3$ was then filtered and washed by EtOAc. H$_2$O was then added, and the organic layer was separated and washed with brine, dried (MgSO$_4$), and concentrated *in vacuo* to give the crude product. Purification by flash column chromatography on silica gel eluting with 30% EtOAc in hexane gave 4 (31.3 g, 83% for two steps) as pale yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 0.85 (t, J = 7.3 Hz, CH_3, 12H), 1.17–1.28 (m, CH_2, 64H), 1.44 (m, CH, 2H), 3.68 (d, J = 7.3 Hz, NCH_2, 4H), 3.86 (s, (C=O)CH_2, 4H), 7.22 (s, ArCH, 4H). ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 14.0 (4 × CH$_3$), 22.5, 26.1, 29.24, 29.16, 29.21, 29.53, 29.84, 30.96, 31.74, 31.79, 35.9 (32 × CH$_2$), 53.2 (2 × CH), 60.5 (2 × (C=O)CH$_2$), 129.4 (4 × ArCH), 140.1 (2 × ArC), 171.7 (2 × C=O). IR (ATR): ν_{max} (cm^{-1}): 2921, 2852, 1657, 1509, 1458, 1383, 1289, 1093. MS m/z (ES$^+$): 808 ([M+Na$^+$] 100%). HRMS (ES$^+$): $C_{50}H_{93}N_2O_4$ requires 785.7130, found 785.7125.

1,5-Bis(2-octyldodecyl)-3,7-bis-phenylsulfanyl-5,7-dihydro-1H,3H-pyrrolo[2,3-f]indole-2,6-dione (5)

To a stirred solution of oxalyl chloride (0.54 g, 4.26 mmol) in CH$_2$Cl$_2$ (5 mL) at −78°C under N$_2$ was added a solution

of DMSO (0.61 g, 7.76 mmol) in CH$_2$Cl$_2$ (5 mL) dropwise via cannula, the resulting solution was then stirred for 30 min before a solution of 4 (1.52 g, 1.94 mmol) in CH$_2$Cl$_2$ (7.4 mL) was added dropwise. The solution was stirred for a further 1 h, then NEt$_3$ (1.96 g, 19.4 mmol) was added at −78 °C, and the solution allowed to warm to 20 °C. The resulting suspension was then stirred for a further 1.5 h. CH$_2$Cl$_2$ (75 mL) and a saturated aqueous solution of NaHCO$_3$ (100 mL) were then added, and the organic layer was separated and washed with a saturated aqueous solution of NaHCO$_3$ (2 × 100 mL), dried with MgSO$_4$ and concentrated *in vacuo* to yield the intermediate glyoxamide as a green oil, which was used immediately without further purification.

To a solution of the glyoxamide in CH$_2$Cl$_2$ (20 mL) was added thiophenol (1.68 g, 3.49 mmol). The resulting solution was stirred for 15 h at 20 °C. TFAA (4.67 mL, 34.9 mmol) was then added, the solution stirred for 1 h, then BF$_3$.OEt$_2$ (2.42 mL, 19.4 mmol) was added. After 2 h, the solution was cooled to 0 °C and carefully quenched with a saturated aqueous solution of NaHCO$_3$ (100 mL), then washed with a saturated aqueous solution of NaHCO$_3$ (3 × 25 mL), dried with MgSO$_4$, and concentrated *in vacuo* to yield 5 as a deep red oil (crude = 1.73 g), which was used without further purification.

^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 0.92 (m, CH_3, 12H), 1.33 (m, CH_2, 64H), 1.77 (m, CH, 2H), 3.48 (m, NCH_2, 4H), 4.61 (s, CHS, 2H, one diastereoisomer), 4.63 (s, CHS, 2H, one diastereoisomer), 6.74 (s, ArH, 2H), 7.26 (m, ArH, 4H), 7.33 (m, ArH, 2H), 7.46 (m, ArH, 4H). ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 14.0 (4 × CH$_3$), 22.5, 26.1, 29.2, 31.8 (32 × CH$_2$), 36.0 (2 × CH), 44.8 (2 × NCH$_2$), 49.3 (2 × CHS), 106.3 (2 × ArCH), 126.6 (2 × ArC), 128.6 (2 × ArCH), 131.1 (2 × ArC), 133.9 (2 × ArCH), 139.1 (2 × ArC), 173.4 (2 × C=O). IR (ATR): ν_{max} (cm^{-1}): 2922, 2852, 1699, 1470, 1346, 1159, 872, 738, 689, 649. MS m/z (ES$^+$): 964 (100%, M$^+$). HRMS (ES$^+$): $C_{62}H_{95}N_2O_2S_2$ requires 963.6840, found 963.6825.

1,5-Bis(2-octyldodecyl)-5,7-dihydro-1H,3H-pyrrolo [2,3-f]indole-2,6-dione (6)

To a stirred solution of 5 (1.73 g, 1.80 mmol) in THF (30 mL) was added SmI$_2$ (89.8 mL of a 0.1 M solution in THF, 5.0 equiv.) at room temperature. After 14 h, the reaction mixture was opened to air and aqueous saturated NaHCO$_3$ (250 mL) was added. The aqueous layer was extracted with EtOAc for three times, the organic layer was dried (Mg$_2$SO$_4$) and concentrated *in vacuo*. Purification by column chromatography using 10% EtOAc in petroleum ether as eluant gave **6** (738 mg, 51% for three steps) as a deep green oil.

^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 0.84 (t, J = 7.1 Hz, CH_3, 12H), 1.21–1.36 (m, CH_2, 64H), 1.82 (m, CH, 2H), 3.52 (d, J = 7.6 Hz, NCH_2, 4H), 3.55 (s, (C=O)CH_2, 4H), 6.71 (s, ArH, 2H). ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 14.0 (4 × CH$_3$), 22.5, 26.3, 29.15, 29.88, 31.7 (32 × CH$_2$), 35.9 (2 × NCH$_2$), 36.1 (2 × CH), 44.5 (2 × (C=O)CH$_2$), 105.7 (2 × ArCH), 123.6 (2 × ArC), 139.9 (2 × ArCN), 174.5 (2 × C=O). IR (ATR): ν_{max} (cm^{-1}): 2920, 2852, 1702 (C=O), 1473, 1376, 1344, 1160, 1125. MS(ES$^+$): 772 ([M+Na]$^+$, 100%). HRMS (ES$^+$): $C_{50}H_{88}N_2O_2Na$ requires 771.6729, found 771.6739.
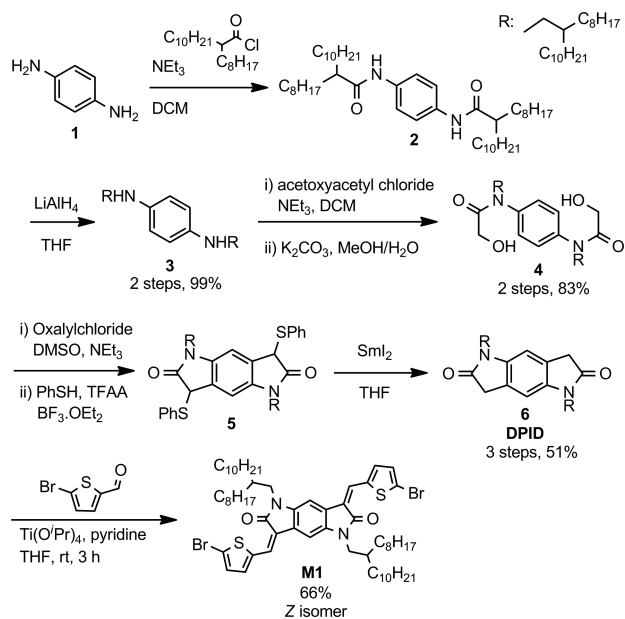
SCHEME 1 Synthesis of the **DPID** monomer **M1**.

(3Z)-(7Z)-1,5-Bis(2-octyldodecyl)-3,7-bis-[(5-bromothiophen-2-yl)-5,7-dihydro-1H,3H-pyrrolo[2,3-f]indole-2,6-dione (M1)

To a solution of 6 (97.6 mg, 0.13 mmol) in THF (2 mL) was added 2-thiophene-carboxaldehyde (54.8 mg, 0.29 mmol), pyridine (41 mg, 0.52 mmol), and Ti(OiPr)$_4$ (222 mg, 0.78 mmol). The reaction mixture was stirred in room temperature for 3 h. Then it was diluted with ethyl acetate (25 mL), washed with water (25 mL), aqueous NaHCO$_3$ (25 mL), and brine (25 mL), dried with MgSO$_4$, and concentrated *in vacuo* to give the crude product. Purification by flash column chromatography on silica gel eluting with 30% CH$_2$Cl$_2$ in hexane gave M1 (93.7 mg, 66%) as a black solid.

^{1}H NMR (400 MHz, C$_6$D$_6$), δ (ppm): 0.92 (t, J = 6.6 Hz, CH_3, 12H), 1.27–1.47 (m, CH_2, 64H), 2.10 (m, CH, 2H), 3.77 (d, J = 7.3 Hz, NCH_2, 4H), 6.73 (d, J = 4.0 Hz, BrC=CH, 2H), 6.86 (s, C=CH, 2H), 6.89 (d, J = 4.3 Hz, SC=CH, 2H), 7.31 (s, ArCH, 2H). ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 14.8 (4 × CH_3), 23.5, 27.2, 30.21, 30.9, 32.7 (32 × CH_2), 37.3 (2 × CH),

44.9 (2 × NCH_2), 100.1 (2 × C=CH), 122.5 (2 × CBr), 123.4 (2 × ArC), 124.8 (2 × C=CH), 127.3 (2 × ArCH), 130.4 (2 × BrC=CH), 137.8 (2 × SC=CH), 138.4 (2 × SC=CH), 140.2 (ArCN), 166.9 (2 × C=O). IR (ATR): ν_{max} (cm^{-1}): 2920, 2850, 1684, 1604, 1478, 1414, 1381, 1121, 785, 662. MS (MALDI-Dithranol): 1095 ([M]$^+$, 100%).

Poly-(3Z)-(7Z)-1,5-bis(2-octyldodecyl)-3,7-bis-[(5-thiophen-2-yl)-5,7-dihydro-1H,3H-pyrrolo[2,3-f]indole-2,6-dione-phenyl (P1)

[PDPIDDT-P: Poly-dihyropyrroloindoledionedithiophenyl-phenyl]. A microwave vial was charged with M1 (76 mg, 0.07 mmol), 1,4-benzenediboronic acid bis(pinacol) ester (37 mg, 0.09 mmol), 5 mol % of tris(dibenzylideneacetone)dipalladium, and 10 mol % of triphenylphosphine and sealed. A degassed solution of Aliquat 336 (two drops) in toluene (1.5 mL) was then added, followed by a degassed aqueous solution (0.3 mL) of potassium phosphate tribasic (63 mg, 0.30 mmol), and the mixture refluxed with vigorous stirring for 3 days at 115 °C. The crude polymer was precipitated in methanol and then purified by Soxhlet extraction with acetone, hexane, and chloroform. Remaining palladium residues were removed by vigorously stirring the latter fraction with aqueous sodium diethyldithiocarbamate for 3 h at 55 °C. The organic phase was then separated, washed (water), concentrated *in vacuo*, and again precipitated in methanol, filtered off, and dried under high vacuum to afford the title compound as a dark purple solid (26 mg, 37% yield). M_n = 106 kDa, M_w = 186 kDa, PDI = 1.75.

Poly-(3Z)-(7Z)-1,5-bis(2-octyldodecyl)-3,7-bis-[(5-thiophen-2-yl)-5,7-dihydro-1H,3H-pyrrolo[2,3-f]indole-2,6-dione-thiophene (P2)

[PDPIDDT-T: Poly-dihyropyrroloindoledionedithiophenyl-thiophene]. A microwave vial was charged with M1 (98 mg, 0.09 mmol), 2,5-bis(trimethylstannyl)thiophene (37 mg, 0.09 mmol), 2.2 mol % of tris(dibenzylideneacetone)dipalladium, and 8.8 mol % of tri(o-tolyl)phosphine. The vial was then sealed, chlorobenzene added, the mixture degassed and submitted to the microwave reactor for: 3 min at each of 100, 120, 140, and 160 °C and finally 50 min at 180 °C. The crude polymer was precipitated in methanol and then purified by Soxhlet extraction with acetone, hexane, and chloroform. Remaining palladium residues were removed by vigorously stirring the latter fraction with
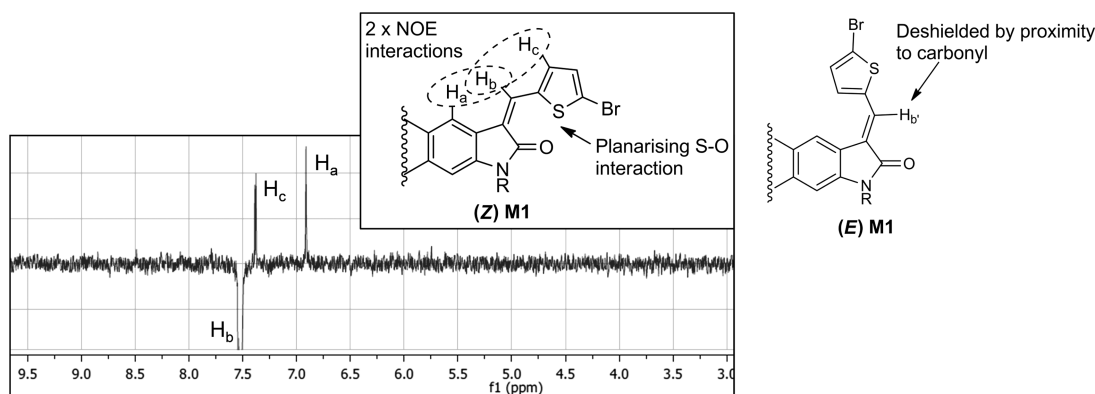
FIGURE 2 Determination of **M1** configuration by NOE and proton NMR analysis.

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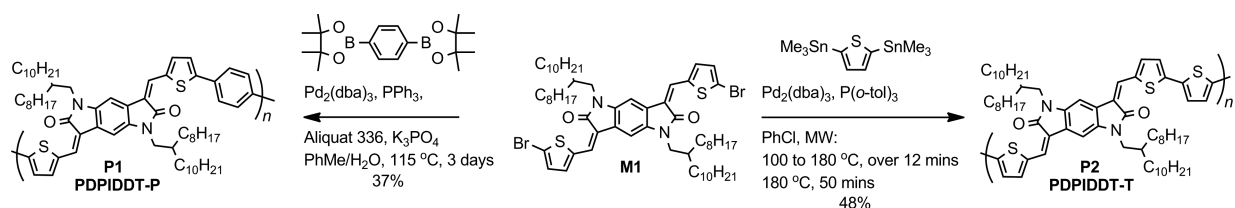
SCHEME 2 Synthesis of **DPID** polymers **P1** and **P2**.

aqueous sodium diethyldithiocarbamate for 3 h at 55 °C. The organic phase was then separated, washed (water), concentrated *in vacuo* and again precipitated in methanol, filtered off, and dried under high vacuum to afford the title compound as a dark purple solid (52 mg, 57% yield). $M_n = 25$ kDa, $M_w = 41$ kDa, PDI = 1.60.

RESULTS AND DISCUSSION

The **DPID** tricycle **6** was synthesized as depicted in Scheme 1. *p*-Phenylenediamine **1** underwent two-directional acylation with 2-octyldodecanoyl chloride to give the diamide **2** and subsequent reduction to give the corresponding diamine **3** in good yield. Reaction with acetoxyacetyl chloride followed by ester hydrolysis proceeds in good yield to give the 1,4-bis(hydroxyacetamide) **4**. Swern oxidation affords the 1,4-bis(glyoxamide), which then undergoes a two-directional Pummerer-type[12] cyclization as previously developed by Procter et al.[13] to close the intermediate tricycle **5**. Reductive cleavage of the sulfanyl groups by samarium iodide[14,15] completes the **DPID** core (**6**). The use of a bulky thiophenol in the Pummerer-type cyclization gave predominantly (>5:1) the *linear* isomer shown (**5**), presumably due to unfavorable steric interactions involved in forming the alternative "bent" isomer.

The "linear" **DPID** tricycle **6** was then subjected to a two-directional Knoevenagel condensation with 5-bromo-2-thiophenecarboxaldehyde. Use of the coordinating Lewis acid titanium(IV) iso-propoxide promotes the reaction forming the *Z* isomer.[16] Separation by column chromatography thus afforded the monomer **M1** almost exclusively in its expected *cis (Z)* configuration, as a waxy black solid[17] (Fig. 2). A nuclear Overhauser effect experiment reveals a through-space interaction between the vinyl proton H_b and both the H_a pro-

ton on the center ring and the H_c proton on the thiophene for the *Z*-isomer, confirming the stereochemistry present.

Meanwhile in the *E*-isomer, the H_b vinyl proton is shifted downfield due to the deshielding effect of the carbonyl group (Fig. 2).[18] The *Z* isomer is desired as this facilitates a planarizing sulfur–oxygen interaction believed to result from a 3-center-4-electron interaction between a lone pair of electrons on the oxygen atom and a σ^*_{S-C} orbital leading to a weak unsymmetrical hypervalent bond.[19]

The synthesis of the polymers is shown in Scheme 2. The phenyl copolymer **P1** was synthesized under standard Suzuki coupling conditions in a toluene/water solvent system, whereas the thiophene copolymer **P2** was synthesized under standard microwave Stille coupling conditions in chlorobenzene. The polymers were purified by precipitation from methanol followed by Soxhlet extraction using acetone, hexane, and finally chloroform. The latter fraction was then heated and vigorously stirred with aqueous sodium diethyl-dithiocarbamate to remove residual catalytic metal impurities. Lower molecular-weight oligomers were readily removed in the acetone and hexane fractions, giving a particularly high number-average molecular weight for **P1** and a satisfactory value for **P2** ($M_n = 106$ and 25 kDa for **P1** and **P2**, respectively) with moderate polydispersity indexes (PDIs) (Table 1).

Optical absorption spectra of the **DPID** monomer **M1** and polymers **P1** and **P2** are shown in Figure 3 and key properties summarized in Table 1. While the monomer displays absorption maxima below 450 nm, both polymers display a maxima above 600 nm due to extended conjugation. The red-shift in solution (~25 nm) from **P1** to **P2** can be attributed to the difference of comonomer from phenyl to the more

**TABLE 1** Properties of DPID Polymers P1 and P2

Compounds	M_n (kDa)[a]	M_w (kDa)[a]	PDI[a]	λ_{max}^{abs} (nm) Solution[c]	λ_{max}^{abs} (nm) Film[d]	E_g^{opt} (eV)	E_{ox}^{onset} (eV vs. Fc/Fc$^+$)	E_{red}^{onset} (eV vs. Fc/Fc$^+$)	Energy Levels (eV)[b] E_{HOMO}	Energy Levels (eV)[b] E_{LUMO}
P1	106	186	1.7	630	635	1.68	0.66	−0.91	−5.47	−3.89
P2	25	41	1.6	655	655	1.57	0.67	−0.85	−5.47	−3.95

[a] Determined by GPC using polystyrene standards and PhCl as the eluent at 80°C.
[b] Calculated using the equations $E_{HOMO} = -E_{ox}^{onset}$ (vs. Fc/Fc$^+$) − 4.8 eV, $E_{LUMO} = -E_{red}^{onset}$ (vs. Fc/Fc$^+$) + 4.8 eV.[20]
[c] Solutions in dilute PhCl.
[d] Thin-films spin-coated from ~5 mg mL^{-1} PhCl solutions on glass substrates.
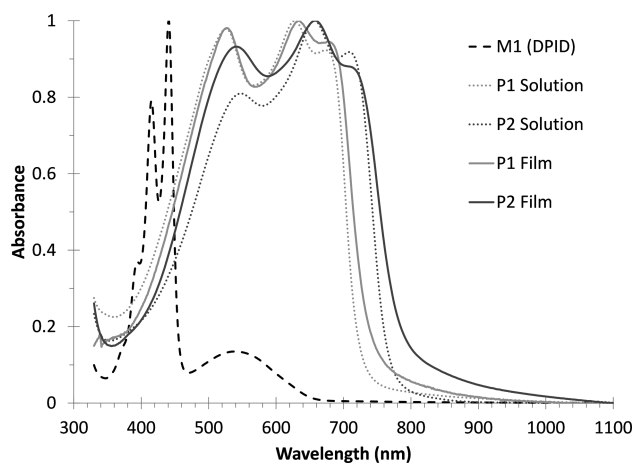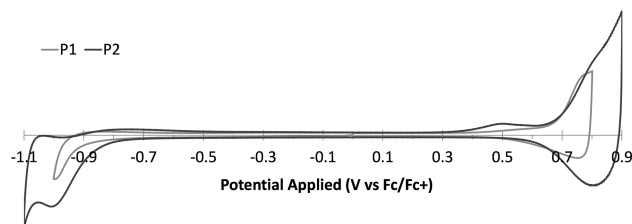
FIGURE 3 Normalized UV–vis absorption spectra of **M1** and polymers **P1** and **P2**; dilute solutions are in chlorobenzene; and thin-films spin-coated from ∼5 mg mL^{-1} chlorobenzene solutions on glass substrates.

electron rich and more planarizing thiophene unit. The redshift (∼20 nm in the onset of absorption) on going from solution to film is not very strong, presumably due to aggregation in the solutions from intermolecular interactions such as solid-state packing effects, which may be beneficial for charge transport. In addition, **P1** and **P2** both display a particularly broad absorption, which may be favorable for light absorption and subsequent charge generation in heterojunction solar cells. The low optical bandgaps show **DPIDs** should be effective units for constructing low-bandgap polymers.

Electrochemical behavior is summarized in Table 1 and shown in Figure 4. The polymers were investigated by cyclic voltammetry (CV) in a three-electrode electrochemical cell with an ITO working electrode, Ag/Ag$^+$ reference electrode and Pt counter electrode. Bu$_4$NPF$_6$ in acetonitrile solution (0.1 M) was used as the electrolyte. Thin-films of the polymers were spin-coated (from chlorobenzene solution, 5 mg mL^{-1}) on ITO conducting glass substrates. The potentials were calibrated using the ferrocene/ferrocenium redox couple (Fc/Fc$^+$).

Both polymers show irreversible reduction at negative potential and pseudoreversible oxidation at positive scan. The highest occupied molecular orbital (HOMO) levels, esti-

mated from the oxidation onset, are both −5.47 eV. The lowest unoccupied molecular orbital (LUMO) energy levels of **P1** and **P2**, estimated from the reduction onset, are −3.89 and −3.95 eV, respectively. Such deep energy levels are comparable to those of **BDP**-based polymers, showing stronger electron affinities and lower electron densities than typical **DPP**-based polymers. These deep HOMO energy levels could lead to a high open-circuit voltage (V_{oc}) in devices and may indicate good air stability.

The difference in bandgap (∼0.1 eV) between **P1** and **P2** is related to a lower **P2** LUMO level, as found by CV. This might be due to the reduced **P2** dihedral angle (between the **DPID** cores and flanking vinyl groups) allowing a more planar conjugated backbone.[21]

Figure 5 displays the optimized structures of **P1** and **P2**, their HOMO and LUMO energy distributions and their calculated bandgaps and dihedral angles (at the B3LYP/6-31G* level, for *N*-methyl-substituted polymers, modeled as tetramers only shown in part). While both polymers are almost fully planar, **P2** shows less torsional twisting (consistently a 0° dihedral angle) between the **DPID** core and the flanking vinyl groups. This supports the notion that the slight twisting of **P1** induces a bandgap ∼0.1 eV wider than more planar **P2**. Interestingly, for both polymers the HOMO and LUMO are both delocalized along the polymer chain, as opposed to being localized on the donor and acceptor parts,
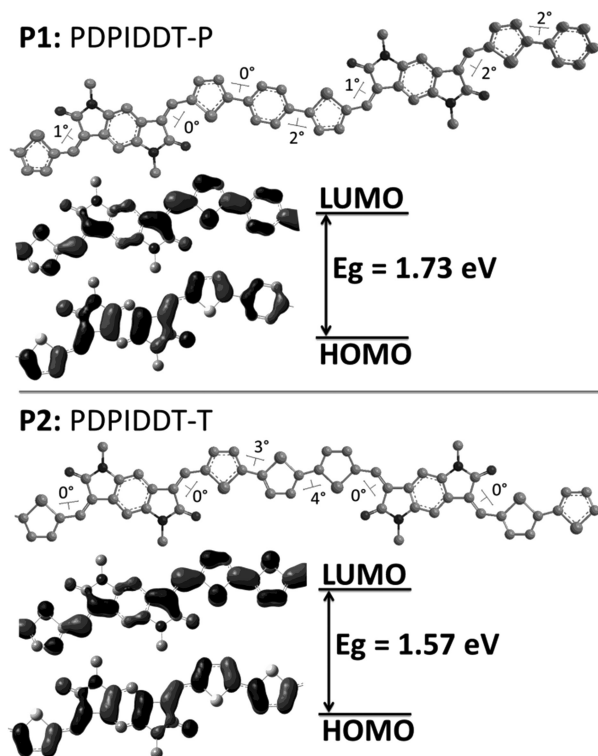
FIGURE 5 Segments of energy minimized structures (B3LYP/6-31G*) of **P1** and **P2** tetramers with *N*-methyl substitution showing calculated dihedral angles, with visualization of the HOMO (bottom) and LUMO (top) energy distributions and calculated bandgap beneath each structure.

FIGURE 4 Cyclic voltammograms of **P1** and **P2** (thin-films spin-coated from chlorobenzene solution [5 mg mL^{-1}] on conducting indium tin oxide [ITO] glass substrates.

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respectively. This large delocalization could facilitate enhanced ambipolar transport.

CONCLUSIONS

In summary, two novel **DPID**-based copolymers were designed and synthesized by a completely two-directional pathway. Both polymers show broad, long wavelength absorption and deep energy levels. PDPIDDT-P [**P1**] and PDPIDDT-T [**P2**] are characterized by UV–vis absorption spectroscopy, electrochemical oxidation and reduction (CV) and computational modeling. The broad absorption profile and planar backbone of PDPIDDT-T [**P2**] makes it a promising donor polymer for both organic transistors and solar cells.

The investigation of organic photovoltaic devices and organic field-effect transistors, both with varied aromatics flanking the **DPID** core, varied comonomers, and linear alkyl chains for transistor applications[22] will be of interest. Work in this direction is in progress and will be reported in due course.

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