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A Three-Step Synthetic Approach to Asymmetrically Functionalized 4*H*-Cyclopenta[2,1-*b*:3,4-*b*′]dithiophenes

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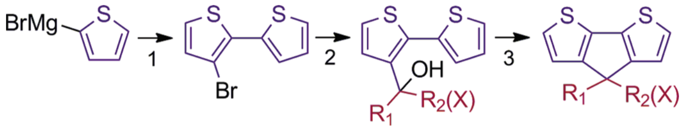

1. 2,3-dibromothiophene, Pd(dppf)Cl_2; 2. *n*-BuLi, ketone;
3. H_2SO_4

A convenient and efficient three-step route toward both symmetrically and asymmetrically functionalized 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophenes has been developed. Using this method a broad collection of functionalized bridged bithiophenes can smoothly be accessed. Starting from 3-bromo-2,2′-bithiophene, prepared by Kumada coupling of 2-thienylmagnesium bromide with 2,3-dibromothiophene under Pd(dppf)Cl_2 catalysis, lithiation and subsequent reaction with dialkyl ketones afforded (a)symmetrically dialkylated tertiary alcohol derivatives. By means of final Friedel−Crafts dehydration cyclization in sulfuric acid medium, these derivatives were converted to 4,4-dialkyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophenes. Upon replacement of the dialkyl ketone reagent by ethyl levulinate, an ester-functionalized 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene was prepared, representing an attractive precursor for variously functionalized cyclopentadithiophene compounds.

Introduction

During the last decades cyclopentadithiophenes have emerged as attractive building blocks for the development of novel materials. These heterocycles have for example been applied in the design of polymerization catalysts and conjugated polymers with various applications.[1−7] Cyclopentadienyl ligands fused with thiophene units have been investigated as structural subunits of homogeneous metallocene catalysts

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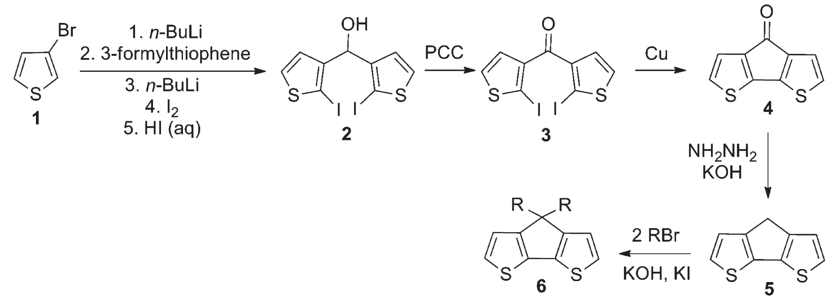
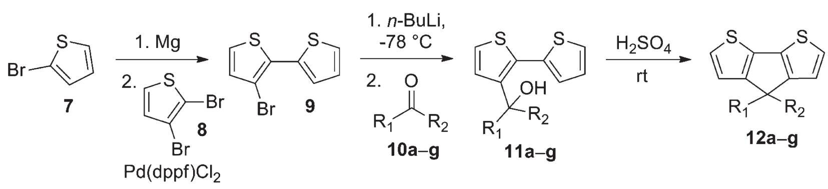
SCHEME 1. **State-of-the-Art Method toward Dialkyl-CPDTs**[8h−j]



SCHEME 2. **Novel Synthetic Route toward 4,4-Dialkyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophenes**



12a $R_1 = R_2$ = Et (55%), **12b** R_1 = Me, R_2 = Nonyl (16%), **12c** $R_1 = R_2$ = Isobutyl (35%),
12d R_1 = Octyl, R_2 = 2-Ethylhexyl (57%), **12e** $R_1 = R_2$ = Pentyl (32%), **12f** $R_1 = R_2$ = Cy (40%),
12g $R_1 = R_2$ = Octyl (53%)

for the polymerization of 1-olefins, affording enhanced control over the polymer microstructure not achievable by traditional Ziegler−Natta catalysts.[1] On the other hand, cyclopentadithiophenes have become popular rigid precursors for polymeric (semi)conducting materials.[2−7] Zotti and others have extensively studied the optical, electrochemical, and conducting properties of poly(cyclopentadithiophenes), immobilized on surfaces by electrochemical polymerization.[2,3] Such polymers could be applied as sensor systems when well-established supramolecular recognition elements (calixarenes or crown ethers) were appended.[2c,h,3f] Electrochromic polymers based on cyclopentadithiophenes have also been reported recently,[4] whereas conducting cyclopentadithiophene-based matrices for electrochemically controlled (DNA) delivery systems have been developed by the group of Cougnon and Pilard.[5]

Out of the six possible cyclopentadithiophene isomers, 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene has majorly been applied for the construction of conjugated polymer materials, whereas the 7*H*-cyclopenta[1,2-*b*:4,3-*b*′]dithiophene analogue has most often been used for the development of metallocene catalysts. The vast majority of 4*H*-cyclopenta[2,1-*b*:3,4-b′]dithiophene (CPDT) building blocks reported to date have been synthesized by rather laborious multistep procedures affording mostly symmetrically dialkylated cyclopentadithiophenes.[8] Consequently, finding a more economic, straightforward, and versatile synthetic protocol would be beneficial and could also facilitate optimization of the CPDT-based material features. In this paper, a three-step pathway toward both symmetrically and asymmetrically substituted dialkyl-CPDTs and functional derivatives thereof is reported.

Results and Discussion

The first synthetic pathway toward the 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene isomer was reported in 1968 by Wynberg and co-workers, affording the parent CPDT **5** in a low overall yield.[8a] Although some improvements to this procedure have been made over the years, synthetic progress has been rather limited.[8b−g] More recently, Reynolds and Brzezinski described a three-step synthesis—one-pot double lithiation and iodination, oxidation, and Ullmann coupling—toward 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophen-4-one (**4**), the ketone analogue of the rigidly bridged bithiophene unit (Scheme 1).[8h] This cyclic ketone could subsequently be reduced with hydrazine according to a Huang−Minlon modification of the Wolff−Kischner procedure, as reported by Turner et al. (Scheme 1).[8i,j] Dialkylation at the methylene bridge (4-position) of the planar bithiophene unit, required for processability in solution, has been performed with various

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TABLE 1. **Tested (Lewis) Acidic Reaction Conditions for the Alkylative Cyclization Reaction toward CPDT 12a**

entry	(Lewis) acid	equiv	reaction time (h)	solvent	T (°C)	**12a** (%)
1	$BF_3 \cdot OEt_2$	159	3	CH_2Cl_2	rt	–[a]
2	$BF_3 \cdot OEt_2$	80	2	CH_2Cl_2	rt	–[a]
3	$BF_3 \cdot OEt_2$	80	3	CH_2Cl_2	rt	–[a]
4	$BF_3 \cdot OEt_2$	1	12	CH_2Cl_2	rt	–[a]
5	HCl	8.5	4	AcOH	120	–[a]
6	HCl	8.5	12	AcOH	120	–[a]
7	HNO_3	12	12	-	rt	–[a]
8	*p*-TsOH	12	12	*n*-octane	rt	–[a]
9	H_3PO_4	12	12	-	rt	–[a]
10	H_2SO_4	12	12	-	rt	45[b]
11	H_2SO_4	12	12	*n*-octane	rt	55[b]
12	H_2SO_4	12	2	AcOH	80	–[a]
13	H_2CrO_4	12	12		rt	35[b]

[a] Mainly a mixture of **13** and **14**, sometimes accompanied by small amounts of **12a**. [b] No remaining alkene isomers.

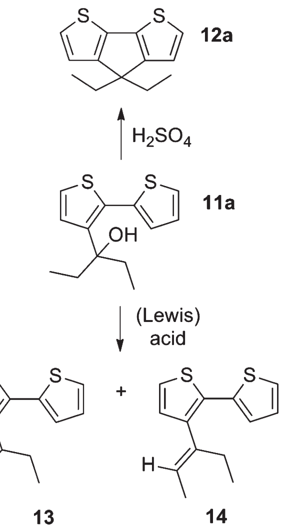
alkyl halides, either employing KOH in DMSO (Scheme 1)[8i,j] or by stepwise lithiation and alkylation.[2a,9]

The synthetic protocol as summarized in Scheme 1 represents the most efficient route toward dialkylated CPDTs to date and is hence applied frequently for the construction of CPDT-based materials. This state-of-the-art synthetic procedure can, however, be regarded as comparatively laborious and more suitable for symmetrically dialkylated CPDT derivatives.[9] This encouraged us to search for an alternative synthetic method, which would be applicable toward a wide range of CPDTs. The major goals were the ability to introduce, using one single straightforward approach, two *identical or different* alkyl chains simultaneously and to enable introduction of basic functional groups on these alkyl chains.

Our novel synthetic approach comprises three main steps, as depicted in Scheme 2. 4,4-Diethyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (**12a**) was used as the model compound during this study, but the optimized procedures were readily extended to other (asymmetrically) dialkylated derivatives (vide infra). According to the reported protocol by Jüttner and co-workers,[10] 3-bromo-2,2′-bithiophene (**9**) was synthesized through a Kumada coupling of the Grignard reagent of 2-bromothiophene (**7**) with 2,3-dibromothiophene (**8**) under Pd(dppf)Cl_2 catalysis. The next step involved regiospecific formation of the lithio derivative by bromo-lithio exchange. The lithiated compound was then in situ reacted with 3-pentanone (1 equiv) affording tertiary alcohol derivative **11a**.[11] Subsequently, after tedious optimization of the ring closure conditions, an acid-catalyzed (H_2SO_4) cyclization reaction afforded the desired diethyl-CPDT **12a**.

To the best of our knowledge, there are no literature reports in which (Lewis) acid-catalyzed alkylative cyclization

SCHEME 3. **Ring Closure vs Alkene Formation**



of bithiophene moieties toward 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]-dithiophenes has been performed.[12,13] Scherf et al. described a series of ring closure reactions promoted by borontrifluoride dietherate ($BF_3 \cdot OEt_2$) toward thiophene–phenylene and thiophene–naphthalene stepladder copolymers.[14] However, application of the same reaction conditions to tertiary alcohol derivative **11a** (Table 1, entry 1) afforded majorly alkene *Z* and *E* isomers **13** and **14** by simple dehydration (Scheme 3). Under all tested reaction conditions (variation of the number of equivalents of $BF_3 \cdot OEt_2$ and the reaction time), formation of these alkene isomers remained dominant (Table 1, entries 1–4). Several attempts were carried out to perform the cyclization reaction with Brönsted acids. However, this effort did not lead to any noticeable improvement (Table 1, entries 5–9). Finally, efficient ring closure was achieved by means of addition of an excess of sulfuric acid (Table 1, entry 10). The as-formed orange solution was diluted with water and dichloromethane followed by extraction and, after purification of the crude oil by column chromatography, CPDT **12a** was obtained in a reasonable yield of 45%. A slightly higher yield (55%) could be achieved upon dilution of the reagents in *n*-octane (Table 1, entry 11), whereas addition of acetic acid afforded once more the alkene mixture (Table 1, entry 12). As an alternative Brönsted acid to promote cyclization, chromic acid could also be used (Table 1, entry 13).

It can be assumed that after dehydration the formed alkene *Z* and *E* isomers **13** and **14** undergo protonation of the double bond and subsequent intramolecular alkylation (Scheme 3). Several test reactions indicated that immediate workup after addition of sulfuric acid to the alcohol derivative **11a** afforded alkene isomers **13** and **14**. On the other hand, all traces of alkenes were converted into ring closed CPDT **12a** after 1 h. Treatment of the isolated alkene mixture with H_2SO_4 also afforded **12a**. Summarizing these observations, the cyclization seems to be thermodynamically controlled with the CPDT as the thermodynamic sink. To support this interpretation,

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(9) A few asymmetrically dialkylated CPDTs have been reported by Zotti et al. (refs 2e, 2f, and 2i).

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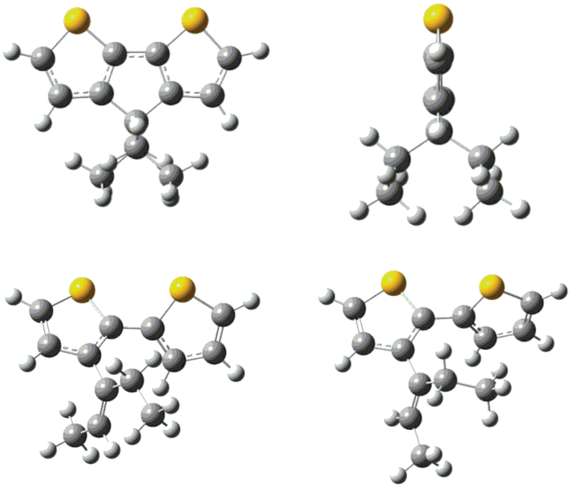

FIGURE 1. Optimized structures of CPDT **12a** (top: front and side view) and alkenes **13** and **14** (bottom).

theoretical calculations on the alkene isomers and diethyl-CPDT **12a** were carried out. At the MP2/6-311+G** level of approximation, the ring closed structure was found to be about 8−9 kcal/mol more stable than the alkene-containing species. As shown in Figure 1, compound **12a** is planar whereas large deviations from planarity are observed for the alkenes.

The two alkene stereoisomers **13** and **14** could not readily be separated resulting in complex NMR spectra for the alkene mixture. The intensity difference of the signals due to the ratio of the two isomers enabled the distinction of the signals for each isomer, i.e. one isomer was formed in 35%, whereas the other was formed in 65%.[15] Complete assignment of the proton and carbon resonances was accomplished by a combination of 2D-HETCOR and one-dimensional NMR techniques (^{1}H, ^{13}C, DEPT, and APT) (cf. the Supporting Information). All chemical shift data of both isomers could be collected, but since they were not separable, NOE(-dif) experiments were required to establish a clear distinction. Two data sets were acquired in one of which selective preirradiation was applied. In Figure 2 only the part of the spectra is shown which changed in intensity. Upon preirradiation at 1.47 ppm, saturating the methyl protons (H_7) of the isomer found in the biggest amount, NOE enhancement was observed for the β-thienyl proton (H_3) at 6.77 ppm (Figure 2). This gave a first indication that *Z* isomer **13** is formed in excess resulting in the highest peak intensities. In addition, NOE enhancement was also observed for the vinyl proton (H_6) at 5.62 ppm (Figure 2). Upon preirradiation at 5.57 ppm, saturating the resonance corresponding to the vinyl proton (H_6) of the isomer formed in the smallest amount, NOE enhancement was observed for the β-thienyl proton (H_3) at 6.85 ppm (Figure 2). This confirmed that the *Z* alkene **13** is majorly formed, whereas the *E* isomer **14** is produced in smaller amounts. In addition, NOE enhancement was also observed for the methyl protons (H_7) at 1.74 ppm. No further NOE's were observed.

Hence, *Z* alkene **13** was formed in 65%, whereas the *E* alkene **14** represented only 35%. This observation might indicate that the *Z* alkene is slightly more thermodynamically stable than the *E* alkene. These results were also confirmed by theoretical ΔG calculations. Using the MP2/6-311+G** method and accounting for solvent effects (AcOH), a slightly lower energy

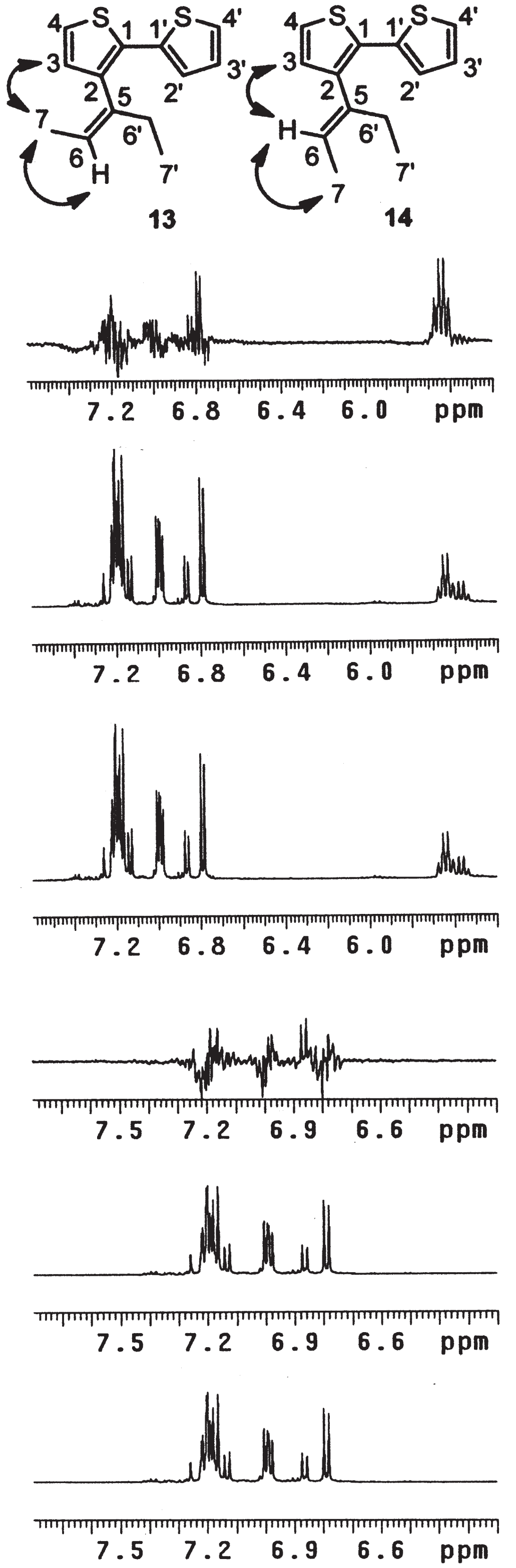

FIGURE 2. NOE spectra for the mixture of alkene isomers **13** and **14**: preirradiation at 1.47 (top) and 5.57 ppm (bottom)—(control) spectrum without preirradiation (bottom), NOE spectrum (middle), and difference spectrum (top).

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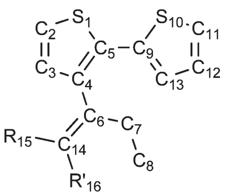
[15] The studied alkene mixture was obtained from the attempt to perform the cyclization with HCl in AcOH (Table 1, entry 6).

TABLE 2. Selected Optimized Parameters for *Z* Alkene 13 and *E* Alkene 14



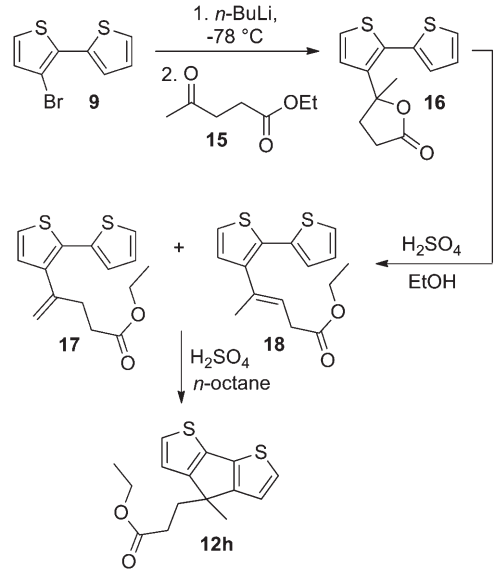
parameters	*Z*: R = Me, R′ = H (**13**)	*E*: R = H, R′ = Me (**14**)
	bond lengths (Å)	
$C_5{-}C_9$	1.454	1.458
$C_4{-}C_6$	1.483	1.481
$C_6{-}C_7$	1.514	1.520
$C_6{=}C_{14}$	1.351	1.354
$C_{14}{-}R_{15}$	1.504	1.091
$C_{14}{-}R'_{16}$	1.089	1.502
	torsion angles (deg)	
$S_1{-}C_5{-}C_9{-}S_{10}$	50.6	73.4
$C_6{-}C_4{=}C_5{-}C_9$	5.0	8.7
$C_3{-}C_4{-}C_6{=}R_{14}$	67.8	56.2
$C_{14}{=}C_6{-}C_7{-}R_8$	6.0	71.0
$C_4{-}C_6{=}C_{14}{-}R_{15}$	3.6	5.1
$C_4{-}C_6{=}C_{14}{-}R'_{16}$	178.0	185.0

(by 1 kcal/mol) was found for *Z* alkene **13** as compared to *E* alkene **14**. This difference in favor of the *Z* form is attributed to the important deviation from planarity, i.e., to the larger interthiophene-ring dihedral angle ($S_1{-}C_5{-}C_9{-}S_{10}$) of the *E* form and the larger distortion of its double bond planarity ($C_4{-}C_6{=}C_{14}{-}R_{15}$ and $C_4{-}C_6{=}C_{14}{-}R'_{16}$), resulting in a slightly larger $C_6{=}C_{14}$ bond length (Figure 1, Table 2).

The main advantages of the presented route compared to the traditionally applied route are the shortened straightforward sequence and the ability to synthesize different materials simply by changing the ketone reagent applied in the formation of the tertiary alcohol. In this way a number of dialkylated CPDTs **12b**−**g**, both symmetrical and asymmetrical derivatives, have been prepared. Reaction with the dialkyl ketone and ring closure both proceeded in moderate to good yields (18−75% for **11a**−**g**, 16−57% for **12a**−**g**). Once again, the yield for the cyclization step could be improved by dilution of the alcohol precursor in *n*-octane (from 17% to 57% for **12d**, from 30% to 53% for **12g**).[16]

The newly developed three-step procedure also readily allows introduction of functional groups on (one of) the alkyl substituents based upon a versatile ester-functionalized CPDT scaffold. Reaction of the lithio derivative of 3-bromo-2,2′-bithiophene (**9**) with ethyl levulinate (ethyl 4-oxopentanoate **15**) afforded lactone **16** by intramolecular transesterification of the intermediate tertiary alcohol with the terminal ethyl ester moiety (Scheme 4). Ring-opening of the lactone in ethanol under acid-catalyzed conditions resulted in alkene isomers **17** and **18** (25:75 ratio), which were converted to ester-functionalized CPDT **12h** with the aid of sulfuric acid (Scheme 4). Starting from this ester derivative (or, alternatively, the lactone precursor), basic functional group conversions (or lactone ring-opening reactions) should enable access to variously substituted CPDT building blocks.

SCHEME 4. Synthetic Strategy toward Ester-Functionalized CPDT 12h



Conclusions

In summary, we have designed an elegant and convenient approach toward 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophenes, shortening the currently applied route while concomitantly extending its synthetic possibilities. Simple variation of the ketone reagent opens new perspectives in the synthesis of (asymmetrically) functionalized CPDT derivatives, and the final ring closing step was optimized. The functionalization scope can be extended further by a versatile ester-functionalized CPDT scaffold. Experimental observations on the plausible reaction pathway have been supported by detailed NMR spectroscopy and theoretical energy calculations.

Experimental Section

NMR chemical shifts (δ) in ppm were determined relative to the residual $CHCl_3$ absorption (7.26 ppm) or the ^{13}C resonance shift of $CDCl_3$ (77.16 ppm).[17] Gas chromatography−mass spectrometry (GC-MS) analyses were carried out applying Chrompack Cpsil5CB or Cpsil8CB capillary columns. Exact mass measurements were performed in the EI mode at a resolution of 10 000. Solution UV−vis absorption measurements were performed with a scan rate of 600 nm/min in a continuous run from 200 to 800 nm. Infrared spectra were collected with a resolution of 4 cm^{-1} (16 scans), using films drop-casted on a NaCl disk from a $CHCl_3$ solution. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Diethyl ether was dried by distillation from Na/benzophenone.

3-Bromo-2,2′-bithiophene (**9**) was synthesized according to a literature procedure.[10] Material identity and purity was confirmed by MS, IR, and ^1H and ^{13}C NMR.

5-Ethylpentadecan-7-one (10d). A Grignard solution of 2-ethylhexylmagnesium bromide in dry diethyl ether (1.0 M, 110 mL, 0.11 mol) was slowly added via a syringe to a stirred mixture of *n*-octylcyanide (4.66 g, 55 mmol) in dry diethyl ether (100 mL) at 0 °C under N_2 atmosphere. After being stirred for 12 h at reflux temperature, the reaction was quenched with an

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(16) Intermolecular reaction (oligomer formation) was observed as a minor side reaction by ESI-MS (less pronounced upon dilution).

(17) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512.

aqueous HCl solution (2.0 M) at 0 °C and subsequently vigorously stirred for an additional 3 h at rt. The organic phase was separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with a saturated bicarbonate solution and brine, dried with $MgSO_4$, and evaporated under reduced pressure to give a yellow oil. The crude oil was purified by vacuum distillation (75 °C, 10^{-2} mbar) resulting in a pure slightly yellow oil (4.51 g, 32%). GC-MS (EI) *m*/*z* 254 [M^+]; HRMS (EI) calcd for $C_{17}H_{34}O$ 254.2610, found *m*/*z* 254.2612; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (t, *J* = 7.5 Hz, 2H), 2.30 (d, *J* = 6.6 Hz, 2H), 1.89−1.81 (m, 1H), 1.60−1.53 (m, 2H), 1.26−1.18 (m, 18H), 0.91−0.81 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.0 (CO), 47.6 (CH_2), 43.5 (CH_2), 35.3 (CH), 33.3 (CH_2), 32.0 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.0 (CH_2), 26.5 (CH_2), 24.0 (CH_2), 23.1 (CH_2), 22.8 (CH_2), 14.2 (CH_3), 11.0 (CH_3), 10.9 (CH_3); IR (NaCl, cm^{-1}) ν_{max} 2959/2926/2859 (s, saturated C−H), 1717 (m, CO).

3-([2,2′-Bithiophen]-3-yl)pentan-3-ol (11a): General Procedure 1 A solution of 3-bromo-2,2′-bithiophene (**9**) (3.0 g, 12 mmol) in dry diethyl ether (100 mL) was added slowly to a solution of *n*-BuLi (1.6 M in hexane, 7.5 mL, 12 mmol) in dry diethyl ether (100 mL) at −78 °C over 2 h under N_2. The mixture was stirred for 15 min at the same temperature. Freshly distilled 3-pentanone (1.29 mL, 12 mmol) was added via a syringe to the mixture at −78 °C, followed by stirring overnight at rt. The reaction was quenched with an aqueous NH_4Cl solution (2.5 M) and water at 0 °C. The organic phase was separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure to give a crude oil. The oily residue was purified by column chromatography (silica, eluent hexane/ethyl acetate 90:10) to afford the title compound as a slightly yellow oil (1.7 g, 56%). GC-MS (EI) *m*/*z* 252 [M^+]; HRMS (EI) calcd for $C_{13}H_{16}OS_2$ 252.0643; found *m*/*z* 252.0652; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 5.0/1.2 Hz, 1H), 7.26 (d, *J* = 5.4 Hz, 1H), 7.13 (dd, *J* = 3.4/1.2 Hz, 1H), 7.03 (dd, *J* = 5.0/3.4 Hz, 1H), 6.98 (d, *J* = 5.4 Hz, 1H), 2.01 (s, 1H), 1.82−1.69 (m, 4H), 0.83 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 135.6, 129.5 (CH), 129.2, 128.4 (CH), 127.3 (CH), 126.9 (CH), 125.0 (CH), 78.8 (C−OH), 35.3 (CH_2), 8.3 (CH_3); IR (NaCl, cm^{-1}) ν_{max} 3584 (w, OH), 3105/3073 (w, unsaturated C−H), 2966/2931/2877/2854 (m, saturated C−H).

2-([2,2′-Bithiophen]-3-yl)undecan-2-ol (11b). 11b was obtained according to general procedure 1 with 3-bromo-2,2′-bithiophene (**9**) (1.00 g, 4.08 mmol), dry diethyl ether (70 mL), *n*-BuLi (1.6 M in hexane, 2.50 mL, 4.0 mmol), and 2-undecanone (0.84 mL, 4.08 mmol); eluent hexane/ethyl acetate 90:10; yield 63% (0.86 g). GC-MS (EI) *m*/*z* 336 [M^+]; HRMS (EI) calcd for $C_{19}H_{28}OS_2$ 336.1582, found *m*/*z* 336.1583; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 5.1/1.1 Hz, 1H), 7.24 (d, *J* = 5.4 Hz, 1H), 7.14 (dd, *J* = 3.5/1.1 Hz, 1H), 7.07 (d, *J* = 5.4 Hz, 1H), 7.03 (dd, *J* = 5.1/3.5 Hz, 1H), 2.12 (s, 1H), 1.82−1.68 (m, 2H), 1.51 (s, 3H), 1.28−1.15 (m, 14H), 0.89 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.8, 135.6, 129.5 (CH), 129.0, 128.1 (CH), 127.2 (CH), 126.9 (CH), 124.8 (CH), 75.2 (C−OH), 44.0 (CH_2), 32.0 (CH_2), 30.4 (CH_2), 30.0 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 24.3 (CH_2), 22.8 (CH_2), 14.2 (CH_3); IR (NaCl, cm^{-1}) ν_{max} 3451 (m, OH), 3105/3087/3074 (w, unsaturated C−H), 2955/2925/2854 (s, saturated C−H).

4-([2,2′-Bithiophen]-3-yl)-2,6-dimethylheptan-4-ol (11c). 11c was obtained according to general procedure 1 with 3-bromo-2,2′-bithiophene (**9**) (3.00 g, 12 mmol), dry diethyl ether (200 mL), *n*-BuLi (1.6 M in hexane, 7.50 mL, 12 mmol), and 2,6-dimethyl-4-heptanone (2.17 mL, 12 mmol); eluent hexane/ethyl acetate 90:10; yield 18% (0.67 g). GC-MS (EI) *m*/*z* 308 [M^+]; HRMS (EI) calcd for $C_{17}H_{24}OS_2$ 308.1269, found *m*/*z* 308.1264; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 5.2/1.3 Hz, 1H), 7.25 (d, *J* = 5.3 Hz, 1H), 7.10 (dd, *J* = 3.6/1.3 Hz, 1H), 7.03 (dd, *J* = 5.2/3.6 Hz, 1H), 7.02 (d, *J* = 5.3 Hz, 1H), 1.92 (s, 1H), 1.80−1.64 (m, 4H), 1.57−1.50 (m, 2H), 0.91 (d, *J* = 6.3 Hz, 6H), 0.71 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7, 135.6, 129.5 (CH), 128.8 (CH), 128.4, 127.3 (CH), 126.8 (CH), 124.9 (CH), 79.3 (C−OH), 52.7 (CH_2), 24.6 (CH_3), 24.4 (CH_3); IR (NaCl, cm^{-1}) ν_{max} 3587 (m, OH), 3106/3074 (w, unsaturated C−H), 2955/2928/2868 (s, saturated C−H).

7-([2,2′-Bithiophen]-3-yl)-5-ethylpentadecan-7-ol (11d). 11d was obtained according to general procedure 1 with 3-bromo-2,2′-bithiophene (**9**) (1.00 g, 4.08 mmol), dry diethyl ether (70 mL), *n*-BuLi (1.6 M in hexane, 2.50 mL, 4.08 mmol), and 5-ethylpentadecan-7-one (**10d**) (1.00 g, 4.08 mmol); eluent gradient hexane to hexane/ethyl acetate 90:10; yield 34% (0.583 g). GC-MS (EI) *m*/*z* 420 [M^+]; HRMS (EI) calcd for $C_{25}H_{40}OS_2$ 420.2521, found *m*/*z* 420.2492; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 5.2/1.2 Hz, 1H), 7.24 (d, *J* = 5.3 Hz, 1H), 7.10 (dd, *J* = 3.5/1.2 Hz, 1H), 7.02 (dd, *J* = 5.2/3.5 Hz, 1H), 6.97 (d, *J* = 5.3 Hz, 1H), 1.93 (s, OH), 1.77−1.58 (m, 4H), 1.44−1.05 (m, 21H), 0.89−0.69 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7, 135.7, 129.5 (CH), 128.7, 128.5 (CH), 127.3 (CH), 126.8 (CH), 124.9 (CH), 78.8 (C−OH), 47.7 (CH_2), 43.4 (CH_2), 34.7 (CH), 33.9 (CH_2), 32.0 (CH_2), 29.7 (CH_2), 29.4 (CH_2), 28.7 (CH_2), 27.1 (CH_2), 23.7 (CH_2), 23.22 (CH_2), 23.16 (CH_2), 22.8 (CH_2), 14.2 (CH_3), 10.7 (CH_3), 10.6 (CH_3); IR (NaCl, cm^{-1}) ν_{max} 3589/3490 (m, OH), 3105/3073 (w, unsaturated C−H), 2956/2926/2856 (s, saturated C−H).

6-([2,2′-Bithiophen]-3-yl)undecan-6-ol (11e). 11e was obtained according to general procedure 1 with 3-bromo-2,2′-bithiophene (**9**) (0.500 g, 2.04 mmol), dry diethyl ether (40 mL), *n*-BuLi (1.6 M in hexane, 1.25 mL, 2.04 mmol), and 6-undecanone (0.42 mL, 2.04 mmol); eluent hexane/ethyl acetate 90:10; yield 62% (0.425 g). GC-MS (EI) *m*/*z* 336 [M^+]; HRMS (EI) calcd for $C_{19}H_{28}OS_2$ 336.1582, found *m*/*z* 336.1580; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, *J* = 5.2/1.3 Hz, 1H), 7.25 (d, *J* = 5.4 Hz, 1H), 7.10 (dd, *J* = 3.5/1.3 Hz, 1H), 7.02 (dd, *J* = 5.2/3.5 Hz, 1H), 6.99 (d, *J* = 5.4 Hz, 1H), 1.80−1.59 (m, 4H), 1.26−1.16 (m, 12H), 0.85 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 135.6, 129.4 (CH), 128.7, 128.4 (CH), 127.3 (CH), 126.8 (CH), 124.9 (CH), 78.2 (C−OH), 43.1 (CH_2), 32.3 (CH_2), 23.5 (CH_2), 22.7 (CH_2), 14.2 (CH_3); IR (NaCl, cm^{-1}) ν_{max} 3584/3474 (m, OH), 3104/3073 (w, unsaturated C−H), 2954/2929/2859 (s, saturated C−H).

1-([2,2′-Bithiophen]-3-yl)cyclohexanol (11f). 11f was obtained according to general procedure 1 with 3-bromo-2,2′-bithiophene (**9**) (0.50 g, 2.04 mmol), dry diethyl ether (40 mL), *n*-BuLi (1.6 M in hexane, 1.25 mL, 2.04 mmol), and cyclohexanone (0.21 mL, 2.04 mmol); eluent hexane/ethyl acetate 90:10; yield 49% (0.264 g). GC-MS (EI) *m*/*z* 264 [M^+]; HRMS (EI) calcd for $C_{14}H_{16}OS_2$ 264.0643, found *m*/*z* 264.0648; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 5.2/1.2 Hz, 1H), 7.24 (d, *J* = 5.4 Hz, 1H), 7.18 (dd, *J* = 3.6/1.2 Hz, 1H), 7.11 (d, *J* = 5.4 Hz, 1H), 7.04 (dd, *J* = 5.2/3.6 Hz, 1H), 1.87−1.82 (m, 4H), 1.70−1.50 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 136.0, 130.0, 129.5 (CH), 127.6 (CH), 127.2 (CH), 127.0 (CH), 124.9 (CH), 73.5 (C−OH), 39.0 (CH_2), 25.5 (CH_2), 22.1 (CH_2); IR (NaCl, cm^{-1}) ν_{max} 3553/3441 (m, OH), 3104 (w, unsaturated C−H), 2932/2851 (s, saturated C−H).

9-([2,2′-Bithiophen]-3-yl)heptadecan-9-ol (11g). 11g was obtained according to general procedure 1 with 3-bromo-2,2′-bithiophene (**9**) (5.00 g, 20 mmol), dry diethyl ether (340 mL), *n*-BuLi (1.6 M in hexane, 12.8 mL, 20 mmol), and heptadecan-9-one (5.08 g, 20 mmol); eluent gradient hexane to hexane/ethyl acetate (90:10); yield 75% (6.3 g). GC-MS (EI) *m*/*z* 420 [M^+]; HRMS (EI) calcd for $C_{25}H_{40}OS_2$ 420.2521, found *m*/*z* 420.2521; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 5.2/1.1 Hz, 1H), 7.24 (d, *J* = 5.3 Hz, 1H), 7.10 (dd, *J* = 3.5/1.1 Hz, 1H), 7.02 (dd, *J* = 5.3/3.5 Hz, 1H), 7.00 (d, *J* = 5.3 Hz, 1H), 1.98 (s, 1H), 1.78−1.63 (m, 4H), 1.31−1.14 (m, 24H), 0.87 (t, *J* = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6, 135.6, 129.4 (CH), 128.7, 128.4 (CH), 127.3 (CH), 126.8 (CH), 124.9 (CH), 78.2 (C−OH), 43.1 (CH_2), 32.0 (CH_2), 30.1 (CH_2), 29.7 (CH_2), 29.4

(CH_2), 23.8 (CH_2), 22.8 (CH_2), 14.3 (CH_3); IR (NaCl, cm^{-1}) ν_{max} 3588/3483 (m, OH), 3105/3073 (w, unsaturated C−H), 2954/2925/2854 (s, saturated C−H).

4,4-Diethyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (12a): General Procedure 2 H_2SO_4 (0.5 mL) was added dropwise to 3-([2,2′-bithiophen]-3-yl)pentan-3-ol (**11a**) (0.193 g, 0.77 mmol) in *n*-octane (10 mL) under stirring at rt. After additional stirring for 12 h, CH_2Cl_2 and water were added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were successively washed with saturated $NaHCO_3$ and brine. After drying with $MgSO_4$, the solvent was removed in vacuo. The crude oil was purified by column chromatography (silica, eluent hexane) to afford a pure dark yellow oil (0.10 g, 55%). GC-MS (EI) *m*/*z* 234 [M^+]; HRMS (EI) calcd for $C_{13}H_{14}S_2$ 234.0537, found *m*/*z* 234.0546; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, J = 5.0 Hz, 2H), 6.94 (d, J = 5.0 Hz, 2H), 1.91 (q, J = 7.7 Hz, 4H), 0.60 (t, J = 7.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 136.9, 124.6 (CH), 121.7 (CH), 54.4, 30.3 (CH_2), 9.2 (CH_3); IR (NaCl, cm^{-1}) ν_{max} 3423 (m, OH), 3102/3070 (w, unsaturated C−H), 2964/2929/2874/2853 (s, saturated C−H); UV−vis ($CHCl_3$, nm) λ_{max} (log ε) 249 (3.880), 320 (4.115).

4-Methyl-4-nonyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (12b). 12b was obtained according to general procedure 2 with H_2SO_4 and (1.33 mL), and 2-([2,2′-bithiophen]-3-yl)undecan-2-ol (**11b**) (0.70 g, 2.08 mmol); eluent hexane; yield 16% (0.106 g). GC-MS (EI) *m*/*z* 318 [M^+]; HRMS (EI) calcd for $C_{19}H_{26}S_2$ 318.1476, found *m*/*z* 318.1472; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, J = 4.9 Hz, 2H), 6.96 (d, J = 4.9 Hz, 2H), 1.84−1.78 (m, 2H), 1.43 (s, 3H), 1.26−1.15 (m, 14H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 136.0, 124.8 (CH), 121.4 (CH), 49.0, 39.2 (CH_2), 32.0 (CH_2), 30.1 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 25.1 (CH_2), 23.9 (CH_2), 22.8 (CH_3), 14.3 (CH_3); IR (NaCl, cm^{-1}) ν_{max} 3103/3069 (w, unsaturated C−H), 2955/2925/2854 (s, saturated C−H); UV−vis ($CHCl_3$, nm) λ_{max} (log ε) 249 (3.819), 320 (4.007).

4,4-Diisobutyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (12c). 12c was obtained according to general procedure 2 with H_2SO_4 (1.45 mL) and 4-([2,2′-bithiophen]-3-yl)-2,6-dimethylheptan-4-ol (**11c**) (0.688 g, 2.23 mmol); eluent hexane; yield 35% (0.226 g). GC-MS (EI) *m*/*z* 290 [M^+]; HRMS (EI) calcd for $C_{17}H_{22}S_2$ 290.1163, found *m*/*z* 290.1168; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (d, J = 4.9 Hz, 2H), 6.93 (d, J = 4.9 Hz, 2H), 1.87 (d, J = 5.7 Hz, 4H), 1.05−0.97 (m, 2H), 0.51 (d, J = 6.8 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 136.8, 124.5 (CH), 122.1 (CH), 53.2, 48.8 (CH), 24.9 (CH_2), 24.6 (CH_3); IR (NaCl, cm^{-1}) ν_{max} 3104/3067 (w, unsaturated C−H), 2954/2925/2867 (s, saturated C−H); UV−vis ($CHCl_3$, nm) λ_{max} (log ε) 249 (3.932), 320 (4.094).

4-(2-Ethylhexyl)-4-octyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (12d). 12d was obtained according to general procedure 2 with H_2SO_4 (0.38 mL) and 7-([2,2′-bithiophen]-3-yl)-5-ethylpentadecan-7-ol (**11d**) (0.25 g, 0.60 mmol); eluent hexane; yield 17% (0.040 g); or with H_2SO_4 (0.38 mL), 7-([2,2′-bithiophen]-3-yl)-5-ethylpentadecan-7-ol (**11d**) (0.25 g, 0.60 mmol), and *n*-octane (8 mL); eluent hexane; yield 57% (0.137 g). GC-MS (EI) *m*/*z* 402 [M^+]; HRMS (EI) calcd for $C_{25}H_{38}S_2$ 402.2415, found *m*/*z* 402.2412; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, J = 5.1 Hz, 2H), 7.02 (dd, J = 4.9/2.2 Hz, 2H), 2.02 (t, J = 7.5 Hz, 2H), 1.96−1.90 (m, 2H), 1.11−1.02 (m, 21H), 0.96 (t, J = 6.6 Hz, 3H), 0.87 (t, J = 6.9 Hz, 3H), 0.72 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.85, 157.79, 136.8, 124.3 (CH), 121.9 (CH), 53.3, 41.9 (CH), 39.7 (CH_2), 35.3 (CH_2), 34.2 (CH_2), 32.0 (CH_2), 30.2 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 28.7 (CH_2), 27.4 (CH_2), 24.5 (CH_2), 22.9 (CH_2), 22.8 (CH_2), 14.3 (CH_3), 10.8 (CH_3); IR (NaCl, cm^{-1}) ν_{max} 3104/3068 (w, unsaturated C−H), 2957/2926/2855 (s, saturated C−H); UV−vis ($CHCl_3$, nm) λ_{max} (log ε) 249 (3.868), 320 (4.064).

4,4-Dipentyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (12e). 12e was obtained according to general procedure 2 with H_2SO_4 (0.63 mL) and 6-([2,2′-bithiophen]-3-yl)undecan-6-ol (**11e**) (0.33 g, 0.98 mmol); eluent hexane; yield 32% (0.10 g). GC-MS (EI) *m*/*z* 318 [M^+]; HRMS (EI) calcd for $C_{19}H_{26}S_2$ 318.1476, found *m*/*z* 318.1479; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, J = 4.8 Hz, 2H), 6.96 (d, J = 4.8 Hz, 2H), 1.88−1.82 (m, 4H), 1.24−1.09 (m, 8H), 1.03−0.93 (m, 4H), 0.80 (t, J = 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 136.6, 124.5 (CH), 121.7 (CH), 53.3, 37.8 (CH_2), 32.4 (CH_2), 24.3 (CH_2), 22.5 (CH_2), 14.2 (CH_3); IR (NaCl, cm^{-1}) ν_{max} 3103/3070 (w, unsaturated C−H), 2955/2929/2858 (s, saturated C−H); UV−vis ($CHCl_3$, nm) λ_{max} (log ε) 249 (3.918), 320 (4.114).

Spiro[4,5]([2,1-*b*:3,4-*b*′]dithieno)decane (12f). 12f was obtained according to general procedure 2 with H_2SO_4 (1.41 mL), 1-([2,2′-bithiophen]-3-yl)cyclohexanol (**11f**) (0.582 g, 2.20 mmol), and *n*-octane (30 mL); eluent hexane; yield 40% (0.217 g). This compound has been prepared before by Zotti et al.[2g] Material identity and purity was confirmed by (HR)MS, IR, UV−vis, and ^{1}H and ^{13}C NMR. HRMS (EI) calcd for $C_{14}H_{14}S_2$ 246.0537, found *m*/*z* 246.0526; ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 135.9, 124.2 (CH), 122.8 (CH), 50.0, 34.2 (CH_2), 25.7 (CH_2), 23.8 (CH_2); IR (NaCl, cm^{-1}) ν_{max} 3102/3079 (w, unsaturated C−H), 2927/2853 (s, saturated C−H); UV−vis ($CHCl_3$, nm) λ_{max} (log ε) 249 (3.588), 320 (3.802).

4,4-Dioctyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (12g). 12g was obtained according to general procedure 2 with H_2SO_4 (9.62 mL) and 9-([2,2′-bithiophen]-3-yl)heptadecan-9-ol (**11g**) (6.32 g, 15 mmol); eluent hexane; yield 30% (1.81 g); or with H_2SO_4 (9.62 mL), 9-([2,2′-bithiophen]-3-yl)heptadecan-9-ol (**11g**) (6.32 g, 15 mmol), and *n*-octane (200 mL); eluent hexane; yield 53% (3.20 g). This compound has been prepared before by several groups.[2a,7i,8j] Material identity and purity was confirmed by MS and ^{1}H and ^{13}C NMR.

(*Z*)-3-(Pent-2-en-3-yl)-2,2′-bithiophene (13). GC-MS (EI) *m*/*z* 234 [M^+]; HRMS (EI) calcd for $C_{13}H_{14}S_2$ 234.0537, found *m*/*z* 234.0524; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (dd, J = 5.1/1.3 Hz, 1H), 7.18 (dd, J = 3.7/1.3 Hz, 1H), 7.17 (d, J = 5.1 Hz, 1H), 6.99 (dd, J = 5.1/3.7 Hz, 1H), 6.79 (d, J = 5.1 Hz, 1H), 5.64 (q, J = 7.3 Hz, 1H), 2.28 (q, J = 6.9 Hz, 2H), 1.47 (d, J = 7.3 Hz, 3H), 1.01 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2, 137.9, 136.7, 131.8, 130.3 (CH), 127.1 (CH), 125.1 (CH), 124.9 (CH), 123.9 (CH), 123.1 (CH), 31.2 (CH_2), 14.9 (CH_3), 13.0 (CH_3); IR (NaCl, cm^{-1}) ν_{max} 3105/3069 (w, unsaturated C−H), 2963/2926/2872/2854 (s, saturated C−H).

(*E*)-3-(Pent-2-en-3-yl)-2,2′-bithiophene (14). GC-MS (EI) *m*/*z* 234 [M^+]; HRMS (EI) calcd for $C_{13}H_{14}S_2$ 234.0537, found *m*/*z* 234.0524; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (dd, J = 5.1/1.3 Hz, 1H), 7.17 (dd, J = 3.9/1.3 Hz, 1H), 7.13 (d, J = 5.2 Hz, 1H), 6.99 (dd, J = 5.1/3.9 Hz, 1H), 6.86 (d, J = 5.2 Hz, 1H), 5.57 (q, J = 7.0 Hz, 1H), 2.35 (q, J = 7.6 Hz, 2H), 1.76 (d, J = 7.0 Hz, 3H), 0.93 (t, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 137.4, 136.8, 131.2, 130.3 (CH), 126.9 (CH), 126.0 (CH), 125.8 (CH), 125.1 (CH), 123.0 (CH), 24.3 (CH_2), 14.3 (CH_3), 13.8 (CH_3); IR (NaCl, cm^{-1}) ν_{max} 3105/3069 (w, unsaturated C−H), 2963/2926/2872/2854 (s, saturated C−H).

5-([2,2′-Bithiophen]-3-yl)-5-methyldihydrofuran-2-(3*H*)-one (16). 16 was obtained according to general procedure 1 with 3-bromo-2,2′-bithiophene (**9**) (1.00 g, 4.08 mmol), dry diethyl ether (70 mL), *n*-BuLi (1.6 M in hexane, 2.50 mL, 4.08 mmol), and ethyl levulinate (**15**) (0.58 mL, 4.08 mmol); eluent CH_2Cl_2; yield 36% (0.39 g). GC-MS (EI) *m*/*z* 264 [M^+]; HRMS (EI) calcd for $C_{13}H_{12}O_2S_2$ 264.0279, found *m*/*z* 264.0255; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (dd, J = 5.2/1.2 Hz, 1H), 7.28 (d, J = 5.4 Hz, 1H), 7.16 (d, J = 5.4 Hz, 1H), 7.11 (dd, J = 3.6/1.2 Hz, 1H), 7.06 (dd, J = 5.2/3.6 Hz, 1H), 2.60−2.15 (m, 4H), 1.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2 (CO), 142.7, 134.1, 130.0 (CH), 129.5, 127.5 (CH), 127.2 (CH), 125.6 (CH), 86.4, 35.1 (CH_2), 29.1 (CH_2), 29.0 (CH_3); IR (NaCl, cm^{-1}) ν_{max} 3106 (m, unsaturated C−H), 2977/2931 (m, saturated C−H), 1775 (s, CO−O lactone).

Ethyl 3-(4-Methyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophen-4-yl)-propanoate (12h). H_2SO_4 (0.73 mL) was added dropwise to

5-([2,2′-bithiophen]-3-yl)-5-methyldihydrofuran-2-(3*H*)-one (**16**) (0.388 g, 1.47 mmol) in ethanol (20 mL) under stirring at rt and the reaction was continuously stirred for 12 h at rt. Workup according to general procedure 2: The crude oily residue was purified by flash column chromatography (silica, eluent CH_2Cl_2) to afford a dark yellow oil (0.302 g, 70%). To the obtained crude alkene mixture (**17**:**18**, 25:75 ratio) (0.302 g, 1.0 mmol) were added H_2SO_4 (0.73 mL) and *n*-octane (15 mL) and the reaction was stirred for 12 h at rt. Workup according to general procedure 2: eluent hexane/ethyl acetate 90:10; yield 20% (60 mg). GC-MS (EI) *m*/*z* 292 [M^+]; HRMS (EI) calcd for $C_{15}H_{16}O_2S_2$ 292.0592, found *m*/*z* 292.0572; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, J = 5.0 Hz, 2H), 6.95 (d, J = 5.0 Hz, 2H), 3.98 (q, J = 7.2 Hz, 2H), 2.28 (t, J = 7.9 Hz, 2H), 1.80 (t, J = 7.9 Hz, 2H), 1.47 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6 (CO), 157.8, 136.6, 125.3 (CH), 121.2 (CH), 60.3, 48.2 (CH_2), 33.7 (CH_2), 29.9 (CH_2), 24.2 (CH_3), 14.2 (CH_3); IR (NaCl, cm^{-1}) ν_{max} 3102/3070 (w, unsaturated C−H), 2974/2925/2869 (w, saturated C−H), 1731 (m, CO-O); UV−vis ($CHCl_3$, nm) λ_{max} (log ε) 320 (3.104).

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Supporting Information Available: Details on the computational procedures, ^{1}H and ^{13}C NMR spectra for all novel CPDTs and precursors, and complete NMR assignment of the proton and carbon resonances of alkene isomers **13** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.