Harnessing Direct(Hetero)Arylation in Pursuit of a Saddle-Shaped Perylene Diimide Tetramer

Joshua Koenig, Audrey Laventure, Gregory Welch

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This contribution explores the direct(hetero) arylation (DHA) cross-coupling of a saddle-like, π-conjugated cyclooctatetrathiophene (Th₄) core with the N-annulated perylene diimide (PDI) chromophore. Replacing the bulky pivalic acid with acetic acid enabled a facile cross-coupling, selectively forming a PDI tetramer (Th₄PDI₄) in a 70% overall yield. The optoelectronic properties of Th₄PDI₄ were characterized and density functional theory (DFT) was used to calculate the optimized molecular geometry and molecular orbitals (MOs). MOs determined by cyclic voltammetry corresponded well with those calculated using DFT. The molecular geometry calculated by DFT showed Th₄PDI₄ adopts two separate PDI-PDI conformations (propeller and double-decker). Organic photovoltaic (OPV) devices were fabricated using a blend of PTB7-Th:Th₄PDI₄, where an initial power conversion efficiency (PCE) of 1.89 % was improved by testing a series of solvent additives and thermal annealing techniques. Through use of 3 % (v/v) 1-chloronaphthalene additive, a combination of higher short circuit current (J_sc = 10.2 mA/cm²) and fill factor (FF = 42 %) led to an overall increase in PCE to 4.26 %.
Harnessing Direct(Hetero)Arylation in Pursuit of a Saddle-Shaped Perylene Diimide Tetramer

Josh D. B. Koenig, Audrey Laventure, and Gregory C. Welch a*

a Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, Alberta, T2N 1N4, Canada.
* Corresponding Author
Email: gregory.welch@ucalgary.ca
Phone Number: 1-403-210-7603

Abstract

This contribution explores the direct(hetero) arylation (DHA) cross-coupling of a saddle-like, π-conjugated cyclooctatetra thiophene (Th4) core with the N-annulated perylene diimide (PDI) chromophore. Replacing the bulky pivalic acid with acetic acid enabled a facile cross-coupling, selectively forming a PDI tetramer (Th4PDI4) in a 70% overall yield. The optoelectronic properties of Th4PDI4 were characterized and density functional theory (DFT) was used to calculate the optimized molecular geometry and molecular orbitals (MOs). MOs determined by cyclic voltammetry corresponded well with those calculated using DFT. The molecular geometry calculated by DFT showed Th4PDI4 adopts two separate PDI-PDI conformations (propeller and double-decker). Organic photovoltaic (OPV) devices were fabricated using a blend of PTB7-Th:Th4PDI4, where an initial power conversion efficiency (PCE) of 1.89 % was improved by testing a series of solvent additives and thermal annealing techniques. Through use of 3 % (v/v) 1-chloronaphthalene additive, a combination of higher short circuit current (Jsc = 10.2 mA/cm²) and fill factor (FF = 42 %) led to an overall increase in PCE to 4.26 %.
Introduction

High performance organic photovoltaic (OPV) devices often make use of a bulk-heterojunction (BHJ), which consists of electron-donor and electron-acceptor materials. Energy from photons is harvested in the BHJ to generate free-charge carriers, which must be subsequently extracted and transported to their respective electrodes to generate current \[^1\]. Conventionally, fullerene derived materials have been used as the electron acceptor component. However, for fullerenes, the high cost of production, low visible light absorptivity, and long-term instability has caused many to explore the viability of alternative small molecule, non-fullerene acceptors (NFAs) \[^2,3\].

One class of high performing NFA materials, well-known for high molar absorptivity and redox stability, are perylene diimides (PDI) \[^4-6\]. The ability to easily functionalize the PDI chromophore means the physical, optoelectronic, and self-assembly properties may be easily altered through simple structural modifications \[^7-19\]. However, a common problem faced by many PDI-based NFA materials is their propensity to self-assemble through π-π stacking in the BHJ, which can limit the efficiency of charge extraction \[^20\]. Two common methods to disrupt PDI π-π stacking and promote favorable phase separation in the BHJ is through dimerization \[^7-9\] or insertion of a core \[^10-13\].

Recent trends in the literature seem to suggest that increasing the number of PDIs appended from the core can lead to improved power conversion efficiencies (PCEs) \[^14-19\]. For example, Yan and co-workers \[^16\] demonstrated that fusing four PDIs to a tetrathienylbenzene core (FTTB-PDI4) can lead to PCEs of >10 %. The downside to FTTB-PDI4 and many other PDI-core materials, however, is the synthesis often necessitates Stille and/or Suzuki cross-couplings, which requires the installation of Sn or B directing groups, respectively. For these materials to become
synthetically viable on large-scale, they must be synthesized using techniques which are more atom-economical \[^{21}\]. Perhaps the most promising technique for large-scale cross-coupling would be direct(hetero) arylation (DHA) because the reaction can be performed without the use of directing groups \[^{22-25}\].

In the past, our research group has exploited DHA cross-couplings to develop a variety of N-annulated PDI-core NFAs \[^{12,26-28}\], including two PDI-tetramers based on indancenodithiophene (IDT) \[^{27}\] and thienothiophene (ThTh) \[^{28}\] cores (Scheme 1). The density functional theory (DFT) calculated molecular geometry of IDT-PDI\(_4\) showed that the sterically hindered N-annulated PDI units oriented orthogonally to the core, causing IDT-PDI\(_4\) to adopt a unique butterfly shape. Proof-of-concept OPV devices using IDT-PDI\(_4\) as an NFA achieved moderate PCEs of 3.41%, when paired with the electron-donor polymer PTB7-Th. Ultimately, the PCE was hindered by the low fill factor (FF) and low shunt resistance. It was rationalized that the butterfly shape of IDT-PDI\(_4\) may be detrimental to OPV performance, relative to the double-decker conformation (pairs of PDI being parallel) of the high-performing FTTP-PDI4. In pursuit of a less rigid core that would be amenable to DHA cross-coupling, we selected the cyclooctatetrathiophene (Th\(_4\)) core (Scheme 1) \[^{29}\]. Interested by how the Th\(_4\) non-planar, saddle-shape might impact OPV performance, we applied our DHA cross-coupling conditions to synthesize an N-annulated PDI cyclooctatetrathiophene tetramer (Th\(_4\)PDI\(_4\)). Herein, we report the optimized synthesis, complete physical and optoelectronic characterization of Th\(_4\)PDI\(_4\), as well as proof-of-concept OPV device data.
**Results and Discussion**

Standard DHA cross-coupling methods utilize a stoichiometric amount of carbonate base, a catalytic amount of bulky carboxylic acid, and a Pd catalyst. Our lab has developed a set of DHA conditions which employs Cs₂CO₃, pivalic acid (PivOH), and a silica-supported Pd catalyst (SiliaCat® DPP-Pd) [[12,26–28]]. Not only can SiliaCat® DPP-Pd be easily separated from the reaction mixture, it may also be recycled and used for additional cross-coupling reactions. Preliminary DHA cross-coupling experiments between Th₄ and Hex-N-PDI-Br afforded Th₄PDI₄ as the major product, as well as some incomplete substituted Th₄PDI₄₋ₙ products (Figure S8). The incomplete substitution of Th₄ may be rationalized by examining the mechanism of DHA (Figure 1) [[24]]. After oxidative addition of Hex-N-PDI-Br, an in-situ generated carboxylate exchanges with the bromide. This carboxylate-bound Pd intermediate participates in a concerted metalation-deprotonation (CMP) step with Th₄, followed by the reductive elimination of Th₄ and Hex-N-PDI.
The crucial step of this catalytic mechanism is the CMP and the carboxylate directly influences the coordination sphere of the catalyst [30]. PivOH is a bulky carboxylic acid, meaning the coordination sphere during the CMP step is relatively small. As the reaction progresses, binding to the catalyst coordination sphere becomes progressively more challenging as the steric bulk of Th₄PDI₄-ₙ increases. We therefore rationalized that the coordination of Th₄PDI₄-ₙ may be facilitated by replacing PivOH with smaller carboxylic acid, namely acetic acid (AcOH), thereby generating a larger catalyst coordination sphere. By exchanging PivOH for AcOH, the desired Th₄PDI₄ product was formed exclusively, with a 70% overall yield.

**Figure 1.** Proposed DHA cross-coupling mechanism between Th₄ and Hex-N-PDI-Br.

In the past, our DHA conditions have successfully allowed unprecedented reactivity towards both the 4- and 5-H of fused-thiophene cores [27,28]. We therefore posited that the synthesis of an octameric cyclooctatetrathiophene N-annulated PDI complex (Th₄PDI₈) could be possible if the
optimized DHA cross-coupling reaction was performed with either 8 equivalents of Hex-N-PDI-Br and Th4 or 4 equivalents of Hex-N-PDI-Br and Th4PDI4. Under both sets of conditions, mass spectrometry was unable to detect any trace of Th4PDI8 (Figure S9). Instead, the major product of both reactions was Th4PDI4. The lack of reactivity is attributed do to steric congestion inhibiting access to the β-hydrogen atoms (vide infra).

The identity of Th4PDI4 was confirmed by MALDI-TOF mass spectrometry (Figure S11) and elemental analysis (Figure S12), as well as 1H and 13C NMR spectroscopy (Figures S3-S5). At 20 °C, the 1H NMR spectrum of the Th4PDI4 was broad and unresolved (Figure 2 and S3). A lack of PDI free-rotation on the NMR timescale at room-temperature suggests steric crowding between PDI moieties and the Th4 core, which may explain why no Th4PDI8 was detected. Elevating the temperature of the 1H NMR spectroscopic experiment caused the broad peaks from δ 8.40 – 8.50 ppm to resolve into three singlets and two doublets. These downfield-shifted aromatic peaks, along with the peak-splitting patterns observed in the aliphatic region, were consistent with the electron-deficient PDI-N-Hex moieties. The singlet at δ 7.10 ppm was assigned to the electron rich Th4 core. The highly symmetric nature of the elevated temperature 1H NMR spectrum of Th4PDI4 suggests activation of only the 5-H of Th4 (see Supporting Information for complete assignment of the 1H NMR spectrum).
Figure 2. Variable temperature $^1$H NMR spectra of Th$_4$PDI$_4$ (600 MHz, tetrachloroethane-d$_2$).

The physical properties of Th$_4$PDI$_4$ were probed using a combination of differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The DSC profile of Th$_4$PDI$_4$ did not exhibit any melt or glass transitions between 100 – 300 °C (Figure S13). By TGA, Th$_4$PDI$_4$ was thermally stable until 395 °C, which is typical of other N-annulated PDI materials $^{[9,12,26–28]}$.

The optical properties of Th$_4$PDI$_4$ were measured using UV-vis absorption spectroscopy (Figure S15). Since Th$_4$ does not absorb visible light, it was unsurprising that the optical absorption spectrum of Th$_4$PDI$_4$ was dominated by the highly absorptive PDI units. The molar absorptivity of Th$_4$PDI$_4$ being 210000 M$^{-1}$ cm$^{-1}$ was consistent with four-fold PDI substitution on Th$_4$. The thin-film absorption profile of Th$_4$PDI$_4$ was nearly identical to the profile measured in solution (Figures S15), suggesting minimal molecular reorganization when transitioning from solution to solid state.
Cyclic voltammetry (CV) was used to probe the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of Th₄PDI₄ (Figure 3A). The onset of oxidation ($\epsilon^{0}_{1/2} = +0.92 \text{ V vs. Fc}^{+/0}$) matched the oxidation event observed with the Th₄ core (Figure S17), while the onset of reduction ($\epsilon^{0}_{1/2} = -1.19 \text{ V vs. Fc}^{+/0}$) was typical for N-annulated PDI-based materials [9,12,26–28]. Therefore, these data would strongly suggest that the HOMO of Th₄PDI₄ is localized near the Th₄ core and the LUMO is largely delocalized over the PDI units.

Figure 3. Cyclic voltammogram (A), DFT calculated optimized geometry (B), and DFT calculated frontier molecular orbitals (C) of Th₄PDI₄.

Structural and electronic properties of Th₄PDI₄ were further investigated by modelling the optimized molecular geometry and molecular orbitals (MOs) using DFT at the B3LYP-6-31G(d,p) level of theory. The DFT optimized structure of Th₄PDI₄ was highly twisted, with the Th₄ core adopting a saddle-shape (Figure 3B and S19). The dihedral angle of adjacent PDIs on Th₄ were near orthogonal, while the dihedral angle of PDIs on opposite sides of Th₄ were near co-planar.
While this combination of PDI-PDI dihedral angles caused $\text{Th}_4\text{PDI}_4$ to largely adopt a propeller conformation, there was small degree of the desirable double-decker conformation. We also note that the calculated MOs of $\text{Th}_4\text{PDI}_4$ (Figures 3C and S20) correspond identically to the HOMO and LUMO determined by CV.

To test the viability of $\text{Th}_4\text{PDI}_4$ as an NFA, we prepared a series of OPV devices using a standard electron-donor polymer, PTB7-Th (Figure S21A). While $\text{Th}_4\text{PDI}_4$ was soluble in the commonly used chlorinated solvents (chloroform, chlorobenzene and o-dichlorobenzene), it was much less soluble in non-halogenated solvents. We note that the solubility of $\text{Th}_4\text{PDI}_4$ could be improved through modification of the imidic and pyrrolic sidechains. But for the purpose of these proof-of-concept OPVs, o-dichlorobenzene (o-DCB) was chosen as the casting solvent, and PTB7-Th was selected as the donor polymer. All devices were air-fabricated and tested using the following inverted architecture: Glass/ITO/ZnO/PTB7-Th:$\text{Th}_4\text{PDI}_4$/MoO$_3$/Ag.

The UV-visible spectra of spin-coated films of PTB7-Th and $\text{Th}_4\text{PDI}_4$ (Figure 4A) showed complementary absorption from 600-750 nm and 400-600 nm, respectively; thus, the potential photocurrent that could be generated from this system was maximized. The offset in energy levels (Figure S21B) of PTB7-Th and $\text{Th}_4\text{PDI}_4$ were also appropriate for the preparation of an active layer in OPV devices. Using a 15 mg/mL total weight concentration, several different processing conditions and donor:acceptor ratios were used (Table S1 and Figure S23A). While a higher concentration of polymer (7:3) produced a higher short-circuit current ($J_{sc}$), the open-circuit voltage ($V_{oc}$) and the FF were found to be similar to the 1:1 and 3:7 donor:acceptor ratios. Overall, the 1:1 blend produced the best compromise of $V_{oc}$, $J_{sc}$ and FF, reaching an average PCE of 1.89%.
Figure 4. UV-visible spectra of spin-coated films from o-DCB of PTB7-Th and Th₄PDI₄ (A). Also depicted are the UV-vis absorption spectra (B) and J-V curves (C) of the OPV devices that used 1:1 PTB7-Th:Th₄PDI₄ (spin-coated from o-DCB), containing 0, 1, 3, or 5 % (v/v) CN.

In the past, we have shown that the use of solvent additives can help control the self-organization and crystallization of N-annulated PDI dimers⁴¹ and PDI tetramer derivatives⁴². To evolve the BHJ towards a more favorable morphology, four common solvent additives, namely 1,8-diiodooctane (DIO), diphenyl ether (DPE), 1-chloronaphthalene (CN) and p-anisaldehyde (AA) were explored. Neat thin films of Th₄PDI₄ were cast using 1% (v/v) concentration of each solvent additive (Figure S16) and the UV-vis absorption spectra revealed that DPE and CN had minimal impact on the morphology of Th₄PDI₄, whereas both DIO and AA induced significant changes. DIO led to the appearance of a low energy shoulder around 575 nm, while AA changed the relative ratio between the 497 and 534 nm absorption peaks.

Next, each of these four additives was added to the 1:1 PTB7-Th:Th₄PDI₄ blend (Table S1). Unlike what was observed in neat films of Th₄PDI₄, the UV-vis absorption profiles of these devices showed that additives had minimal influence on the morphology (Figures 4B and S22A), likely due to viscosity of the PTB7-Th matrix limiting the intra- and intermolecular mobility of Th₄PDI₄. Although adding DIO did not influence device Vₒc, both the J_sc and the PCE were found to marginally decrease. The addition of DPE simultaneously lowered the Vₒc and the J_sc value.
(compared to no additive) leading to an average PCE value < 1 %. Although the addition of CN and AA did not affect the V<sub>oc</sub>, both additives enabled an impressive two-fold boost in the J<sub>sc</sub> relative to the 1:1 PTB7-Th:Th<sub>4</sub>PDI<sub>4</sub> active layer without additive. Despite FF staying around 40% for all four additives, adding 1% (v/v) CN or AA led to improved average PCE values of 3.42% and 3.21%, respectively. It is important to note that AA had a similar influence of the OPV metrics than that of CN, highlighting that it could be a viable non-halogenated solvent additive for PDI tetramer derivatives in the future.

Since adding 1% (v/v) CN to the processing solvent led to the highest J<sub>sc</sub> and PCE values, 1:1 PTB7-Th:Th<sub>4</sub>PDI<sub>4</sub> devices were prepared with higher concentrations of CN to explore if device performance could be further improved. The device metrics (Table 1) and the J-V curves (Figure 5D) reveal that the optimal concentration of CN additive is 3 % (v/v). Using this concentration, OPV devices achieved an average J<sub>sc</sub> of 10.2 mA/cm<sup>2</sup>, a V<sub>oc</sub> of 0.99 V and an FF of 42%, leading to PCE values as high as 4.52 %. The 5 % (v/v) CN containing devices showed similar metrics to that containing 3 % (v/v) CN, but with slightly lower J<sub>sc</sub> values. The over two-fold increase in J<sub>sc</sub> going from 0% and 3% (v/v) CN additive was reflected in their external quantum efficiency (EQE) spectra (Figure S24), where the generated photocurrent spanned from 300-800 nm, with contribution from both the PTB7-Th and the Th<sub>4</sub>PDI<sub>4</sub> compounds.

**Table 1.** OPV devices average data of PTB7-Th:PDI<sub>4</sub> blends spin-coated from o-DCB with 0-5% (v/v) CN. Metrics corresponding to the devices with the highest PCE are in parenthesis.

| % CN (v/v) | V<sub>oc</sub> (V) | J<sub>sc</sub> (mA/cm<sup>2</sup>) | FF (%) | PCE (%) |
|-----------|-----------------|-------------------------------|--------|---------|
| 0         | 1.01 (1.02)     | 4.5 (5.1)                     | 42 (42)| 1.89 (2.20) |
| 1         | 0.98 (0.98)     | 9.2 (9.5)                     | 38 (39)| 3.42 (3.61) |
| 3         | 0.99 (0.99)     | 10.2 (10.6)                   | 42 (43)| 4.26 (4.52) |
| 5         | 0.99 (1.00)     | 9.4 (9.3)                     | 43 (45)| 3.99 (4.16) |
Another method which can often improve OPV device performance is thermal annealing of the active layer \[^1,^16\]. In our case, the thermal annealing did not alter the $J_{sc}$, but rather the $V_{oc}$ decreased and dropped the PCE to 1.31% (Table S1 and Figure S23B). On the other hand, hot-casting done with the PTB7-Th:$\text{Th}_4\text{PDI}_4$ solution and a glass/ITO/ZnO substrate heated at 100 °C, lead to a 20% increase in $J_{sc}$ (relative to devices spin-coated at room temperature). It is proposed that heating could help the free rotation of the PDI-moieties (as illustrated by the variable temperature $^1$H NMR experiments), assisting the $\text{Th}_4\text{PDI}_4$ compound to find an improved conformation for charge separation and transport within the BHJ.

The surface morphology of the films studied by atomic force microscopy (AFM) revealed that the 1:1 PTB7-Th:$\text{Th}_4\text{PDI}_4$ was smooth with very small domains, giving a root-mean-square (RMS) roughness value of 0.71 nm (Figure 5). Adding 1, 3 and 5% (v/v) CN to the blend led to even smoother films, with RMS values ranging from 0.36 nm to 0.41 nm. While a lower roughness seems to be correlated to better performances for this system, no clear correlation could be established in terms of phase separation as per the AFM phase images (Figure S26). The photoluminescence (PL) spectra (Figure S25) of PTB7-Th and the corresponding 1:1 blend with $\text{Th}_4\text{PDI}_4$ containing 0 or 3% (v/v) CN further confirmed this trend, when no significant difference in terms of PL quenching was observed between these two systems. AFM height and phase images of the 1:1 PTB7-Th:$\text{Th}_4\text{PDI}_4$ films prepared with 1% (v/v) DIO, DPE and AA (Figure S27) also confirmed the trend between the roughness and the OPV device metrics, where these films have a RMS of 1.17, 2.30 and 0.61 nm, respectively, corresponding to average PCE values of 1.44, 0.99 and 3.21%.
The behavior of the devices prepared using \textbf{Th$_4$PDI$_4$} can be compared to other PDI tetramers used as NFAs in OPV devices. Our previously reported PTB7-Th:IDT-PDI$_4$ OPV devices reached, on average, a PCE of 3.41 \%, with a $V_{oc}$ of 1.02 V, a $J_{sc}$ of 9.62 mA/cm$^2$ and an FF of 35 \% \cite{27}. These metrics were achieved using 5 \% (v/v) CN, which is the same additive as that was used to improve the performance of the PTB7-Th:Th$_4$PDI$_4$ system. The PTB7-Th:Th$_4$PDI$_4$ devices prepared using 3 \% (v/v) CN had a similar $V_{oc}$ (0.99 V), but a slightly higher $J_{sc}$ (10.2 mA/cm$^2$), FF (42\%) and PCE (4.26 \%). Relative to other reported PDI-core tetramer systems with highly-twisted conformations \cite{14,18}, our Th$_4$PDI$_4$ system obtained very comparable performance metrics. But with respect to the champion PDI-based NFA (FTTB-PDI$_4$) that was paired with electron donor polymer P3TEA\cite{16}, our PCE and FF were much lower than the reported 10.4\% and 66 \%, respectively. This discrepancy in OPV performance highlights two important OPV design features. First, NFA molecular geometry is extremely important to the BHJ, where a balance between core rigidity and PDI steric hindrance must be achieved. Second, the choice of electron donor polymer

\textbf{Figure 5}. AFM height images of the 1:1 PTB7-Th:Th$_4$PDI$_4$ films spin-coated from \textit{o}-DCB containing 0, 1, 3 or 5\% (v/v) CN.
selection is also critically important, where the selected electron donor polymer can be optimized to further maximize OPV performance.

**Conclusion**

In summary, we exploited an optimized DHA cross-coupling reaction to afford a novel flexible, saddle-shaped N-annulated PDI-tetramer ($\text{Th}_4\text{PDI}_4$). The optical properties of $\text{Th}_4\text{PDI}_4$ were dominated by the PDI-moieties, while the CV determined electronic properties suggest the HOMO is $\text{Th}_4$ centered and the LUMO is PDI delocalized. DFT calculated molecular geometry of $\text{Th}_4\text{PDI}_4$ showed two separate PDI-PDI dihedral angles, consistent with propeller and double-decker conformations. Preliminary proof-of-concept OPV devices, cast from $o$-DCB using a 1:1 blend of PTB7-Th:$\text{Th}_4\text{PDI}_4$, gave an initial PCE of 1.89%. OPV performance was improved by screening a series of solvent additives, where the use of 3% (v/v) CN additive led to an over two-fold increase in $J_{sc}$ (10.2 mA/cm$^2$) and PCE (4.26%). Our lab is actively investigating the effects of side-chain engineering on $\text{Th}_4\text{PDI}_4$ to enable better solubility in non-halogenated solvents. We are also exploring the potential use of other less sterically hindered cores, which may enable the development of PDI-tetramers or higher order oligomers with more favorable molecular geometries.

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*Chem. Rev.* **2018**, 118 (7), 3447–3507. https://doi.org/10.1021/acs.chemrev.7b00535.
Voltage Bias (V)

Current Density (mA/cm²)

PCE = 4.3 %

Th4PDI4
Harnessing Direct(Hetero)Arylation in Pursuit of a Saddle-Shaped Perylene Diimide Tetramer

(Supporting Information)

Josh D. B. Koenig, Audrey Laventure, and Gregory C. Welch a*

a Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, Alberta, Canada T2N 1N4

* Corresponding Author

Email: gregory.welch@ucalgary.ca;
Phone number: 1-403-210-7603

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1. Methods and Materials

**Materials:** Polymer PTB7-Th was purchased from 1-Material. SiliaCat® DPP-Pd was purchased from SiliCycle. All other reactants, reagents, and catalysts were purchased from Sigma-Aldrich or VWR and used without further purification.

**CHN Elemental Analysis:** Elemental analyses were performed by Johnson Li in the Chemical Instrumentation Facility at the University of Calgary. A Perkin Elmer 2400 Series II CHN Elemental Analyzer was used to obtain CHN data, using ~1.5 mg of sample (with particle sizes ranging between 0.2 and 0.5 mm in diameter).

**Nuclear Magnetic Resonance (NMR):** $^1$H and $^{13}$C NMR spectroscopy experiments were recorded using either a Bruker Avance III 500 or 600 MHz spectrometer. All experiments were performed in either chloroform-d (CDCl$_3$) or tetrachloroethane-d$_2$. Chemical shifts (referenced to residual solvent) were reported in parts per million (ppm). Multiplicities were reported as follows: singlet (s), doublets (d), triplets (t), quartet (q), pentet (p), hexet (h), doublet of doublets (dd), doublet of triplets (dt), doublet of quartets (dq), triplet of doublets (td), triplet of triplets (tt), and multiplets (m).

**High-resolution MALDI-TOF (HR MALDI-TOF):** High-resolution MALDI-TOF mass spectrometry measurements were performed courtesy of Jian Jun (Johnson) Li in the Chemical Instrumentation Facility at the University of Calgary. The sample solution (~ 1 µg/ml in dichloromethane) was mixed with matrix trans2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) solution (~5 mg/ml in methanol). All spectra were acquired using a Bruker Autoflex III Smartbeam MALDI-TOF, set to the positive reflective mode (Na:YAG 355 nm laser settings: laser offset = 62-69; laser frequency = 200Hz; and number of shots = 300). The target used was Bruker MTP 384 ground steel plate target.

**UV-Visible Spectroscopy (UV-Vis):** All absorption measurements were recorded using Agilent Technologies Cary 60 UV-Vis spectrometer at room temperature. All solution UV-Vis spectra were measured with 2 mm quartz cuvettes, using CH$_2$Cl$_2$ as solvent. Stock solutions (1.0 mg/mL) of each compound were prepared, serially diluted to concentrations between $10^{-5}$ - $10^{-6}$ M, and then used to construct calibration curves for determining molar absorptivity. Neat films were prepared by spin-coating from a 1 % wt/v solution onto clean Corning glass micro slides. Prior to use, glass slides were cleaned with soap and water, acetone and isopropanol, and followed by UV/ozone treatment using a Novascan UV/ozone cleaning system.

**Photoluminescence (PL):** All emission measurements were recorded using an Agilent Technologies Cary Eclipse fluorescence spectrophotometer at room temperature.

**Atomic Force Microscopy (AFM):** AFM measurements were performed by using a TT2-AFM (AFM Workshop) in tapping mode and WSxM software with an 0.01-0.025 Ohm/cm Sb (n) doped Si probe with a reflective back side aluminum coating. Samples for AFM measurement were the same ones that were used to collect the respective the device parameters.
Cyclic Voltammetry (CV): Electrochemical measurements were performed using a CH Instruments Inc. Model 1200B Series Handheld Potentiostat. A standard 3-electrode setup was utilized, consisting of a freshly polished glassy carbon disk working electrode (WE), Pt-wire counter electrode (CE), and Ag-wire pseudo-reference electrode (RE). All measurements were referenced to ferrocene (Fc+/0) as internal standard. All cyclic voltammetry experiments were performed at a scan rate of 100 mV/s. Sample solutions, with 1 mM compound and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) supporting electrolyte, were prepared in anhydrous CH₂Cl₂. All electrochemical solutions were sparged with dry gas (either N₂ or argon) for 5 minutes to deoxygenate the system prior to measurements. The ionization potentials (IP) and electron affinities (EA) were estimated by correlating the 1ˢᵗ oxidation and 1ˢᵗ reduction potentials (Eᵒₓ ½ Fc⁰⁺, Eᵣᵉᵈ ½ Fc⁰⁺) to the normal hydrogen electrode (NHE), assuming the IP of Fc⁰⁺ to be 4.80 eV, respectively. [¹]

Power Conversion Efficiency (PCE) and External Quantum Efficiency (EQE): The current density-voltage (J-V) curves were measured by a Keithley 2420 source measure unit. The photocurrent was measured under AM 1.5 illumination at 100 mW/cm² under a Solar Simulator (Newport 92251A-1000). The standard silicon solar cell (Newport 91150V) was used to calibrate light intensity. EQE was measured in a QEX7 Solar Cell Spectral Response/QE/IPCE Measurement System (PV Measurement, Model QEX7, USA) with an optical lens to focus the light into an area about 0.04 cm², smaller than the dot cell. The silicon photodiode was used to calibrate the EQE measurement system in the wavelength range from 300 to 1100 nm.

Organic Photovoltaic (OPV) Devices: Devices were fabricated using ITO-coated glass substrates cleaned by sequentially ultra-sonicating with detergent and de-ionized water, acetone, and isopropanol followed by exposure to UV/ozone for 30 min. ZnO was subsequently deposited as a sol-gel precursor solution in a N₂ purge box following the method of Sun et al. [²] The room temperature solution was spin-coated at a speed of 4500 rpm and then annealed at 200 °C for at least 15 min. Active layer solutions of PTB7-Th and Th₄PDI₄ were prepared in air with a total concentration of 10-20 mg/mL in o-dichlorobenzene (o-DCB) with 0-5 % (v/v) 1-chloronaphthalene (CN) additive, unless otherwise noted. Solutions were stirred for 4 h at room temperature. Active layer materials were combined in a 1:1 donor/acceptor weight ratio, unless otherwise noted. The active layer solution was coated at room temperature at a speed of 1000 rpm for 60 s. The substrates with the cast active layers were kept in an N₂ atmosphere glovebox overnight before evaporating MoO₃ and Ag. The 10 nm of MoO₃ followed by 100 nm of Ag were thermally deposited under vacuum (10⁻⁵ Torr). The active areas of the devices were 0.14 cm².

Computational Details: Gas-phase B3LYP/6-31G(d,p) ground-state equilibrium geometry optimizations were considered within Gaussian 09. [³] To reduce the computational cost, all alkyl-substituents were truncated to methyl groups. Molecular dihedral angles were systematically altered to help ensure that lower energy minimum was not missed. The resulting structure was characterized through frequency calculations at the same level of theory. TD-SCF calculations were also performed from this optimized geometry. Single point calculations were performed on this structure to generate molecular orbitals and electrostatic potential maps.
2. Synthetic/Experimental Procedures

2,5,8,11-tetrakis(trimethylsilyl)cyclooctatetrathiophene (Th₄TMS₄)

TMS₄Th₄ was synthesized by iteratively combining two known literature preparations \(^{[4,5]}\).

\[
\begin{align*}
&\text{Br} \quad \text{Br} \\
&\text{Br} \quad \text{Br} \\
&\text{Br} \quad \text{Br}
\end{align*}
\]

Into a 250 mL Schlenk flask, add 3,3',5,5'-tetrabromobithiophene (2.0g, 4.16 mmol, 1 eq.) and seal the flask with a septum. Complete three vacuum purge and nitrogen backfill cycles on the Schlenk line. Once filled with N₂, cannula transfer over dried THF (80 mL). Stir to dissolve the 3,3',5,5'-tetrabromobithiophene and then cool reaction mixture to -78°C. Dropwise add n-butyllithium (3.7 mL, 9.2 mmol, 2.2 eq.) and leave the reaction to stir for 1 hour. Then trimethylsilylchloride (1.3 mL, 10.4 mmol, 2.5 eq.) was added dropwise to the cooled solution and left to stir overnight. The stirring reaction mixture (containing in-situ generated intermediate) was cooled to -78°C. n-butyllithium (4.0 mL, 9.8 mmol, 2.3 eq.) was dropwise added and left to stir for 1 hour. Under a stream of N₂, the septum was opened and CuCl₂ (1.70g, 12.6 mmol, 3 eq.) was added to the reaction. The system was re-sealed and left to stir overnight. The reaction was quenched with water (75 mL), and then extracted using diethyl ether (3 × 50 mL). Diethyl ether extracts were dried over Na₂SO₄. The drying agent was filtered off and the solvent was concentrated under reduced pressure. The resulting crude oil was purified by silica gel column chromatography (eluted with hexanes) to afford pale yellow solid (452 mg, 0.73 mmol, 35%). The isolated compound matched previously reported spectroscopic properties \(^{[5]}\).

Cyclooctatetrathiopene (Th₄)

Th₄ was synthesized using slightly modified literature procedure \(^{[6]}\).

\[
\begin{align*}
&\text{TMS} \quad \text{TMS} \\
&\text{TMS} \quad \text{TMS}
\end{align*}
\]

Into a 100 mL rbf, Th₄TMS₄ (300 mg, 0.48 mmol, 1 eq.) was dissolved in minimal CHCl₃. Trifluoroacetic acid (1 mL, 5.9 mmol, 12 eq.) was added dropwise to the rapidly stirring solution. After 15 minutes, the reaction was quenched by adding H₂O (40 mL). The aqueous mixture was extracted with CHCl₃ (3 × 30 mL), and then those extracts were washed with H₂O (2 × 50 mL). After drying organic extracts over Na₂SO₄, the extracts were filtered through Celite and solvent was removed under reduced pressure. Precipitating from MeOH, the resulting off-white solid was collected by vacuum filtration (128 mg, 0.47 mmol, 98%). The isolated compound also matched previously reported spectroscopic properties \(^{[6]}\).
**Tetrakis(N-hexyl-peryleneimide)cyclooctatetrathiophene (Th₄PDI₄)**
Starting material, hexyl-N-peryleneimide bromide (Hex-N-PDI-Br), was synthesized using previously reported literature procedure.[7]

![Chemical structure](image)

Th₄ (32.8 mg, 0.10 mmol, 1 eq.), Hex-N-PDI-Br (320 mg, 0.45 mmol, 4.5 eq.), Cs₂CO₃ (163 mg, 0.50 mmol, 5 eq.), and SiliaCat-Pd-DPP (0.1 eq., 40 mg, 0.01 mmol) were all added to a 10 mL microwave vial. The vial was sealed and purged with N₂ for 30 minutes. Dried dimethylacetamide (6 mL) was cannula transferred into the vessel and the reaction mixture was sparged for an additional 15 minutes. Acetic acid (3 mg, 0.05 mmol, 0.5 eq.) was injected into the microwave vial and then it was placed in a 120 °C bead bath for 24 hours. The reaction mixture was poured into methanol (150 mL), stirred for 1 hour, and then vacuum filtered. This crude solid was dissolved in CHCl₃, adhered to silica, and further purified by silica gel column chromatography (eluting with CHCl₃). The resulting crimson red solid was precipitated into methanol and collected by vacuum filtration. (187 mg, 0.07 mmol, 70%).

**1H NMR** (600 MHz, tetrachloroethane-d₂, 120 °C) δ 8.50 (s, 1H, H_{abc}), 8.46 (s, 1H, H_{abc}), 8.41 (s, 1H, H_{abc}), 8.31 (d, J = 8.3 Hz, 1H, H_{i}), 8.00 (d, J = 8.3 Hz, 1H, H_{c}), 7.10 (s, 1H, H_{f}), 4.64 – 4.57 (m, 1H, H_{g}), 4.38 (m, 1H, H_{h}), 4.32 (t, J = 7.3 Hz, 2H, H_{i}), 1.76 (dq, J = 15.8, 7.9 Hz, 2H, H_{j}), 1.69 (p, J = 7.4 Hz, 2H, H_{k}), 1.53 (tt, J = 16.1, 8.1 Hz, 2H, H_{l}), 1.45 (dt, J = 14.1, 7.0 Hz, 2H, H_{m}), 1.28 (dq, J = 14.3, 7.4 Hz, 2H, H_{n}), 0.97 (p, J = 7.3 Hz, 2H, H_{o}), 0.86 (dt, J = 15.6, 6.9 Hz, 2H, H_{p}), 0.78 (dt, J = 14.6, 7.2 Hz, 2H, H_{q}), 0.43 (t, J = 7.4 Hz, 6H, H_{r}), 0.31 (t, J = 7.3 Hz, 3H, H_{s}), 0.24 (dt, J = 7.4, 3.5 Hz, 6H, H_{t}).

**13C NMR** (151 MHz, tetrachloroethane-d₂, 120 °C) δ 165.17, 165.09, 163.67, 163.57, 144.89, 137.50, 134.81, 134.68, 134.04, 132.64, 132.55, 131.76, 131.15, 129.51, 127.41, 127.02, 124.47, 124.41, 122.91, 122.78, 122.68, 122.14, 121.82, 119.61, 119.51, 118.13, 117.73, 57.70, 57.33, 46.41, 30.74, 30.67, 26.27, 24.88, 24.69, 21.70, 12.98, 10.73, 10.60.

**HRMS ([M+Na]^+) calculated for M = C₁₇₆H₁₆₄N₁₂O₁₆S₄:** 2852.1163; detected [M+Na]^+: 2852.1254

**UV-Vis** λ (M⁻¹ cm⁻¹) 298 nm (140000), 497 nm (180000), 534 nm (210000)

**CHN** theoretical (%) C: 74.66, H: 5.84, N: 5.94; found (%) C: 74.34; H: 5.68; N: 5.80
3. **$^1$H and $^{13}$C NMR Spectroscopy**

![Figure S1. $^1$H NMR spectrum of Th₄ (500 MHz, CDCl₃).](image1)

![Figure S2. $^{13}$C NMR spectrum of Th₄ (126 MHz, CDCl₃).](image2)
Figure S3. $^1$H NMR spectrum of Th$_4$PDI$_4$ (600 MHz, tetrachloroethane-d$_2$, 20 ºC).

Figure S4. $^1$H NMR spectrum of Th$_4$PDI$_4$ (600 MHz, tetrachloroethane-d$_2$, 120 ºC).
Figure S5. $^{13}$C NMR spectrum of Th$_4$PDI$_4$ (151 MHz, tetrachloroethane-d$_2$, 120 °C).

Figure S6. Concentration-dependent $^1$H NMR spectra of Th$_4$PDI$_4$ (600 MHz, tetrachloroethane-d$_2$, 20 °C).
Figure S7. $^1$H-$^1$H COSY spectrum of Th$_4$PDI$_4$ (600 MHz, tetrachloroethane-d$_2$, 120 °C).
4. HR-MALDI-TOF

**Figure S8.** HR-MALDI-TOF mass spectrum showing incomplete substitution of Th$_4$ core.

**Figure S9.** HR-MALDI-TOF mass spectrum showing no formation of Th$_4$PDI$_8$. 
Figure S10. HR-MALDI-TOF mass spectrum of Th₄.

Figure S11. HR-MALDI-TOF mass spectrum of purified Th₄PDI₄.
5. Elemental Analysis and Thermal Properties

Figure S12. CHN elemental analysis of Th₄PDI₄.

Figure S13. Differential scan calorimetry (A) and thermal gravimetric analysis (B) profiles of Th₄PDI₄. All features observed in the DSC trace of Th₄PDI₄ near 150 °C are artifacts of the instrument, as they were also observed in the blank.
6. UV-Visible Spectroscopy

Figure S14. UV-visible absorption spectrum of \( \text{Th}_4 \) in \( \text{CHCl}_3 \), with calibration curve inset.

Figure S15. UV-visible absorption spectrum of \( \text{Th}_4\text{PDI}_4 \) in \( \text{CHCl}_3 \), with calibration curve inset.
Figure S16. Directly comparing the UV-vis absorption spectra of Th₄PDI₄ in solution (CHCl₃) and in thin film. The influence of 1,8-diiodooctane (A), diphenyl ether (B), chloronaphthalene (C), and p-anisaldehyde (D) on the thin film UV-vis absorption spectra of Th₄PDI₄ are also depicted.
7. Voltammetry

Figure S17. Cyclic voltammogram of Th₄ (~1 mM) in CH₂Cl₂, recorded at 100 mV/s.

Figure S18. Cyclic voltammogram (A) and differential pulse voltammogram (B) of Th₄PDI₄ (~1 mM) in CH₂Cl₂, recorded at 100 mV/s.
8. Density Functional Theory

Figure S19. Optimized geometry of Th₄PDI₄ at B3LYP/6-31G(d,p) ground-state.

Figure S20. Molecular orbital diagram of Th₄PDI₄ at B3LYP/6-31G(d,p) ground-state.
9. OPV Device Optimization

Figure S21. Chemical structure of PTB7-Th (A), CV determined energy levels (using $E_{1/2}$) for PTB7-Th and Th$_4$PDI$_4$ (B), and proof-of-concept OPV device architecture (C).

Figure S22. UV-visible spectra (A) and J-V curves (B) of 1:1 PTB7-Th:Th$_4$PDI$_4$ films and devices, respectively, spin-coated from o-DCB containing 0 or 1% (v/v) of DIO, DPE or AA.

Figure S23. J-V curves of the PTB7-Th-Th$_4$PDI$_4$ devices spin-coated from o-DCB using different (A) donor:acceptor weight ratio and (B) different processing.
Figure S24. External quantum efficiency of 1:1 PTB7-Th:Th₄PDI₄ films spin-coated from o-DCB containing 0 or 3% (v/v) CN.

Figure S25. Photoluminescence spectra of PTB7-Th and of 1:1 PTB7-Th:Th₄PDI₄ films spin-coated from o-DCB containing 0 or 3% (v/v) CN. The excitation wavelength is 705 nm.
Figure S26. AFM phase images of the 1:1 PTB7-Th:Th₄PDI₄ films spin-coated from o-DCB containing 0, 1, 3 or 5% (v/v) CN.

Figure S27. AFM height (top) and phase (bottom) images of the PTB7-Th:Th₄PDI₄ devices spin-coated from o-DCB using different processing conditions.
Table S1. OPV data of PTB7-Th:Th4PDI4 blends spin-coated from o-DCB with different additives. Best PCE results are highlighted in bold. Averages are in italics.

| Active layer | V<sub>oc</sub> (V) | J<sub>sc</sub> (mA/cm<sup>2</sup>) | FF (%) | PCE (%) |
|--------------|------------------|-------------------------------|--------|---------|
| o-DCB, 15 mg/mL, 1:1 ratio |
| No additive | 1.00 | 4.3 | 40 | 1.72 |
| 1.02 | 5.1 | 42 | 2.20 |
| 1.02 | 4.8 | 43 | 2.10 |
| 1.01 | 4.7 | 44 | 2.10 |
| 1.03 | 3.8 | 43 | 1.68 |
| 1.01 | 4.3 | 40 | 1.72 |
| 1.01 | 4.4 | 39 | 1.73 |
| 1.01 | 4.5 | 42 | 1.89 |
| 1% (v/v) DIO | 1.01 | 3.0 | 46 | 1.39 |
| 1.01 | 3.0 | 45 | 1.36 |
| 1.03 | 2.9 | 44 | 1.31 |
| 1.01 | 2.9 | 45 | 1.30 |
| 1.04 | 3.6 | 45 | 1.67 |
| 1.02 | 3.6 | 44 | 1.63 |
| 1.02 | 3.2 | 45 | 1.44 |
| 1% (v/v) DPE | 0.97 | 2.6 | 40 | 1.02 |
| 0.93 | 2.5 | 40 | 0.95 |
| 0.91 | 2.5 | 43 | 0.99 |
| 0.94 | 2.6 | 41 | 0.99 |
| 1% (v/v) AA | 0.98 | 6.9 | 40 | 2.72 |
| 1.00 | 8.1 | 44 | 3.53 |
| 1.00 | 7.5 | 44 | 3.32 |
| 1.00 | 7.4 | 44 | 3.27 |
| 1.00 | 7.5 | 43 | 3.21 |
| 1% (v/v) CN | 0.97 | 9.6 | 37 | 3.51 |
| 0.97 | 9.4 | 39 | 3.50 |
| 0.96 | 8.9 | 35 | 3.00 |
| 1.00 | 8.8 | 38 | 3.32 |
| 0.98 | 9.0 | 38 | 3.34 |
| 0.98 | 9.5 | 39 | 3.61 |
| 0.99 | 9.1 | 39 | 3.51 |
| 0.99 | 9.4 | 38 | 3.54 |
| 0.98 | 9.2 | 38 | 3.42 |
| 3% (v/v) CN | 0.99 | 10.7 | 41 | 4.32 |
| 0.99 | 10.6 | 43 | 4.52 |
| 0.99 | 10.3 | 42 | 4.33 |
| 0.98 | 10.6 | 40 | 4.15 |
| 0.99 | 10.4 | 42 | 4.36 |
| 0.99 | 10.2 | 42 | 4.21 |
| 1.00 | 8.8 | 45 | 3.93 |
| 0.99 | 10.2 | 42 | 4.26 |
| 5% (v/v) CN | 0.99 | 9.6 | 41 | 3.89 |
| 1.00 | 9.2 | 44 | 4.10 |
| 1.00 | 9.3 | 45 | 4.16 |
| 0.98 | 9.3 | 42 | 3.82 |
| 0.99 | 9.4 | 43 | 3.99 |
| Method                                         |   0.94 |  4.0  |   37 |  1.40 |
|-----------------------------------------------|--------|-------|------|-------|
| Thermal annealing, 150°C, 10 min              |  0.93  |  3.6  |   38 |  1.28 |
|                                               |  0.93  |  3.7  |   38 |  1.31 |
|                                               |  0.92  |  3.9  |   38 |  1.36 |
|                                               |  0.91  |  3.5  |   38 |  1.22 |
|                                               |  0.93  |  3.8  |   38 |  1.31 |
| Hot casting 100°C                              |  0.97  |  5.8  |   42 |  2.36 |
|                                               |  0.97  |  5.0  |   43 |  2.06 |
|                                               |  0.97  |  5.1  |   42 |  2.09 |
|                                               |  0.99  |  4.0  |   41 |  1.63 |
|                                               |  0.98  |  5.0  |   42 |  2.03 |
| o-DCB, 15 mg/mL, 3:7 ratio                     |  0.97  |  3.7  |   42 |  1.50 |
| No additive                                   |  0.98  |  3.4  |   41 |  1.40 |
|                                               |  0.98  |  3.5  |   41 |  1.43 |
|                                               |  0.97  |  3.4  |   37 |  1.22 |
|                                               |  0.99  |  3.1  |   41 |  1.24 |
|                                               |  0.97  |  3.1  |   41 |  1.25 |
|                                               |  0.98  |  3.4  |   40 |  1.34 |
| o-DCB, 15 mg/mL, 7:3 ratio                     |  1.00  |  5.3  |   40 |  2.12 |
| No additive                                   |  1.00  |  5.1  |   39 |  1.98 |
|                                               |  1.01  |  4.8  |   39 |  1.90 |
|                                               |  0.99  |  5.1  |   39 |  1.99 |
|                                               |  0.99  |  5.0  |   39 |  1.96 |
|                                               |  0.99  |  5.1  |   41 |  2.05 |
|                                               |  1.00  |  5.1  |   40 |  2.00 |
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