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# Synthesis of π-Conjugated Molecules Based on 3,4-Dioxypyrroles *via* Pd-Mediated Decarboxylative Cross-Coupling

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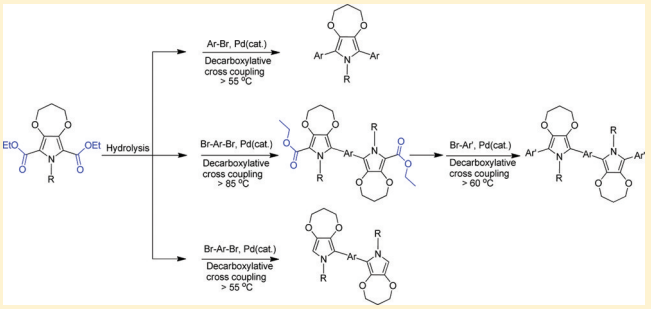
Supporting Information

**ABSTRACT:** A general scheme for the synthesis of π-conjugated molecules based on 3,4-dioxypyrroles is presented. The π-conjugated molecules were synthesized *via* Pd-mediated decarboxylative cross-coupling using various 3,4-propylenedioxypyrrole carboxylic acids and aryl bromides, including the base-sensitive electron acceptor 4,7-dibromobenzo[*c*][1,2,5]-thiadiazole (BTD). *N*-Methylpyrrolidone was used as solvent, $Pd(acac)_2$ was employed as the palladium source and $P(o\text{-tol})_3$ as the ligand. The methodology was applied to 3,4-dioxypyrrole monoacids and 3,4-dioxypyrrole diacids to produce multi-ring π-conjugated systems containing phenyl, thiophenyl, BTD, and pyridinyl units. In general, the method has yielded a practical approach for the synthesis of 3,4-dioxypyrrole-based π-conjugated molecules in acceptable to high yields of 44−94%.




## INTRODUCTION

Carboxylic acids can be used as substrates in a wide variety of chemical reactions,[1] and although their use as sacrificial groups in organometallic coupling was initially reported by Nilsson in 1966, the utilization of the tendency toward decarboxylation of some organic molecules for cross-coupling became well-known with the report made by Myers and co-workers in 2002.[2] Nilsson's reaction requires copper(I) oxide as the catalyst and resembles the Ullmann cross-coupling;[3] on the other hand, Myers' reaction utilizes a palladium catalyst and resembles the Heck reaction. Another remarkable contribution to this type of organometallic cross-coupling was presented in 2006[4] by Goossen and co-workers, who reported a Pd-mediated reaction using a copper(I) catalyst as the transmetallating agent and demonstrated the practical use of the decarboxylative cross-coupling by synthesizing a variety of biaryls and showing that it can be applied in the large-scale production of an intermediate of the agricultural fungicide Boscalid.

As shown in Scheme 1, we reported the synthesis of various π-conjugated oligomers based on 3,4-dialkyloxypyrrole (XDOP)[5] employing a 3,4-propylenedioxy (ProDOP) monocarboxylic acid and demonstrated that the decarboxylative cross-coupling is a suitable reaction to create π-conjugated molecules based on XDOPs. Here, we complement the previous report showing that the methodology can be expanded to XDOP dicarboxylic acids and also applied to create XDOP π-conjugated molecules containing the base-sensitive benzo[*c*]-[1,2,5]thiadiazole (BTD) system.

## RESULTS AND DISCUSSION

Electroactive polymers based on 3,4-dioxypyrrole molecules [poly(3,4-alkylenedioxypyrroles), PXDOPs] display characteristic optical and electrochemical properties, such as high conductivity, multicolor cathodic and anodic coloring electrochromism, rapid redox switching,[6] and stability to bioreductants.[7] These properties make PXDOPs suitable candidates for a wide range of applications, such as electrochromic and light-emitting devices, conducting coatings, chemical sensors, bioactive materials, and mechanical actuators.[6] Due to their electron-rich nature and tunability, XDOPs can produce polymers able to combine high electronic band gaps with low oxidation potentials;[6] however, these desirable properties can render XDOP monomer syntheses difficult and time-consuming, and thus, non-2,5-substituted XDOPs must be handled carefully—that is, under acid- and oxygen-free conditions.

Pd-mediated decarboxylative cross-coupling chemistry offers a practical and useful approach for 3,4-dialkyloxypyrrole molecules. Typically, organometallic cross-couplings involve halo derivatives, yet monohalo-XDOPs tend to dimerize or to decompose,[8] and dihalo-XDOPs polymerize even at relatively low temperatures.[9] Direct arylation is possible for XDOPs, but in this case, the reaction conversions and yields tend to be low.[5] Another possibility in carrying out organometallic cross-coupling on XDOPs is to synthesize the XDOP boron derivative *via* direct borylation,[10] with the boronic ester then employed in the Suzuki coupling, but this approach adds two steps to the synthetic route (decarboxylation[5] and borylation[10])

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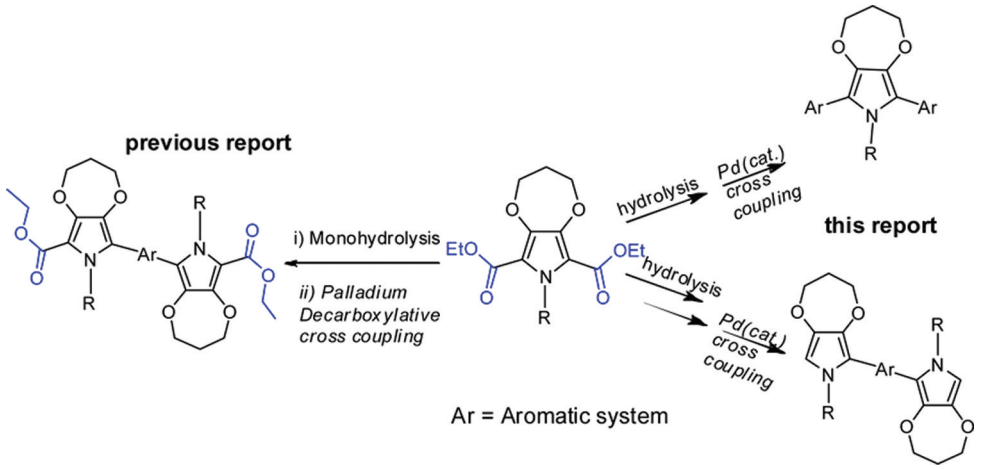
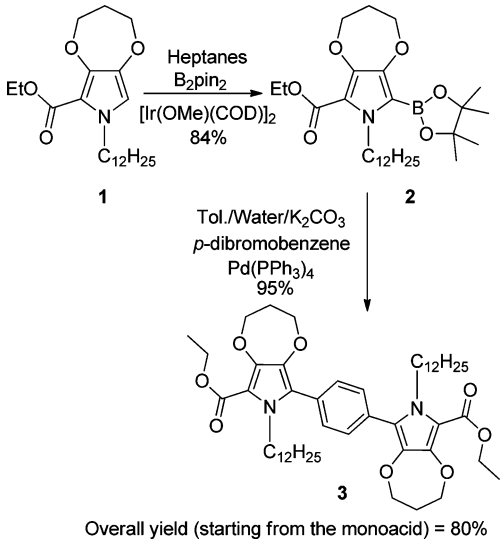
**Scheme 1. Synthesis of ProDOP-Based Molecules *via* Decarboxylative Cross-Coupling of ProDOP Carboxylic Acids**




and requires the expensive iridium catalyst $[Ir(OMe)(COD)]_2$. To compare the Suzuki–Miyaura approach with the decarboxylative cross-coupling,[5] we synthesized the boronate compound **2** and used it in the Suzuki coupling to produce compound **3**, as shown in Scheme 2, with an overall yield of 80%. We also

**Scheme 2. Alternative Route for the Synthesis of XDOP-Based $\pi$-Conjugated Oligomers *via* Suzuki Coupling**

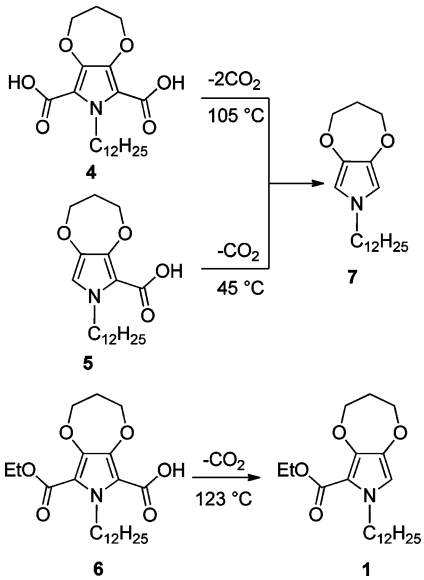



synthesized the dipinacolyl diboronate analogue of 3,4-propylenedioxypyrrole but were unable to purify it, as it decomposed on both silica or alumina, and high vacuum distillation also failed. These results showed that, in the case of XDOPs, the decarboxylative cross-coupling can be a suitable alternative to common cross-coupling methods such as the Suzuki coupling.

Several reports of Pd-mediated decarboxylative cross-coupling on aromatic rings have been made.[1,5,11−22] It has been previously demonstrated that the appropriate temperature for the decarboxylative cross-coupling varies with the tendency of the carboxylic acid to undergo decarboxylation, along with other factors such as aryl halide, solvent, and ligand employed.[5,13] The reaction has been successfully applied to monocarboxylic acids, but reports of decarboxylative cross-coupling for a dicarboxylic acid have yet to be shown. In this work, we demonstrate that the Pd-mediated cross-coupling reaction can be applied to dicarboxylic acids of the readily decarboxylable 3,4-dioxypyrrole molecule.

In order to assess the appropriate decarboxylation temperature and thermal stability of the XDOP carboxylates, we performed thermogravimetric analysis (TGA) measurements on the 3,4-propylenedioxypyrroles (ProDOPs) **4**, **5**, and **6** and also on some corresponding potassium carboxylates (see Supporting Information). As described in Scheme 3, the data

**Scheme 3. Protodecarboxylation of Three Different ProDOP Carboxylic Acids As Measured by TGA**




reveal that the decarboxylation temperature of the dicarboxylic ProDOP diacid **4** is lower than the temperature needed to decarboxylate the monoacid containing the ester group (**6**) and higher than the temperature needed to decarboxylate the corresponding monoacid **5**. The temperatures presented in Scheme 3 correspond to the minimum required temperature for the protodecarboxylation to occur in the bulk molten compound. Although we did not expect to have the same reactivity on the respective potassium carboxylates, the TGA data provide insight into the reactivity and relative stability of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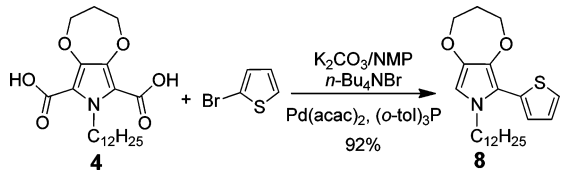
each carboxylate—acids and potassium salts, with the latter decomposing around 300 °C (see Supporting Information).

For our reactions, we used a 3,4-dioxypyrrole containing a propylene bridge because the presence of the dioxepine ring offers higher stability to the pyrrole ring than the ethylenedioxy (EDOP) analogue and the open chain substituents such as methoxy or hexyloxy. The relatively higher stability comes from the torsion generated in the seven-membered ring, which decreases the electron donation from the oxygen atoms into the pyrrole ring, thus decreasing the electron density in the pyrrole ring. In addition, ProDOPs also possess higher solubility than their EDOP analogues, which we attribute to the lower symmetry of the dioxepine ring, which decreases the possibility of $\pi$-stacking.

Our initial experiments using the dicarboxylic acid **4** with cesium or potassium carbonates failed under the previously reported conditions,[5] as even at high temperature (180 °C) the reaction did not take place, and precipitation of the potassium carboxylate was commonly observed. In an attempt to increase the solubility of the dioxypyrrole dicarboxylate, the amount of solvent (*N*-methylpyrrolidone) was increased, and the base was switched to $Li_2CO_3$, but it did not produce any change in the reaction outcome. Tetra(*n*-butyl)ammonium bromide was added to the reaction mixture to increase the solubility of the carboxylate, which had a favorable effect, and several products were observed by TLC. A combination of 1−2 equiv of tetra(*n*-butyl)ammonium bromide with 2−3 equiv of $K_2CO_3$ almost exclusively produced the monosubstituted product **8** in 92% yield (Scheme 4), which indicates that the potassium carbonate is not sufficiently basic to form the potassium dicarboxylate of **4**, which leads to a monodecarboxylative cross-coupling, followed by a proto-decarboxylation to produce compound **8**.

**Scheme 4. Sequential Decarboxylative Cross-Coupling and Proto-decarboxylation on a ProDOP Diacid**




Scheme 4 demonstrates how the Pd-decarboxylative cross-coupling reaction has been employed to build $\pi$-conjugated molecules containing the ProDOP unit. The synthesis of the ProDOP acids was carried out by controlled saponification of the ProDOP diester **9** (shown in Scheme 5), and this way the diacid **4** (shown in Scheme 3) and monoacid **6** can be obtained. To synthesize the monoacid **5**, compound **6** has to be decarboxylated first and then subjected to a second hydrolysis (as shown in Scheme 5). In all cases, the ProDOP acids were isolated and then employed for the decarboxylative cross-coupling according to the routes described in Scheme 5. As aforementioned, potassium carbonate is not a suitable base to carry out the cross-coupling in ProDOP diacids since it will lead to monosubstitution; therefore, the best results for route A were observed when the anhydrous potassium dicarboxylate **10** (shown Scheme 5) was presynthesized from the diacid **4** using a strong base (e.g., KOH or *t*-BuOK) and employed in the Pd-decarboxylative cross-coupling in combination with tetra(*n*-butyl)ammonium bromide (compounds **11** and **12**, presented in entries 1 and 2, Table 1). In this case, the reaction temperature was relatively low, and the reactions proceeded slowly at 55 °C, thus, to speed up the chemical reactions, the temperatures were typically increased to ∼70 °C. Route A produced a $\pi$-conjugated system containing the ProDOP as central core, and these types of molecules may be further employed in the construction of more complex $\pi$-conjugated systems such as oligomers and polymers.

Using route B presented in our previous report,[5] we now demonstrate that the coupling can be applied to synthesize $\pi$-conjugated systems containing the base-sensitive benzo[*c*]-[1,2,5]thiadiazole (BTD) unit (compounds **13** and **14**, entries 3 and 4, Table 1). Inclusion of the BTD unit in a $\pi$-conjugated molecule is a practical approach to decrease the band gap of the system—oligomer or polymer through an electron donor−acceptor interaction, and to increase its stability toward oxidation.[23] Unfortunately, the thiadiazole ring tends to

**Scheme 5. General Scheme for the Synthesis of ProDOP-Based $\pi$-Conjugated Molecules *via* Palladium-Mediated Decarboxylative Cross-Coupling (R = $C_{12}H_{25}$ in All Instances)**

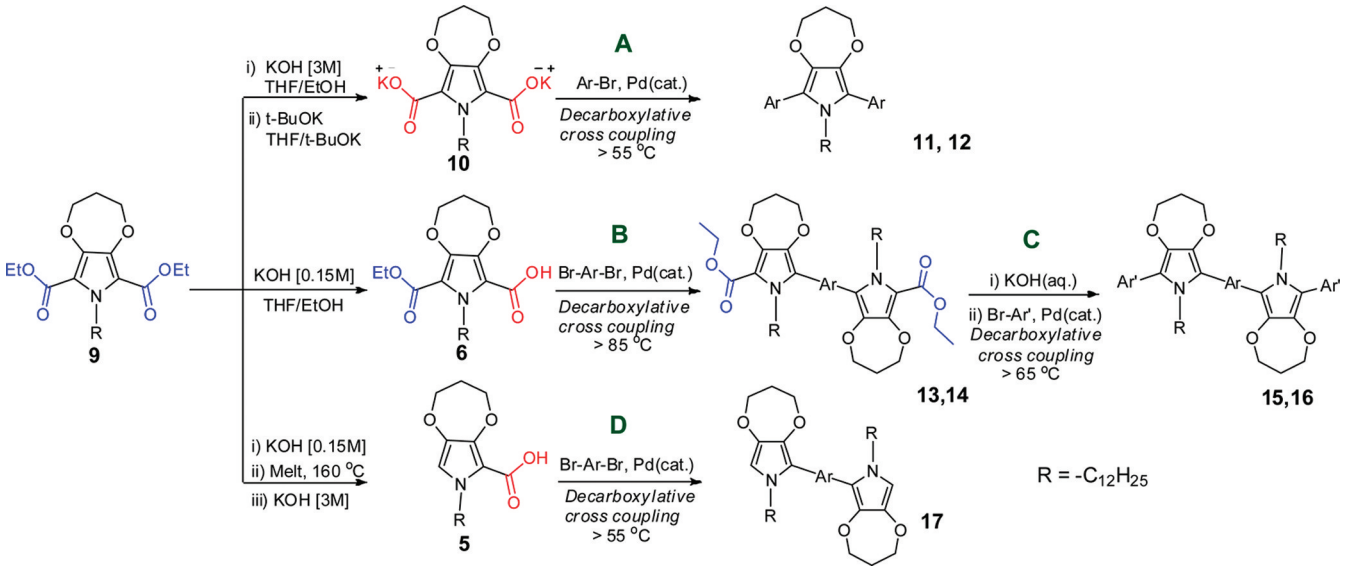




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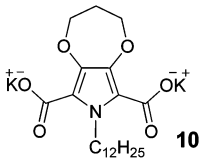
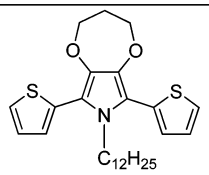
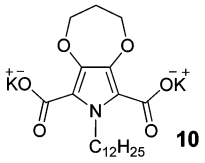
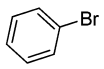
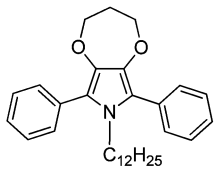
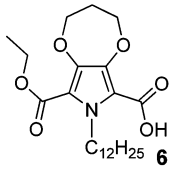
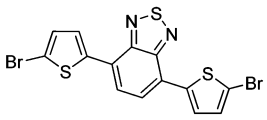
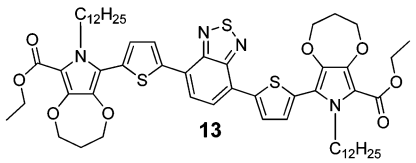
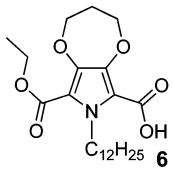
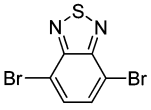
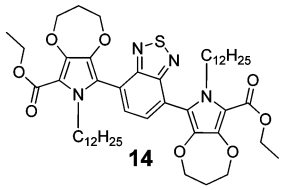
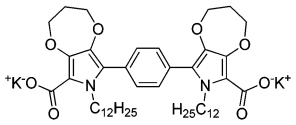
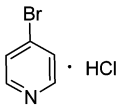
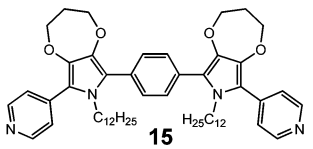
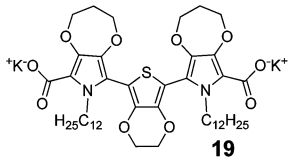
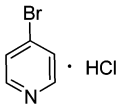
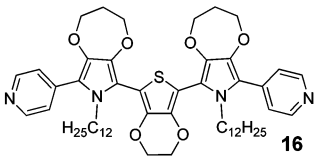
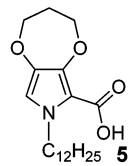
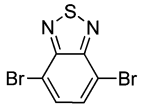
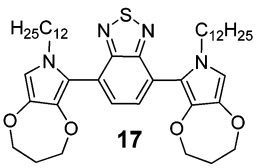
**Table 1. Several ProDOP-Based $\pi$-Conjugated Molecules Synthesized *via* Decarboxylative Cross-Coupling**

| entry | dioxypyrrole | aryl bromide | product | yield (%) |
|---|---|---|---|---|
| 1 |  **10** |  |  **11** | 69[a] |
| 2 |  **10** |  |  **12** | 72[a] |
| 3 |  **6** |  |  **13** | 89[b] |
| 4 |  **6** |  |  **14** | 94[b] |
| 5 |  **18** |  · HCl |  **15** | 64[c] |
| 6 |  **19** |  · HCl |  **16** | 79[c] |
| 7 |  **5** |  |  **17** | 44[d] |

[a]NMP, $Bu_4NBr$, 2 mol % of $Pd(acac)_2$, 4 mol % of $(o\text{-tol})_3P$. [b]NMP, $KHCO_3$, 3 mol % of $Pd(acac)_2$, 6 mol % of $(o\text{-tol})_3P$. [c]NMP, $K_2CO_3$, $Bu_4NBr$, 2 mol % of $Pd(acac)_2$, 4 mol % of $(o\text{-tol})_3P$. [d]NMP, $KHCO_3$, 3 mol % of $Pd(acac)_2$, 6 mol % of $(o\text{-tol})_3P$.

decompose under basic reaction conditions, such as those employed for decarboxylative cross-coupling. Initial attempts to include the BTD moiety in the ProDOP $\pi$-conjugated molecules using the Pd-decarboxylative cross-coupling failed because the bases $K_2CO_3$ and $Cs_2CO_3$ in *N*-methylpyrrolidone (NMP) caused decomposition of 4,7-dibromo-BTD. Switching to the milder base $KHCO_3$, while keeping the temperature under 90 °C and increasing dilution, allowed the reaction to proceed in high yield (89% for **13** and 94% for **14**).

Route B produces a $\pi$-conjugated system that still possesses two ester groups and, as depicted in route C (Scheme 5), the ester groups can be hydrolyzed and further employed to carry out an additional decarboxylative cross-coupling to expand the $\pi$-conjugated system (e.g., compounds **15** and **16**, entries 5 and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6, Table 1). These potassium dicarboxylates obtained from the hydrolysis of the ProDOP oligomers[5] have low solubility in water, which allowed a facile isolation after the basic hydrolysis, and additionally, due to the low solubility of the potassium salts also in organic solvents, route C requires tetra(*n*-butyl)-ammonium bromide. Route C cannot be applied to BTD-containing molecules since the BTD unit will decompose during the basic hydrolysis, but this problem is circumvented by employing route D, which generates a $\pi$-conjugated molecule containing two unsubstituted positions on the 3,4-dioxypyrrole molecule that may be employed for further reaction or derivatization (e.g., compound **17**, entry 7 in Table 1). We assume that the moderate yield for formation of compound **17** was due to decomposition and possible ill-defined oligomerization since, in addition to the desired compound, several side products were also observed by TLC after 24 h of reaction, which probably corresponds to oligomerization *via* direct arylation, as has been observed previously under these reaction conditions.[5]

In general, palladium acetylacetonate was used in combination with tri(*o*-tolyl)phosphine as the catalytic system, and the amount employed was varied from 1 to 3% for the palladium catalyst and 2 to 6% for the phosphine ligand; also it is possible to use triphenylphosphine as the ligand, but lower yields may be expected.[5] *N*-Methylpyrrolidone proved to be a suitable solvent since it can dissolve both the potassium and the tetra(*n*-butyl)ammonium salts as well as the $\pi$-conjugated molecule that is being formed.

In most cases, the cross-coupling reactions were monitored by TLC to determine the optimal reaction time, which varied depending of the ProDOP and the aryl bromide employed (24−72 h; see Experimental Section). Time and temperature of the reaction are two important factors that have to be controlled; on one hand, temperatures higher than the ones presented in Table 1 may lead to decomposition of the carboxylates, and on the other hand, a long reaction time may lead to decomposition of the $\pi$-electron-rich molecule, as was observed in the case of route D (shown in Scheme 5), where both decomposition and ill-defined oligomerization occurred.

## CONCLUSIONS

The decarboxylation of 3,4-dioxypyrrole carboxylic acids is a feature that can be exploited in the Pd-mediated decarboxylative cross-coupling to yield a practical and efficient methodology for the synthesis of 3,4-dioxypyrrole-based $\pi$-conjugated molecules, which may be of interest to the organic electronics community. The methodology was successfully used to create a family of $\pi$-conjugated systems, and some of these molecules may be suitable for further derivatization to produce more complex $\pi$-systems, or may be polymerized by chemical or electrochemical methods. Importantly, we have shown that the Pd-mediated decarboxylative cross-coupling can be applied to build $\pi$-conjugated systems containing the base-sensitive BTD unit which allows the inclusion of electron acceptor units in electron-rich $\pi$-conjugated molecules. As has been illustrated with numerous thiophene-based systems, creating new donor−acceptor-based XDOP oligomers and polymers is expected to increase their stability toward oxidation and also allow fine-tuning of their redox and optoelectronic properties.

## EXPERIMENTAL SECTION

**General Information.** All reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. *N-H*-(2,5-COOEt)ProDOP, [diethyl 3,4-(propylene-1,3-dioxy)pyrrole-2,5-dicarboxylate], was generously provided by BASF. All reactions were carried under argon atmosphere unless otherwise mentioned.

**Ethyl *N*-Dodecyl-3,4-(propylene-1,3-dioxy)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole-2-carboxylate (2).** The literature procedure[10] was slightly modified as follows: To a dry 25 mL round-bottom flask, containing a stir bar and under argon atmosphere, and equipped with a condenser, were added $[Ir(OMe)(COD)]_2$ (5.1 mg, 0.008 mmol, 1.5 mol %), 2,2′-bipyridine (2.4 mg, 0.015 mmol, 3 mol %), and bis(pinacolato)diboron (0.1295 g, 0.510 mmol, 1.1 equiv). Compound **1**[5] was dissolved in 3 mL of degassed heptanes and then transferred *via* syringe to the flask containing the other reagents, the system was equipped with a bubbler. The mixture was stirred at 75 °C for 24 h. The reaction mixture was cooled to room temperature and filtered through a short path of a mixture 4:1 of decolorizing carbon/alumina activity 3. The decolorizing carbon/alumina mixture was flushed with 80 mL of 30% diethyl ether in hexanes to recover the entire product. After removal of the solvent, the crude was subjected to high vacuum for 1 h at 60 °C to remove boron byproducts. The product was isolated as a colorless oil, 0.198 g (84% yield): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.41 (t, 2H, $J$ = 7.4 Hz), 4.30 (q, 2H, $J$ = 7.0 Hz), 4.15−4.08 (m, 4H), 2.22−2.12 (m, 2H), 1.59 (m, 2H), 1.40−1.20 (br, 33H), 0.88 (t, 3H, $J$ = 6.4 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 161.1, 146.7, 142.6, 129.9, 113.3, 83.4, 71.7, 71.6, 60.1, 48.0, 33.8, 32.9, 32.1, 29.88, 29.85, 29.82, 29.64, 29.57, 27.0, 24.9, 22.9, 14.6, 14.3; HRMS (ESI, M + H$^+$) $m/z$ calcd for $C_{28}H_{48}BNO_6H$ 506.3653, found 506.3696, (ESI, M + Na$^+$) $m/z$ calcd for $C_{28}H_{48}BNO_6Na$ 528.3472, found 528.3480.

**Diethyl 5,5′-(1,4-Phenylene)bis(*N*-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (3).** To a 100 mL round-bottom flask equipped with a condenser and containing a stir bar and under argon atmosphere were added compound **2** (0.183 g, 0.3602 mmol, 2.1 equiv), $K_2CO_3$(0.320 g), *n*-$Bu_4NBr$(28 mg, 0.0865 mmol, 0.5 equiv), and 1,4-dibromobenzene (40.7 mg, 0.1724 mmol, 1 equiv). The system was purged with vacuum-argon four times and then toluene (4.5 mL, previously degassed), and deionized water (4 mL, previously degassed) was added. The mixture was stirred for 30 s, and $Pd(PPh)_4$ (approximately 3 mg) was added. The mixture was warmed up to 85−90 °C and stirred vigorously for 18 h. The mixture was cooled to room temperature and partitioned between water and diethyl ether, washed with water (4×) and brine (1×), and dried over $Na_2SO_4$; an oily material was obtained, which produced a white solid after treatment with MeOH. For quantification purposes, the entire crude was purified by a chromatographic column (silica, neutralized with $Et_3N$, and ethyl ether/hexanes 1:1), producing 137 mg of a white solid in 95% yield. The compound showed the same spectroscopic characteristics as previously reported.[5]

**Diethyl *N*-Dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2,5-dicarboxylate (9).** *N-H*-(2,5-COOEt)ProDOP (5.952 g, 21.0112 mmol, 1 equiv), *n*-dodecylbromide (6.284 g, 25.2135 mmol, 1.2 equiv), ground anhydrous $K_2CO_3$ (8.7119 g, 63.0336 mmol, 3 equiv), and DMF (80 mL) were stirred at 95 °C. The reaction was monitored by TLC (silica, 1:2 ethyl ether/hexanes) until disappearance of the starting material (approximately 48 h), then the solvent was removed by rotary evaporation, and the resulting crude was partitioned between water and ethyl acetate, the ethyl acetate was washed with water (3×) and brine (1×), and dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporation, and the resulting crude was purified by column (silica, 1:2 ethyl ether/hexanes). The product was isolated as a colorless oil, 8.538 g (90% yield): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.54 (t, 2H, $J$ = 7.6 Hz), 4.32 (q, 4H, $J$ = 7.1 Hz), 4.14 (t, 4H, $J$ = 5.3 Hz), 2.21 (td, 2H, $J$ = 5.3 Hz, $J$ = 10.5 Hz), 1.70−1.55 (m, 2H), 1.35 (t, 6H, $J$ = 7.1 Hz), 1.31−1.15 (m, br, 18H), 0.86 (t, 3H, $J$ = 6.7 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 160.9, 142.0, 113.8, 71.8, 60.7, 46.5, 33.5, 32.2, 32.1, 29.9, 29.8, 29.8, 29.8, 29.5, 26.9, 22.9, 14.5, 14.3; FTIR (NaCl, disc) $\bar{\nu}_{max}$ (cm$^{-1}$) 2925.7 (s), 2854.9 (m), 1713.7 (vs), 1531.0 (m), 1456.0 (m), 1435.5 (m), 1365.1 (m), 1351.3 (m), 1308.8 (m), 1249.5 (s), 1154.7 (s), 1082.3 (m), 1028.9 (m), 776.9 (w).


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***N*-Dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2,5-dicarboxylic acid (4).** To a 250 mL round-bottom flask containing a stir bar were added compound **9** (1.534 g, 3.397 mmol), THF (15 mL), and ethanol (30 mL), After the solid dissolved, 30 mL of KOH (3 M) was added, and argon was bubbled through the reaction mixture for 5 min. The flask was equipped with a condenser, and the reaction mixture was heated to 75 °C with strong stirring under argon for 36 h. The organic volatiles were carefully removed in a rotary evaporator, and the aqueous solution was cooled in an ice bath, then the reaction mixture was carefully acidified by slow addition of 3 M HCl. The resulting white precipitate was filtered and washed with deionized water, air-dried for about 40 min, then put under high vacuum overnight. The resulting solid was stirred at ∼40 °C in 25 mL of a mixture 1:25 of ethyl ether/pentanes for 5 min; the mixture was allowed to cool to room temperature, filtered, and washed with cold pentanes. The product was isolated as a white solid, 1.303 g (97% yield): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 10.13−8.80 (br, 2H), 4.82 (t, 2H, $J$ = 7.6 Hz), 4.32 (t, 4H, $J$ = 4.8 Hz), 2.38 (quint, 2H, $J$ = 4.4 Hz), 1.64−1.72 (m, 2H), 1.29−1.24 (m, 18H), 0.87 (t, 3H, $J$ = 6.3 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 159.2, 139.0, 112.8, 73.6, 46.5, 33.5, 32.1, 31.8, 29.9, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 26.7, 22.9, 14.3; FTIR (KBr, pellet) $\overline{\nu}_{max}$ ($cm^{-1}$) 3223.6 (br, s), 2918.9 (br, s), 2850.5 (br, s), 2630.2 (br, m), 1749.2, 1669.2, 1550.9, 1438.5, 1314.7 (s), 1270.8 (s) 1169.4 (s), 1082.0 (s), 733.2 (s).

***N*-Dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylic acid (5).** To a 100 mL round-bottom flask was added compound **6**[5] (1.2 g, 3.1618 mmol), then the flask was equipped with an vacuum adapter and purged with argon-vacuum three times. The solid was melted at 130 °C under vacuum until no bubbling was observed. The resulting oil was dissolved in 1:1 DCM/hexanes and filtered through a short path of basic alumina (or silica previously neutralized with triethylamine). The solvent was removed by rotary evaporation, and the resulting colorless oil was subjected to high vacuum for 1 h. The product was redissolved using 10 mL of THF and 20 mL of EtOH, and transferred to a 100 mL round-bottom flask equipped with a stir bar and a condenser; then 15 mL of KOH (5 M) was added, and the mixture was degassed by bubbling argon for 10 min. The mixture was stirred under argon at 35−40 °C for 5 days. The volatiles were removed by rotary evaporation at room temperature. Deionized water (∼20 mL) was added to the resulting heterogeneous solution, and then cooled to 5 °C and acidified by adding HCl (2 M) dropwise (alternatively, the potassium salt can be isolated by filtration, and then dried under vacuum). The resulting solid was washed with deionized water and dried under high vacuum. The solid was stored under argon at −20 °C, 0.780 g (70% yield). The NMR showed that the product is a mixture 20:1 of compound **5** and ProDOP ester **1**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 9.93−9.02 (br, 1H), 6.49 (s, 1H), 4.23 (t, 2H, $J$ = 4.9 Hz), 4.16 (t, 2H, $J$ = 7.2 Hz), 4.01 (t, 2H, $J$ = 4.9), 2.24 (td, 2H, $J$ = 5.0 Hz, $J$ = 10.0 Hz), 1.61−1.76 (m, 2H), 1.36−1.17 (m, 18H), 0.87 (t, 3H, $J$ = 6.6 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 159.6, 141.9, 135.6, 116.0, 106.6, 73.8, 72.2, 49.5, 34.4, 32.1, 31.5, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 26.7, 22.9, 14.3; FTIR (NaCl Disc) $\overline{\nu}_{max}$ ($cm^{-1}$) 3324.8 (br, w), 3105.4 (br, w), 2924.7, 2924.7 (vs), 2854.4 (s) 2645.5 (br, w), 1732.4 (s), 1652.3 (s), 1525.1 (m), 1456.2 (s), 1407.9 (s), 1365.2 (s), 1294.6 (m), 1062.9 (s), 795.7 (w).

***N*-Dodecyl-3,4-(propylene-1,3-dioxy)-2-(thiophen-2-yl)-pyrrole (8).** To a dry 25 mL round-bottom flask containing a stir bar and under argon atmosphere were added diacid **4** (0.137 g, 0.3462 mmol, 1 equiv), finely ground anhydrous potassium carbonate (0.144 g, 1.0386 mmol, 3 equiv), and *n*-$Bu_4NBr$ (0.112 g, 0.3462 mmol, 1 equiv). The flask was equipped with an air-cooled condenser; a vacuum adapter was connected to the top of the condenser, and the system was purged with vacuum-argon four times; then *N*-methylpyrrolidone (4 mL, previously degassed) was added *via* syringe. The mixture was warmed to 70 °C and stirred for 1 h, and then 0.074 mL of 2-bromothiophene (0.124 g, 0.7615 mmol, 2.2 equiv), tri(*o*-tolyl)phosphine (4.7 mg, 0.0152 mmol, 2 mol %), and palladium(II) acetylacetonate (2.3 mg, 0.0076 mmol, 1 mol %) was added. The system was then equipped with a septum and a bubbler (containing silicon oil); the reaction mixture was stirred at 70−75 °C for 48 h. The mixture was cooled to room temperature and partitioned between diethyl ether and water in a separatory funnel, then washed with plenty water (5×) and brine (1×) and dried over $Na_2SO_4$; the solvent was removed in a rotary evaporator, and the resulting crude was purified by chromatographic column on silica (previously neutralized with triethylamine; using 1:2 diethyl ether/hexanes as eluent). The product was isolated as a pale yellow oil, which was subjected to high vacuum for 6 h, and then stored under argon atmosphere, 0.124 g (92% yield): $^1$H NMR (300 MHz, $CD_2Cl_2$) $\delta$ 7.34 (ddd, 1H, $J$ = 1.3 Hz, $J$ = 5.0 Hz, $J$ = 15.9 Hz), 7.09−7.04 (m, 1H), 7.01 (dd, 1H, $J$ = 1.2 Hz, $J$ = 3.5 Hz), 6.29 (s, 1H), 4.02−3.96 (m, 4H), 3.79 (t, 2H, $J$ = 7.4 Hz), 2.02−2.17 (m, 2H), 1.61 (td, 2H, $J$ = 5.2 Hz, $J$ = 10.4 Hz), 1.48−1.00 (m, br, 18H), 0.88 (t, 3H, $J$ = 6.7 Hz); $^{13}$C NMR (75 MHz, $D_2CCl_2$) $\delta$ 138.9, 127.5, 127.4, 127.3, 126.5, 125.9, 125.3, 107.6, 73.1, 72.9, 48.2, 35.8, 32.5, 31.7, 30.2, 30.1, 30.0, 29.9, 29.7, 29.5, 27.1, 23.3, 14.5; HRMS (ESI-DART, M + $H^+$) $m/z$ calcd for $C_{23}H_{35}NO_2SH$ 390.2461, found 390.2459.

**Potassium *N*-Dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2,5-dicarboxylate (10).** This compound can be prepared by two different methods: To a dry 50 mL round-bottom flask containing a stir bar and under argon atmosphere was added 0.2270 g of *t*-BuOK (2.0228 mmol, 2 equiv); the flask was equipped with a septum, and then 4 mL of anhydrous *t*-BuOH and 15 mL of anhydrous THF were added *via* cannula. After the *t*-BuOK dissolved, a solution of compound **4** (0.4000 g, 1.0114 mmol, 1 equiv) in 10 mL of anhydrous THF was slowly added *via* cannula. The mixture was stirred for 30 min, and then the solvent was carefully removed in a rotary evaporator (anhydrous conditions were assured by flushing the rotary evaporator with nitrogen). A pale tan solid was obtained, which was subjected to high vacuum overnight, 0.4771 g (100% yield); FTIR (KBr, pellet) $\overline{\nu}$ ($cm^{-1}$) 3391.1 (br, w), 2925.8 (s), 2853.7 (s), 1618.5 (s), 1589.9 (s), 1419.5 (s), 1340.5 (s), 1132.9 (m), 1081.3 (s), 806.1 (m). Alternatively, the procedure was also carried out using deionized water (4 mL), potassium hydroxide (0.1135 g, 2.0228 mmol, 2 equiv), and compound **4** (0.4000 g, 1.0114 mmol, 1 equiv). After removal of the water by rotary evaporation, the resulting solid was dried under vacuum at 60 °C for 3 h.

**Route A: *N*-Dodecyl-2,5-di(thiophen-2-yl)-3,4-(propylene-1,3-dioxy)pyrrole (11).** To a dry 25 mL round-bottom flask containing a stir bar and under argon atmosphere were added compound **10** (0.112 g, 0.2375 mmol, 1 equiv), *n*-$Bu_4NBr$ (0.153 g, 0.4749 mmol, 2 equiv), tri(*o*-tolyl)phosphine (6.4 mg, 0.021 mmol, 4 mol %), and palladium(II) acetylacetonate (3.2 mg, 0.011 mmol, 2 mol %). The flask was equipped with an air-cooled condenser; then an inlet vacuum adapter was connected to the top of the condenser, and the system was purged with vacuum-argon four times; then 0.05 mL of bromothiophene (0.0852 g, 0.5224 mmol, 2.2 equiv) and anhydrous *N*-methylpyrrolidone (2 mL, previously degassed) was added *via* syringe. The system was then equipped with silicone oil bubbler, and the reaction mixture was warmed to 70−75 °C and stirred for 36 h. On cooling to room temperature, the mixture was partitioned between diethyl ether and water, washed with water (5×) and brine (1×), and dried over $Na_2SO_4$. The organic solvent mixture (including the residual NMP) was removed in a rotary evaporator. The resulting crude was purified by chromatographic column on silica (previously neutralized with $Et_3N$) using 1:4 $Et_2O$/hexanes as eluent. The product was isolated as a pale yellow paraffin-like solid, 0.078 g, 69% yield: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.35 (dd, 2H, $J$ = 2.4 Hz, $J$ = 3.8 Hz), 7.11−7.07 (m, 4H), 4.05 (t, 4H, $J$ = 5.0 Hz), 4.00 (t, 2H, $J$ = 7.9 Hz), 2.07 (quint, 2H, $J$ = 5.0 Hz), 1.49−1.41 (m, 2H), 1.34−1.09 (br, m, 18H), 0.90 (t, 3H, $J$ = 6.8 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 137.3, 132.0, 127.2, 126.9, 125.5, 113.1, 72.5, 45.4, 35.0, 32.1, 31.1, 29.8, 29.7, 29.5, 29.1, 26.5, 22.9, 14.3; HRMS (ESI-TOF, M + $H^+$) $m/z$ calcd for $C_{27}H_{37}NO_2S_2H$ 472.2338, found 472.2357.

***N*-Dodecyl-2,5-diphenyl-3,4-(propylene-1,3-dioxy)pyrrole (12).** The reaction was performed using the same procedure as for compound **11** using the potassium dicarboxylate **10** (0.100 g, 0.2120 mmol, 1 equiv), *n*-$Bu_4NBr$ (0.137 g, 0.4240 mmol, 2 equiv), tri(*o*-tolyl)phosphine (5.7 mg, 0.019 mmol, 4 mol %), palladium(II) acetylacetonate (2.8 mg, 0.009 mmol, 2 mol %), 0.05 mL of

bromobenzene (0.0732 g, 0.4664 mmol, 2.2 equiv), and 2 mL of *N*-methylpyrrolidone (previously degassed). The product was isolated as a colorless paraffin-like solid, 70 mg (72% yield): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.47−7.38 (m, 8H) 7.32−7.26 (m, 2H), 4.01 (t, 4H, $J$ = 5.0 Hz), 3.88 (t, 2H, $J$ = 7.1 Hz), 2.17 (quint, 2H, $J$ = 5.0 Hz), 1.22−0.66 (br, m, 23H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 137.3, 131.6, 129.8, 128.4, 126.6, 120.7, 72.4, 45.6, 35.2, 32.1, 30.1, 29.8, 29.8, 29.6, 29.5, 29.4, 28.9, 26.2, 22.9, 14.3; HRMS (ESI-TOF, M + H$^+$) $m/z$ calcd for $C_{31}H_{41}NO_2H$ 460.3210, found 460.3196.

**Route B: Diethyl 5,5′-(Benzo[*c*][1,2,5]thiadiazole-4,7-diyl)-bis(thiophene-5,2-diyl)bis(*N*-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (13).** To a dry 25 mL round-bottom flask containing a stir bar and under argon atmosphere were added compound **6**[5] (0.060 g, 0.1417 mmol, 2.2 equiv) and finely ground anhydrous potassium bicarbonate (0.0142 g, 0.1417 mmol, 2.2 equiv). The flask was equipped with an air-cooled condenser; an inlet vacuum adapter was connected to the top of the condenser, and the system was purged with vacuum-argon four times, then NMP (5.5 mL, previously degassed) was added *via* syringe. The mixture was warmed to 50 °C and stirred for 1 h (vacuum was slightly applied several times to remove $CO_2$ and help the neutralization process), then 4,7-bis(5-bromothiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (29.5 mg, 0.0644 mmol, 1 equiv), tri(*o*-tolyl)phosphine (1.2 mg, 0.0039 mmol, 6 mol %), and palladium(II) acetylacetonate (0.6 mg, 0.0019 mmol, 3 mol %) were added. The system was then equipped with a septum and a bubbler (containing silicon oil); the reaction mixture was warmed to 90 °C and stirred for 24 h. The solvent was removed in a rotary evaporator at 80 °C, then the crude was dissolved in 3:1 hexanes/ethyl acetate and filtered through a short path (∼1 cm) of neutral alumina (activity 3); the alumina was flushed with the hexanes/AcOEt mixture to recover the entire product. The solvent was removed in a rotary evaporator, and the resulting crude oil was dissolved in hexanes, washed with deionized water (3×) and brine (1×), and dried over $Na_2SO_4$. The mixture was filtered, and the solvent was removed in a rotary evaporator; the resulting sticky solid was put under vacuum overnight, then 2 mL of ethanol was added and the mixture was slightly warmed; then diethyl ether was added until the solid dissolved. Slow evaporation of the diethyl ether produced a purple powdery solid, which was filtered, washed with ethanol, and air-dried for 2 min, then put under vacuum to remove the solvent traces, 60.8 mg (89% yield): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.17 (d, 2H, $J$ = 3.9 Hz), 7.89 (s, 2H), 7.24 (d, 2H, $J$ = 3.9 Hz), 4.35 (q, 8H, $J$ = 7.1 Hz), 4.20 (t, 4H, $J$ = 4.9 Hz), 4.09 (t, 4H, $J$ = 5.1 Hz), 2.27−2.22 (m, 4H), 1.75−1.60 (m, 4H), 1.38 (t, 6H, $J$ = 7.1 Hz), 1.15−1.10 (m, 34H), 0.84 (t, 6H, $J$ = 6.8 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 161.3, 152.8, 144.0, 140.5, 136.5, 131.8, 129.3, 127.9, 125.9, 125.7, 119.9, 109.3, 72.2, 72.1, 60.1, 46.5, 34.2, 32.1, 32.0, 29.9, 29.8, 29.8, 29.8, 29.6, 29.4, 26.8, 22.9, 14.8, 14.3; HRMS (DART-TOF, M + H$^+$) $m/z$ calcd for $C_{58}H_{78}N_4O_8S_3H$ 1055.5055, found 1055.5089.

**Diethyl 5,5′-(Benzo[*c*][1,2,5]thiadiazole-4,7-diyl)bis(*N*-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (14).** Using compound **6**[5] (0.1700 g, 0.4014 mmol, 2.1 equiv), finely ground anhydrous potassium bicarbonate (0.0398 g, 0.3976 mmol, 2.08 equiv), NMP (9 mL, previously degassed), 4,7-dibromobenzo-[*c*][1,2,5]thiadiazole (56.2 mg, 0.1911 mmol, 1 equiv), tri(*o*-tolyl)phosphine (4.6 mg, 0.0153 mmol, 8 mol %), and palladium(II) acetylacetonate (2.3 mg, 0.0077 mmol, 4 mol %), the reaction was run for 72 h, using the same procedure as for **13**, although the workup was modified as follows: The solvent was concentrated by rotary evaporation at 80 °C to ∼1 mL, then the mixture was dissolved in diethyl ether, washed with water (5×) and brine (1×), and dried over $Na_2SO_4$, then purified by chromatographic column on silica using 1:1 diethyl ether/hexanes as eluent. The product was isolated as an orange solid (paraffin like), 0.160 g (94% yield): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.63 (s, 2H), 4.50−3.80 (m, br, 16H), 2.30−2.10 (m, 4H), 1.50−1.28 (m, 10H), 1.28−0.88 (m, 36H), 0.84 (t, 6H, $J$ = 7.1 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 161.3, 154.2, 144.3, 136.8, 131.5, 123.5, 122.6, 109.5, 72.0, 72.0, 60.0, 46.9, 34.3, 32.0, 31.8, 29.8, 29.7, 29.6, 29.6, 29.5, 29.2, 26.6, 22.8, 14.7, 14.2; HRMS (DART, M + H$^+$) $m/z$ calcd for $C_{50}H_{74}N_4O_8SH$ 891.5300, found 891.5295.

**Potassium 5,5′-(1,4-Phenylene)bis(*N*-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (18).** To a 50 mL round-bottom flask containing a stir bar were added diester[5] **3** (0.262 g, 0.3145 mmol), THF (6 mL), and ethanol (6 mL). After the solid dissolved, 3.8 mL of 5 M KOH (19 mmol, 60 equiv) was added, and the mixture was degassed by bubbling argon for 10 min. The flask was equipped with a condenser, and the reaction mixture was heated to 55−60 °C with strong stirring under argon for 72 h. The reaction mixture was filtered using glass wool (to remove traces of palladium black), and then the organic solvents (THF and ethanol) and part of the water were carefully removed in a rotary evaporator at 25 °C, which produced precipitation of the potassium decarboxylate salt. The resulting solid was filtered, washed with slightly basic cold water, air-dried for 5 min, and washed with hexanes. The pale yellow solid (hydrated) was then put under vacuum (0.1 mmHg) at 115 °C for 72 h. The final product was received as a white solid, 0.247 g, 92% yield: $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 7.24 (s, 4H), 4.23 (t, 4H, $J$ = 6.9 Hz), 3.82 (dd, 8H, $J$ = 5.9 Hz, $J$ = 9.5 Hz), 2.04−1.90 (m, 4H), 1.32−0.90 (br, m, 40H), 0.84 (t, 6H, $J$ = 6.5 Hz); FTIR (KBr, pellet) $\bar{\nu}_{max}$ (cm$^{-1}$) 3395.5 (br, w), 2924.7 (s), 2853.5 (s), 1566.0 (s), 1447.9 (s), 1417.5 (s), 1356.9 (s), 1081 (s), 1138.1 (w), 806.3 (m).

**Potassium 5,5′-(3,4-(Ethylene-1,2-dioxy)thiophene-2,5-diyl)-bis(*N*-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (19).** The reaction was performed using a similar procedure as for **18**, using 2.521 g of the EDOT derivative[5] (2.810 mmol), 54 mL of THF, 54 mL of EtOH, and 34 mL of 5 M KOH. The workup was slightly modified as follows: After removal of the volatiles, the resulting gum-like solid was filtered, washed with slightly basic cold water, and air-dried for 10 min. The pale yellow solid was subjected to vacuum overnight at room temperature, yielding an amber solid which was ground in a mortar, producing a fine yellow powder, 2.548 g, 99% yield: $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 4.25−4.10 (m, 8H), 3.90−3.78 (m, 8H), 2.03−1.90 (m, 4H), 1.44−0.09 (m, 40H), 0.84 (t, 6H, $J$ = 6.5 Hz); $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 163.7, 138.3, 137.2, 137.2, 136.7, 120.2, 105.9, 105.9, 71.3, 71.0, 64.0, 34.6, 31.4, 31.4, 31.2, 29.1, 29.0, 29.0, 28.9, 28.6, 26.4, 22.0, 13.8; FTIR (KBr, pellet) $\bar{\nu}_{max}$ (cm$^{-1}$) 3392.1 (m), 2924.2 (s), 2853.7 (s), 1580.8 (s), 1510.7 (m), 1462.0 (s), 1420.6, 1420.6 (s), 1358.6 (s), 1080.6, 954.9 (w), 806.9 (w).

**Route C: 5,5′-(1,4-Phenylene)bis(*N*-dodecyl-2-(pyridin-4-yl)-3,4-(propylene-1,3-dioxy)pyrrole) (15).** To a dry 50 mL round-bottom flask containing a stir bar and under argon atmosphere were added compound **18** (0.233 g, 0.2725 mmol, 1 equiv), 4-bromopyridine hydrochloride (0.1113 g, 0.5723 mmol, 2.1 equiv), anhydrous $K_2CO_3$ (0.083 g, 0.600 mmol, 2.2 equiv), *n*-$Bu_4NBr$ (0.220 g, 0.6814 mmol, 2.5 equiv), tri(*o*-tolyl)phosphine (7 mg, 0.0229 mmol, 4 mol %), and palladium(II) acetylacetonate (3.5 mg, 0.0114 mmol, 2 mol %). The flask was equipped with an air-cooled condenser; then an inlet vacuum adapter was connected to the top of the condenser, and the system was purged with vacuum-argon four times; then *N*-methylpyrrolidone (6 mL, previously degassed) was added via syringe. The system was then equipped with a silicone-oil bubbler, and the reaction mixture was warmed to 70−75 °C and stirred for 60 h. The reaction mixture was concentrated to ∼1 mL by rotary evaporation at 80 °C, and then it was cooled to room temperature, partitioned between diethyl ether and water, and then washed with water (5×) and brine (1×), and dried over $Na_2SO_4$. The resulting crude was purified by chromatographic column on basic alumina, using a gradient 1:0 to 0:1 $Et_2O$/EtOAc as eluent, yielding 0.147 g of a yellow solid, 64% yield: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.60 (d, 4H, $J$ = 5.5 Hz), 7.49 (s, 4H) 7.37 (d, 4H $J$ = 5.5 Hz), 4.03 (dd, 8H, $J$ = 5.0 Hz, $J$ = 9.7 Hz), 3.78 (t, 4H, $J$ = 7.0 Hz), 2.28−2.13 (m, 4H), 1.24−0.72 (br, m, 46H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 149.8, 139.6, 139.1, 137.7, 129.6, 129.4, 122.96−123.17 (br), 123.0, 118.5, 72.3, 46.4, 34.8, 30.1, 29,81−29.75 (br), 29.6, 29.50, 29.46, 29.0, 26.2, 22.9, 14.3; HRMS (MALDI, M + H$^+$) $m/z$ calcd for $C_{54}H_{74}N_4O_4H$ 843.5783, found 843.5765.

**5,5′-(3,4-(Ethylene-1,2-dioxy)thiophene-2,5-diyl)bis(*N*-dodecyl-2-(pyridin-4-yl)-3,4-(propylene-1,3-dioxy)pyrrole) (16).** The reaction was performed using the same procedure as for **15**,


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using **19** (0.250 g, 0.2725 mmol, 1 equiv), 4-bromopyridine hydrochloride (0.1113 g, 0.5723 mmol, 2.1 equiv), anhydrous $K_2CO_3$ (0.083 g, 0.600 mmol, 2.2 equiv), *n*-$Bu_4NBr$ (0.220 g, 0.6814 mmol, 2.5 equiv), tri(*o*-tolyl)phosphine (7 mg, 0.0229 mmol, 4 mol %), palladium(II) acetylacetonate (3.5 mg, 0.0114 mmol, 2 mol %), and 6 mL of NMP. The product was isolated as a pale orange solid, 0.195 g (79% yield): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.56 (d, 4H, $J$ = 6.1 Hz), 7.31 (d, 4H, $J$ = 6.2 Hz), 4.28 (s, 4H) 4.07−3.98 (m, 8H), 3.92 (t, 4H, $J$ = 7.1 Hz), 2.26−2.07 (m, 4H), 1.40−0.89 (br, m, 40), 0.84 (t, 6H, $J$ = 6.8 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 149.8, 138.9, 138.6, 138.5, 138.2, 123.2, 118.4, 112.3, 106.8, 72.3, 64.8, 46.0, 34.8, 32.0, 30.6, 29.77, 29.75, 29.71, 29.6, 29.6, 29.5, 29.2, 26.6, 22.8, 14.2; HRMS (ESI-TOF, $[M + H]^{2+}$) $m/z$ calcd for $C_{54}H_{74}N_4O_6SH_2$ 454.2737, found 454.2743.

**Route D: 4,7-Bis(*N*-dodecyl-3,4-(propylene-1,3-dioxy)pyrrol-2-yl)benzo[*c*][1,2,5]thiadiazole (17).** To a dry 25 mL round-bottom flask containing a stir bar and under argon atmosphere were added compound **5** (0.3 g, 0.8535 mmol, 2.5 equiv) and finely ground anhydrous potassium bicarbonate (0.089 g, 0.8877 mmol, 2.6 equiv). The flask was equipped with an air-cooled condenser; an inlet vacuum adapter was connected to the top of the condenser, and the system was purged with vacuum-argon four times; then NMP (15 mL, previously degassed) was added *via* syringe. The mixture was warmed to 35 °C and stirred for 1 h (vacuum was slightly applied several times to remove $CO_2$ and to help the neutralization process), then 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (0.100 g, 0.3414 mmol, 1 equiv), tri(*o*-tolyl)phosphine (6.2 mg, 0.0205 mmol, 6 mol %), and palladium(II) acetylacetonate (3.11 mg, 0.0102 mmol, 3 mol %) were added. The system was then equipped with a septum and a bubbler (containing silicon oil), and the reaction mixture was warmed to 80−82 °C and stirred for 42 h. The solvent was removed in a rotary evaporator at 80 °C. The crude was dissolved in dichloromethane and washed with water. The dichloromethane was removed by rotary evaporation, and the resulting crude was purified by chromatographic column on silica (previously neutralized with triethylamine), using a 2:1 ether/hexanes mixture as eluent, yielding 0.112 g of a bright red oil (44% yield): $^1$H NMR (300 MHz, DCM-$d_2$) $\delta$ 7.55 (s, 2H), 6.45 (s, 2H), 4.03 (t, 4H, $J$ = 4.3 Hz), 3.96 (t, 4H, $J$ = 4.8 Hz), 3.71 (t, 4H, $J$ = 7.2 Hz), 2.21−2.06 (m, 4H), 1.67−0.98 (m, br, 40 H), 0.87 (t, 6H, $J$ = 6.7 Hz); $^{13}$C NMR (75 MHz, DCM-$d_2$) $\delta$ 154.9, 139.4, 138.0, 131.1, 123.8, 115.7, 108.0, 73.1, 73.0, 48.9, 35.9, 32.5, 31.6, 30.2, 30.2, 30.1, 30.0, 29.9, 29.7, 27.1, 23.3, 14.5; HRMS (APCI, $[M + H]^+$) $m/z$ calcd for $C_{44}H_{66}N_4O_4SH$ 747.4878, found 747.4876.

## ■ ASSOCIATED CONTENT

### Supporting Information

$^1$H and $^{13}$C NMR for target products and TGA data for compounds **4**, **5**, **6**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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