



## Diketopyrrolopyrrole-based oligomers accessed *via* sequential C–H activated coupling for fullerene-free organic photovoltaics



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### ABSTRACT

Exploring sustainable chemistry for renewable energy plays a key role in meeting the ever increasing energy demand without sacrificing the environment. In this study, two novel diketopyrrolopyrrol(DPP)-based  $\pi$ -conjugated oligomers (named as **TPE-DPP<sub>4</sub>** and **BP-DPP<sub>4</sub>**) have been readily synthesized *via* a ligand-free Pd-catalyzed sequential activation of C–H bond in two steps with good yields starting from simple building blocks. Poly(3-hexylthiophene) is employed as an electron donor to blend with the new DPP-derived electron acceptors for the fullerene-free bulk heterojunction organic photovoltaics. The power conversion efficiency of 2.49% has been achieved, corresponding with an open-circuit voltage of 1.16 V, which is among the highest open-circuit voltages for the single-junction organic photovoltaics. The readily accessible electron acceptors blended with cost-effective poly(3-hexylthiophene) donor for fullerene-free organic photovoltaics opens a new pathway to access renewable solar energy *via* sustainable chemistry.

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### 1. Introduction

Bulk heterojunction organic photovoltaics (BHJ OPV) has emerged as a promising renewable energy technology due to its merits of low-cost, light-weight, solution-processability and good flexibility [1–4]. Typically, the active layers of OPVs consist of fullerenes as electron acceptors (A) and conjugated (macro) molecules as electron donors (D) [5]. In spite of their widespread usage, fullerene-based acceptors do suffer from drawbacks including weak absorption of visible light, poor stability of morphology, limited chemical and electronic tunability, and high production cost, which may suppress the sustainability of OPV technology. In recent years, the conjugated semiconducting polymers and oligomers [6], which possess broad tunability in all the aspects of light absorption, frontier orbital energy levels (FOEL), electron affinity, molecular geometry and synthetic complexity, have been explored

as electron acceptors in place of fullerenes for BHJ OPVs [7–14]. These fullerene-free OPVs have raised extensive attention and led to a rapid progress very recently [15–22], e.g., the indacenodithieno [3,2-b]thiophene-2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile (ITIC) acceptor developed by the Zhan group [15]. Nevertheless, to ensure the cost-effectiveness and sustainability of fullerene-free OPVs, the accessibility of both acceptor and donor materials need to be carefully evaluated [23–25]. Green and sustainable synthetic strategies [26–39] to the  $\pi$ -conjugated materials using readily available building blocks are favorable to reach the above goal [23]. Moreover, the use of commercially available and well-developed semiconducting materials with relatively low price is recommendable [23–25].

In the current work, two novel DPP-based oligomer acceptors have been designed and synthesized *via* direct arylation of C–H bond (DACH) to pair with polymeric donor P3HT for fullerene-free BHJ OPV applications. Concerning the sustainability, this P3HT-DPPs donor-acceptor combination has some distinct advantages. DPP is not only a commercialized dye chromophore [40], but also a sustainable and readily available building block for the organic semiconducting materials [41–44]. Previous investigation shows that DPP unit is among the most synthetically accessible electron-poor monomers due to its low synthetic complexity [23]. Also, as

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demonstrated by our previous study, the accessibility of DPP derivatives can be further increased by employing the atom-efficient C–H activation reaction [45]. As for the donor applied herein, P3HT is one of the most frequently studied 2nd generation semi-conducting polymers, which has a relatively lower price compared with other high performance 3rd generation D–A semiconducting polymers [25,46]. It is known that P3HT donor has a wide bandgap, and high-lying LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital) levels. Meanwhile, the conjugated polymers or oligomers containing a DPP block typically have narrow or medium bandgaps with higher LUMO levels compared to the commonly-used acceptors such as PC<sub>61</sub>BM or perylene diimide (PDI) which has four electron-withdrawing carbonyl groups [47,48]. Therefore, the P3HT-DPP BHJ OPVs are expected to achieve high open-circuit voltages ( $V_{OC}$ ) and a broad range of light harvesting, due to the enlarged gap between LUMO of DPP and HOMO of P3HT, and the complementary light absorptions of the wide-bandgap P3HT and narrow-bandgap DPPs [49–53].

Taking all of the abovementioned aspects into account, two novel non-planar oligomers both containing four DPP blocks have been design and synthesized in good yields by direct arylation of mono-phenyl capped DPP respectively using tetrakis(4-bromophenyl)ethene (TBPE) and tetrabromo-biphenyl (TBBP) as arylating reagents. From the viewpoint of molecular design, the twisted non-planar [20–22,54,55], quasi-3D [56] and 3D [52,53,57–59] molecular acceptors suggest that the optimization of the morphology of BHJ layer and thus fill factors ( $FF$ ) can be realized by molecular geometry engineering. Tetraphenylethene (TPE) has been widely used as a building block in the field of aggregation-induced emission (AIE) [60,61] and very recently as a core for PDI-based 3D non-fullerene acceptor [54]. In this study, for the first time, the TPE and biphenyl (BP)-cored tetra-DPP (named as **TPE-DPP<sub>4</sub>** and **BP-DPP<sub>4</sub>**, Scheme 1) have been easily obtained via sequential C–H activation starting from simple building blocks. To the best of our knowledge, there are no previous reports using strategy of sequential C–H activation for accessing structurally complicated DPP-based oligomers. The non-planar conjugated oligomers obtained herein were further evaluated as non-fullerene acceptors in BHJ OPVs by using cost-effective P3HT as donor, affording a highest PCE of 2.49% with an open-circuit voltage ( $V_{oc}$ ) of 1.16 V, which is among the highest  $V_{oc}$  for the single-junction OPVs reported. The integration of easily accessible acceptors with an economical donor for fullerene-free OPVs provided by us represents a step toward accessing renewable solar energy by sustainable chemistry.

## 2. Experimental section

The general synthetic routes toward Ph-DPP, **TPE-DPP<sub>4</sub>** and **BP-DPP<sub>4</sub>** are outlined in Scheme 1. The detailed synthetic procedures are as follows.

### 2.1. Synthesis of Ph-DPP

DPP (1000 mg, 524.78, 1.90 mmol), PivOH (60 mg, 0.3 equiv.), and anhydrous K<sub>2</sub>CO<sub>3</sub> (316 mg, 1.2 equiv.) were added into a Schlenk tube. The mixed solid in the tube was purged by repetitions of vacuum and nitrogen filling ( $\times 3$ ). Then a mixture of bromobenzene (300 mg, 1.90 mmol) and an anhydrous DMA (25 mL) solution of Pd(OAc)<sub>2</sub> ( $8 \times 10^{-5}$  M) was added into the tube. The reaction solution was put through freeze-vacuum-thaw cycles three times to remove dissolved gases, and then rigorously stirred at 110 °C for 10 h under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into an aqueous solution of NaCl (saturated, 250 mL) to remove the high boiling point solvent

DMA. The precipitate was extracted with CH<sub>2</sub>Cl<sub>2</sub> ( $3 \times 40$  mL). The combined organic layer was washed with distilled water. Removal of the solvent by rotary evaporator afforded the crude product, which was then purified by column chromatography on silica gel using the mixtures of CH<sub>2</sub>Cl<sub>2</sub> and hexane as eluent (1.5:1, v/v) and gave a deep red solid (790 mg, 70%). The thin layer chromatography (TLC) analysis for the reaction is shown in Fig. S1 (see Supplementary Information, SI). Ph-DPP is a known compound [45].

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.97 (d,  $J = 4.0$  Hz, 1H), 8.89 (d,  $J = 3.5$  Hz, 1H), 7.68 (d,  $J = 7.5$  Hz, 2H), 7.62 (d,  $J = 5.0$  Hz, 1H), 7.42 (ddd,  $J = 5.0, 6.5, 4.0$  Hz, 4H), 7.30–7.27 (m, 1H), 4.16–3.89 (m, 4H), 1.93 (d,  $J = 5.5$  Hz, 2H), 1.37–1.25 (m, 16H), 0.88 (ddd,  $J = 5.5, 6.0, 3.5$  Hz, 12H).

### 2.2. Synthesis of TPE-DPP<sub>4</sub>

Ph-DPP (300 mg, 0.5 mmol), 1,1,2,2-tetrakis(4-bromophenyl) ethene (TBPE) (65 mg, 0.1 mmol), PivOH (15 mg, 0.15 mmol), and anhydrous K<sub>2</sub>CO<sub>3</sub> (83 mg, 0.6 mmol) were added into a Schlenk tube. The mixed solid in the tube was purged by repetitions of vacuum and nitrogen filling ( $\times 3$ ). Then 10 mL anhydrous DMA solution of Pd(OAc)<sub>2</sub> ( $5 \times 10^{-5}$  M) was added into the tube via syringe. The reaction solution was put through freeze-vacuum-thaw cycles three times to remove dissolved gases, and then rigorously stirred at 110 °C for 10 h under nitrogen atmosphere. The post-treatment of the reaction are similar to that of Ph-DPP. The crude product was purified by column chromatography on silica gel using the mixtures of CHCl<sub>3</sub> and ethyl acetate (EA) as eluent (100:1, v/v) and gave a dark blue solid (235 mg, yield 86%, calculated from TBPE).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.93 (dd,  $J = 11.4, 4.2$  Hz, 8H), 7.64 (d,  $J = 7.5$  Hz, 8H), 7.49 (d,  $J = 8.1$  Hz, 8H), 7.37 (dd,  $J = 38.7, 7.3$  Hz, 20H), 7.13 (d,  $J = 7.7$  Hz, 8H), 4.04 (s, 16H), 1.91 (s, 8H), 1.30 (d,  $J = 68.0$  Hz, 65H), 0.86 (dd,  $J = 34.4, 15.3$  Hz, 48H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  164.26, 152.32, 152.56, 146.39, 142.54, 142.23, 139.52, 135.77, 134.98, 134.45, 131.77, 131.51, 128.72, 128.20, 127.05, 111.01, 110.78, 48.61, 41.96, 32.99, 31.25, 26.33, 25.86, 16.71, 13.26.

MALDI-TOF MS ( $m/z$ ): [M]<sup>+</sup> calcd for C<sub>170</sub>H<sub>188</sub>N<sub>8</sub>O<sub>8</sub>S<sub>8</sub>, 2727.90; found, 2728.42. Elemental Anal.: calcd: C, 74.85; H, 6.95; N, 4.11. Found: C, 74.86; H, 6.95; N, 4.12.

### 2.3. Synthesis of BP-DPP<sub>4</sub>

Ph-DPP (300 mg, 0.5 mmol), 3,3',5,5'-tetrabromo-1,1'-biphenyl (TBBP) (47 mg, 0.1 mmol), PivOH (15 mg, 0.15 mmol), and anhydrous K<sub>2</sub>CO<sub>3</sub> (83 mg, 0.6 mmol) were added into a Schlenk tube. The mixed solid in tube was purged by repetitions of vacuum and nitrogen filling ( $\times 3$ ). Then an anhydrous DMA (10 mL) solution of Pd(OAc)<sub>2</sub> ( $5 \times 10^{-5}$  M) was added into the tube via syringe. The reaction solution was put through freeze-vacuum-thaw cycles three times to remove dissolved gases, and then rigorously stirred at 110 °C for 10 h under nitrogen atmosphere. The post-treatment of the reaction are similar to that of Ph-DPP. The crude product was purified by column chromatography on silica gel using the mixtures of CHCl<sub>3</sub> and ethyl acetate (EA) as eluent (100:1, v/v) and gave a dark blue solid (216 mg, yield 85%, calculated from TBBP).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  9.00 (s, 8H), 7.82 (d,  $J = 26.8$  Hz, 6H), 7.56 (m, 12H), 7.33 (m, 16H), 3.98 (s, 16H), 1.90 (s, 8H), 1.31 (d,  $J = 78.8$  Hz, 64H), 0.80 (d,  $J = 77.5$  Hz, 48H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  168.32, 163.96, 163.74, 152.46, 144.92, 140.06, 137.47, 135.68, 133.54, 132.53, 131.84, 131.28, 128.48, 126.99, 111.23, 110.32, 110.09, 48.62, 42.01, 32.46, 32.02, 31.28, 29.93, 26.36, 25.77, 16.78.

MALDI-TOF MS ( $m/z$ ): [M]<sup>+</sup> calcd for C<sub>156</sub>H<sub>178</sub>N<sub>8</sub>O<sub>8</sub>S<sub>8</sub>, 2549.67;

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