

Communication

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# An Alternating 5,5-Dimethylcyclopentadiene and Diketopyrrolopyrrole Copolymer prepared at Room Temperature for High Performance Organic Thin-Film Transistors

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*Supporting Information Placeholder*

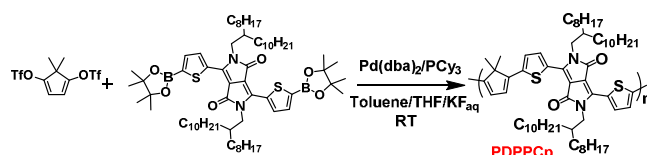
**ABSTRACT:** We report that the inclusion of non-aromatic 5,5-dimethylcyclopentadiene monomer into a conjugated backbone is an attractive strategy to high performance semiconducting polymers. The use of this monomer enables a room temperature Suzuki copolymerization with a diketopyrrolopyrrole comonomer to afford a highly soluble, high molecular weight material. The resulting low band gap polymer exhibits excellent photo and thermal stability, and despite a large  $\pi$ - $\pi$  stacking distance of 4.26 Å, it demonstrates excellent performance in thin-film transistor devices.

Poly(aromatic)s are  $\pi$ -conjugated materials that are highly attractive for organic electronic device applications. Despite inherent aromatic resonance stabilization energies that can confine  $\pi$ -electrons to individual rings and suppress charge-carrier transport,<sup>1</sup> the chemical flexibility, processability, and environmental stability of these systems render them superior to polyenes for most (opto)electronic device applications. Recently, however, there has been a growing interest to impart polyene character to poly(aromatic)s in order to destabilize their electronic ground states and form quinoid structures that are required under operationally-relevant scenarios.<sup>2-10</sup> In this regard, 5,5-dimethylcyclopentadiene (5,5-dimethylCp) has emerged as a useful building block that can enhance the polyene character of a system without affecting its planar topology,<sup>11</sup> a feature made possible by its five-membered ring structure that is akin to common aromatic building blocks such as furan, thiophene, selenophene and tellurophene. Indeed, studies have shown that replacing thiophenes with 5,5-dimethylCp can both reduce the HOMO-LUMO band gap and oxidation potential of  $\pi$ -conjugated macromolecules without compromising their solubility and atmospheric stability to a significant extent.<sup>12,13</sup> Moreover, studies on molecular wires have shown that their single-molecule junction conductance can increase when replacing thiophene and furan components with 5,5-dimethylCp, results that are attributed to a lower energy penalty associated with breaking aromaticity in the molecular wire containing the latter.<sup>14</sup>

In this Communication, we report the synthesis of a low band gap alternating co-polymer comprising 5,5-dimethylCp and

diketopyrrolopyrrole (DPP) for field-effect transistor applications. The use of 5,5-dimethylCp enables a room temperature copolymerization to afford a highly soluble copolymer **PDPPCp** that exhibits excellent thermal and atmospheric stability. Thin-film transistors incorporating **PDPPCp** exhibited close to ideal behavior, with extracted mobilities peaking around  $3.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  that were almost independent of gate voltage. This is in contrast to many DPP copolymers in which high mobility is only observed at low gate voltages due to significant deviations from ideal transistor behavior.<sup>15-17</sup> In addition, the mobility values reported herein surpass those measured from comparable DPP-based polymers bearing alternating phenylene,<sup>18</sup> thiophene,<sup>19-21</sup> and selenophene<sup>22</sup> congeners suggesting that this remarkably simple building block can lead to devices with enhanced performance.

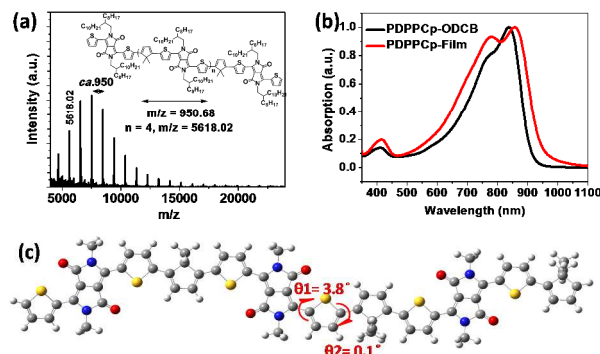
The synthetic route to the copolymer is shown in Scheme 1. Remarkably, we find that high molecular weight polymer is observed after polymerization at room temperature, a feature that is in marked contrast to most Suzuki polymerizations involving thienyl boronic esters (or acids), in which molecular weight tends to be limited by protodeboroylation under basic reaction conditions.<sup>23-25</sup> This is especially problematic at the elevated temperatures required to ensure solubility of the growing polymer chain. In this case, the high reactivity of organotriflate **1** to Suzuki cross-coupling,<sup>11</sup> in combination with the good solubility of the resulting polymer facilitates the room temperature polymerization (Scheme 1). After purification, the copolymer has a number-average molecular weight  $M_n$  of ca. 79 kDa ( $D = \text{ca. } 2.0$ ). Qualitatively, the polymer was found to be highly soluble at room temperature in several common organic solvents (toluene, dichloromethane, chloroform, tetrahydrofuran, chlorobenzene and *o*-dichlorobenzene (ODCB)) in marked contrast to the thiophene analogue which requires elevated temperature for dissolution in non-chlorinated solvents.<sup>19-21</sup>



**Scheme 1.** Synthesis of **PDPPCp** at room temperature.

The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum of **PDPPCp** (Figure 1a) confirmed

the alternating order of the repeat units and provided insight into the identity of the copolymer end groups. For instance, the peak at *ca.*  $m/z = 5618.68$  amu (Figure 1a) corresponds to a thiophene-end-capped chain comprised of five pairs of alternating repeat units (note that the presence of thiophene end-caps was not particularly surprising as protodeboroylation was observed to occur slowly under our polymerization conditions, see Figure S2). We relate the differences in molecular weight between MALDI and GPC to a combination of the poor volatility of the higher molecular weight material by MALDI in addition to the overestimation of molecular weight by GPC against polystyrene.<sup>26</sup>



**Figure 1.** (a) MALDI-TOF mass spectrum of PDPPCp. (b) Normalized UV-vis spectra of PDPPCp in ODCB and film; (c) trimer-minimized conformation (B3LYP/6-31G\*) of a DPPCp trimer.

PDPPCp exhibits excellent thermal stability by TGA as evidenced by its *ca.* 95% weight retention at 400 °C (Figure S3a). The second heating cycle of the DSC thermogram exhibits a glass-transition temperature  $T_g$  at *ca.* 140 °C (Figure S3b) along with endothermic melting transitions  $T_m$  at 233 °C and 240 °C, while the cooling cycle shows a single exothermic crystallization transition  $T_c$  at 207 °C and the corresponding  $T_g$ . This backbone melt is substantially lower than those observed for analogous polymers,<sup>27</sup> in agreement with the higher solubility observed for PDPPCp which likely relates to the presence of the geminal dimethyl group on the cyclopentadiene.<sup>11,12</sup>

The normalized UV-vis absorption spectra of PDPPCp dissolved in ODCB and as a thin film exhibit absorption maxima ( $\lambda_{max}$ ) at 838 nm and 857 nm respectively (Figure 1b). The red shift of absorption peaks from solution to film, together with broadening of the full width at half-maximum of  $\lambda_{max}$  indicates strong polymer aggregation in the solid state, a feature observed in many ordered semiconducting polymers.<sup>28-31</sup> Notably, solutions of PDPPCp in chlorobenzene were unchanged after exposure to air and light over a period of 24 hours, indicating excellent solution-phase stability (Figure S4).

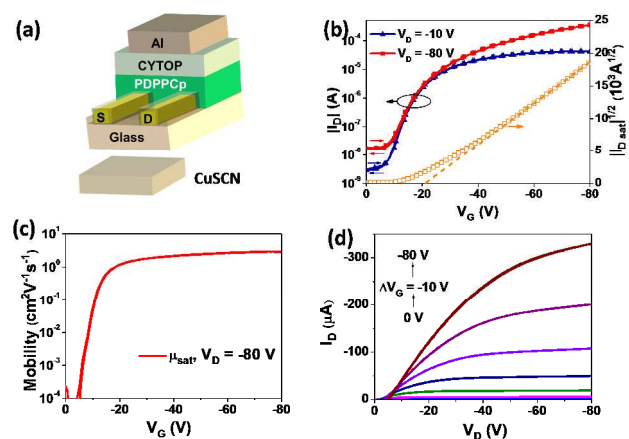
The ionization potential energy of a PDPPCp thin film by photo-electron spectroscopy in air (PESA) was 5.07 ( $\pm 0.05$ ) eV. This value is *ca.* 0.13 eV smaller than that measured from the thiophene analogue by the same technique,<sup>2,21</sup> indicating that the inclusion of 5,5-dimethylCp makes the polymer more susceptible to oxidation. To further verify this observation, the orbital energies of trimers were calculated using density theory functional theory (DFT, B3LYP/6-31 G\* level) and compared against congeners bearing thiophene (PDPPTh) and phenyl (PDPPPh) groups in lieu of 5,5-dimethylCp (Figure S6). Indeed the HOMO level of PDPPCp is predicted to be *ca.* 0.18 and 0.26 eV higher than PDPPTh and PDPPPh, respectively. Furthermore the minimum energy conformation of the PDPPCp trimer reveals  $\theta_1$  and  $\theta_2$  twist angles of 3.8° and 0.1° respectively (Figure 1c), suggesting

that the inclusion of 5,5-dimethylCp does not compromise backbone planarity in these systems. The PDPPCp values are similar with those observed in PDPPTh (*i.e.*,  $\theta_1 = ca. 1.5^\circ$  and  $\theta_2 = ca. 3.1^\circ$ ) and are significantly smaller than PDPPPh (*i.e.*,  $\theta_1 = ca. 13.5^\circ$  and  $\theta_2 = ca. 21.7^\circ$ ) (Figure S7).

Organic thin-film transistors (OTFTs) with a bottom-contact/top gate configuration were fabricated using pentafluorobenzene thiol (PFBT) modified gold source-drain (S-D) electrodes to promote hole-injection.<sup>30</sup> The transfer characteristics of the annealed (120 °C) devices exhibit pronounced hole-transporting character with good drain current saturation (Figure S9), negligible operating hysteresis, and maximum and average hole mobility of 1.9  $cm^2 V^{-1} s^{-1}$  and 1.8  $cm^2 V^{-1} s^{-1}$  respectively. These values are higher than those reported from PDPPTh-based OTFTs (0.6  $cm^2 V^{-1} s^{-1}$ ) fabricated with the same architecture,<sup>21</sup> suggesting that the diene building block can enhance the performance of a device when used in lieu of thiophene. In addition, the gate voltage ( $V_G$ ) dependence of hole mobility measured in both the linear and saturation regime (Figure S9c) is typical of many semicrystalline semiconducting polymer-based devices such as P3HT and pBTTT.<sup>17</sup> Importantly, we do not observe the undesirable peak in the hole mobility at low  $V_G$  bias often reported for many high performance donor-acceptor polymers.<sup>17</sup>

**Table 1.** Summary of OTFT devices performance based on PDPPCp annealed at 120 and 200 °C.

Contact modification and Annealing temperature	$\mu_{lin\ ave}$ ( $cm^2 V^{-1} s^{-1}$ )	$\mu_{sat\ ave}$ ( $\mu_{sat\ max}$ ) ( $cm^2 V^{-1} s^{-1}$ )	$V_{th}$ (V)	$I_{on/off}$
Au-PFBT/120 °C	0.95 $\pm$ 0.04	1.8 $\pm$ 0.10 (1.9)	-25.5 $\pm$ 0.8	10 <sup>4</sup> ~10 <sup>5</sup>
CuSCN/120 °C	0.91 $\pm$ 0.01	2.1 $\pm$ 0.06 (2.1)	-24.4 $\pm$ 0.7	10 <sup>4</sup> ~10 <sup>5</sup>
CuSCN/200 °C	1.10 $\pm$ 0.06	3.0 $\pm$ 0.11 (3.1)	-21.2 $\pm$ 0.5	10 <sup>4</sup> ~10 <sup>5</sup>

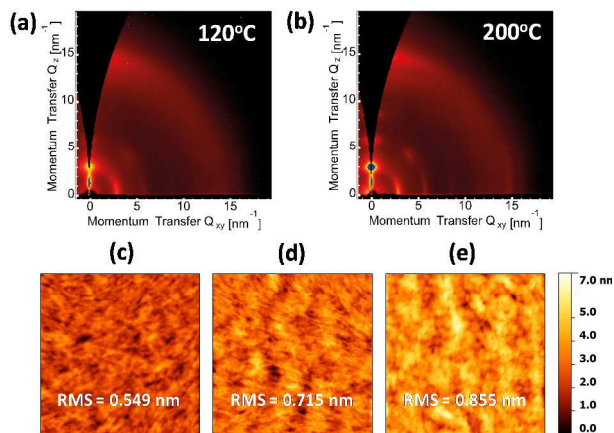


**Figure 2.** Device structure (a) and transfer characteristics (b) of an OTFT device with PDPPCp/Au-CuSCN annealed at 200 °C. (c) Mobility calculation based on the first derivative of the linear regime transfer curve and the first derivative of the square root of the saturation regime transfer curve. (d) Output characteristics of the same device.

In order to improve performance, we investigated the use of a copper(I) thiocyanate (CuSCN) interlayer that serves as a hole-conducting and electron-blocking electrode modifier (Figure 2 & S10).<sup>32</sup> After annealing at 120 °C, the OTFTs were found to ex-

hibit an average mobility of  $2.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (Table 1), a modest improvement over those fabricated with PFBT-modified electrodes. Increasing the annealing temperature to  $200 \text{ }^\circ\text{C}$  produced OFETs with average and maximum hole mobilities of 3 and  $3.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  respectively, indicating that thermal annealing between the  $T_g$  and  $T_m$  of **PDPPCp** results in a significant enhancement in device performance. Despite the remarkable mobility, however, the nonlinear dependence of the channel current ( $I_D$ ) observed at low drain voltages ( $V_D$ ) in Figure 2d, indicates the possibility for further improvements.

Two-dimensional grazing-incidence wide-angle X-ray scattering (2D-GIWAXS)<sup>33</sup> was used to probe the molecular ordering of **PDPPCp** thin films annealed at  $120 \text{ }^\circ\text{C}$  and  $200 \text{ }^\circ\text{C}$ , with diffraction patterns shown in Figures 3 and their integrated cake slices across the horizon and meridian in Figures S10a and b respectively. Both films exhibit alkyl stacking (100) peaks at a value of  $q \approx 2.95 \text{ nm}^{-1}$  corresponding to an interlayer alkyl stacking  $d$ -spacing of  $21.1 - 21.6 \text{ \AA}$  (Table S1). Moreover, these stacking peaks are observed both in-plane and out-of-plane indicating a mixture of face-on and edge-on stacking. Herman's orientation parameter,  $S$ , was calculated to quantify the texture of the film with  $S$  running from  $S = 1$  for a fully edge-on packing to  $S = -0.5$  for a fully face-on packing.  $S$  values of  $\sim -0.35$  are calculated in both cases indicating that the predominant packing geometry is face-on. Apart from the first-order (100) alkyl stacking peak, a progression of peaks up to (300) is also observed suggestive of relatively well ordered crystallites. In both films, mixed index peaks indicate the presence of 3D translational order, while a prominent  $\pi$ -stacking peak at  $q \approx 14.41 \text{ nm}^{-1}$  corresponds to a  $\pi$ - $\pi$  stacking distance of  $4.30 \text{ \AA}$ . The latter is most prominent in the out of plane direction (consistent with the predominantly face-on packing) and is significantly longer than the thiophene<sup>21</sup> analogue of DPP, or other DPP polymers with comparably good OFET performance including the fluorinated benzothiadiazole<sup>34</sup> and 3,4-difluorothiophene<sup>27</sup> analogues of **PDPPCp** that are reported to be less than *ca.*  $4.0 \text{ \AA}$ . Considering that these analogous polymers also contain a branched 2-octyldecyl<sup>21,34</sup> or 2-hexyldecyl<sup>27</sup> group on the DPP, the increased  $\pi$ - $\pi$  distance likely arises from the steric bulk of the geminal dimethyl groups on the cyclopentadiene repeat unit. Both films also show a minority population of stacking at the same momentum transfer as the second order alkyl stacking approximately  $45$  degrees from in-plane, indicating a possible paracrystalline herringbone-like polymorph. While the same general features are seen in both films, upon annealing at  $200 \text{ }^\circ\text{C}$ , the films shows a (100) peak with a slightly longer  $d$ -spacing of  $21.56 \text{ \AA}$  and a  $\pi$ -stacking peak with a slightly shorter  $\pi$ - $\pi$  stacking distance of  $4.26 \text{ \AA}$ . The peak intensities increase with annealing to  $200 \text{ }^\circ\text{C}$  indicating an increase in the degree of crystallinity.



**Figure 3.** Two-dimensional GIWAXS images of **PDPPCp** films annealed at  $120 \text{ }^\circ\text{C}$  (a) and  $200 \text{ }^\circ\text{C}$  (b), and AFM topography im-

ages of **PDPPCp** (a) on glass surface and annealed at  $120 \text{ }^\circ\text{C}$ ; (b) on CuSCN surface and annealed at  $120 \text{ }^\circ\text{C}$ ; and (c) on CuSCN surface and annealed at  $200 \text{ }^\circ\text{C}$ . Scan size:  $1 \times 1 \text{ } \mu\text{m}^2$ .

The coherence lengths of alkyl-stacking and  $\pi$ -stacking peaks also both increase with higher temperature annealing, going from  $13.7$  and  $3 \text{ nm}$  when annealed at  $120 \text{ }^\circ\text{C}$  to  $18.1$  and  $6 \text{ nm}$  after annealing at  $200 \text{ }^\circ\text{C}$ , respectively (Table S1). The improved intensities of peaks and coherence lengths, corresponding to enhanced crystallinity and better ordering, are likely related to the increased hole-transporting mobility annealed at higher temperature.

Atomic force microscopy (AFM) was also used to further characterise the film morphology and crystallinity of **PDPPCp**. The topography and phase images are shown in Figure 4 and S12. Interconnected polycrystalline fibrillar networks were observed after being annealed at  $120 \text{ }^\circ\text{C}$  on top of glass, with a root mean square roughness (RMS) of  $0.549 \text{ nm}$ . The film annealed at the same temperature on top of CuSCN layer exhibited a similar polycrystalline morphology, and the film surface became slightly rougher to  $\text{RMS} = 0.715 \text{ nm}$ . We attribute the increase in surface roughness to the influence of the underlying CuSCN interlayer, which had a rough surface of nanocrystals with  $\text{RMS} = 3.18 \text{ nm}$  (Figure S13). The polycrystalline grains grew larger and the RMS was increased to  $0.855 \text{ nm}$  upon annealing at higher temperature ( $200 \text{ }^\circ\text{C}$ ) on top of the CuSCN layer. Similar increases are often observed in other **DPP**-based polymers.<sup>35,36</sup> We further note that treatment of the film with the solvent used to deposit Cytop (CT180), does not appear to influence the surface morphology of the semiconducting film (Figure S14).

In conclusion, we have reported a novel cyclopentadiene containing DPP co-polymer. The Pd catalysed Suzuki polymerization occurred at room temperature to afford high molecular weight polymer (**PDPPCp**) with good solubility. The resulting cyclopentadiene containing polymer shows a reduction of ionization potential compared to its thiophene analogue in combination with good thermal and optical stability. **PDPPCp** shows excellent thin-film transistor performance with a hole mobility up to  $3.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  observed in top-gate, bottom-contact devices using a CuSCN interlayer. GIWAXS analysis shows the polymer films have a combination of both edge-on and face-on orientation with a notably large  $\pi$ - $\pi$  stacking distance of  $4.26 \text{ \AA}$ . Our results demonstrate that cyclopentadiene unit is a superb building block to design new high performance OFET polymers under mild polymerization conditions.

## ASSOCIATED CONTENT

### Supporting Information

This Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>. Experimental procedures, NMR spectrum, TGA, DSC, UV-vis, Modeling, Transistor plots and AFM data (PDF).

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