Synthesis of Dithienocyclohexanones (DTCHs) as a Family of Building Blocks for π-Conjugated Compounds in Organic Electronics

Gabriele Bianchi,*,[†] Riccardo Po,[†] Mauro Sassi,[‡] Luca Beverina,[‡] Stefano Chiaberge,[†] Silvia Spera,[†] and Alessandra Cominetti[†]

[†]Renewable Energies & Environmental R&D Center - Istituto Guido Donegani, Eni S.p.A., Via Giacomo Fauser 4, 28100 Novara, Italy

[‡]Department of Materials Science, University of Milano-Bicocca, Via Roberto Cozzi 55, 20125 Milano, Italy

Ⓢ Supporting Information

ABSTRACT: The development and widespread application of organic electronic devices require the availability of simple and cost-effective suitable materials. In this study, the preparation of a new class of conjugated compounds on the basis of a dithienocyclohexanone (DTCH) core is reported. Several synthetic strategies for the preparation of dialkyl DTCH derivatives are explored, with special emphasis on the establishment of a sustainable synthetic access. Two successful synthetic pathways, both consisting of five steps, are identified: the first one featuring readily available 3-thiophenecarboxaldeyde and the second one 3-ethynylthiophene as the starting materials. Both procedures are characterized by reasonably high overall yields (over 30%) and remarkably low E factors (<400). Preliminary evidences of the use of such building blocks in the micellar Suzuki−Miyaura cross-coupling reactions leading to promising molecular semiconductors are also given. Moreover, on a small molecule containing DTCH moiety, solar cell performance was investigated.
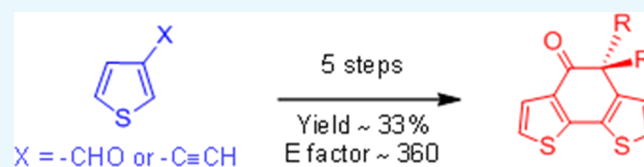
INTRODUCTION

Conjugated polymers[1] play a fundamental role both as active layer and/or interlayer in several plastic electronic and optoelectronic devices, including new-generation photovoltaic cells (OPVs), field-effect transistors, light-emitting diodes, photodetectors, sensors, and so forth. Mostly, polymeric materials are discussed focusing on performances alone, even though the synthetic accessibility, cost of raw materials, and ease of purification and processing are at least as relevant on an industrial level as the absolute performance.[2] Some of us have recently proposed a criterion enabling to rank the synthetic complexity of both conjugated polymers[3] and monodisperse low-molecular-weight molecules[4] generally considered as suitable active materials for the fabrication of organic solar cells. On doing so, we proposed to take into account five parameters: (i) the number of synthetic steps; (ii) the reaction yields; (iii) the number of unit operations required for the isolation/purification of the intermediate compounds, in particular (iv) the number of column chromatographic purifications; and (v) the number of hazardous chemicals used for their preparation. Alongside with synthetic complexity, it is worthwhile to take into account—particularly when scaling up—the reaction E factor.[5] Such number is defined as kilograms of organic wastes produced for every kilogram of product. The pharmaceutical industry is very familiar with this parameter and would accept only processes characterized by E factor in the order of a few hundreds. On the contrary, the E factor is very seldom considered in the OPV field, and the very few documented examples show E factor in tens of thousands

of orders of magnitude.[6] Minimizing both synthetic complexity and E factor ensures the establishment of a protocol that is simple, hazard free, and sustainable.

The literature dedicated to polymeric materials for OPV includes hundreds of structurally very diverse polymers, discussed in several review articles.[7−15] Such vast database of polymers enabled the formulation of structure−property relationships,[16−26] eventually leading to the development of the now generally accepted lead guideline of the donor−acceptor (D−A) concept.[17,27−29] D−A conjugated copolymers feature alternating electron-rich ("donor") and electron-poor ("acceptor") monomer units and are known to exhibit a low energy gap and tunable highest occupied molecular orbital−lowest unoccupied molecular orbital energy levels, which is beneficial for light harvesting and photoinduced electron transfer. The more common donor and acceptor monomer units have been thoroughly reviewed.[9,10,12,29]

According to efficiency alone, the best acceptor building blocks are thieno[3,4-c]pyrrole-4,6-dione[30] and pyrrolo[3,4-c]pyrrole-1,3-dione.[31] The best donors mostly pertain to the benzo[1,2-b:4,5-b′]dithiophenes[32] class. Unfortunately, all of them feature relevant synthetic complexity. The relative E factor is not available in the dedicated literature, but because of the fact that column purifications involving halogenated solvents are frequently mentioned, values would probably

exceed industrial requirements. In short, alongside the efforts to constantly raise the record efficiency bar with whatever can be made, regardless of the cost, it is still worthwhile to design simpler structures, potentially accessible (and scalable) through sustainable approaches. In this context, our groups have recently designed a novel class of monomers on the basis of 5H-dithieno[3,2-b:2',3'-d]cyclohexan-4-one (DTCH) (Figure 1).[33]
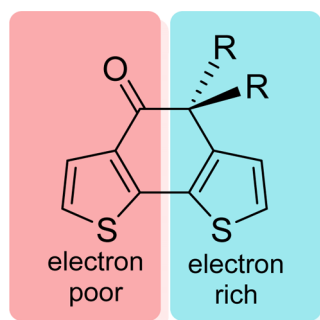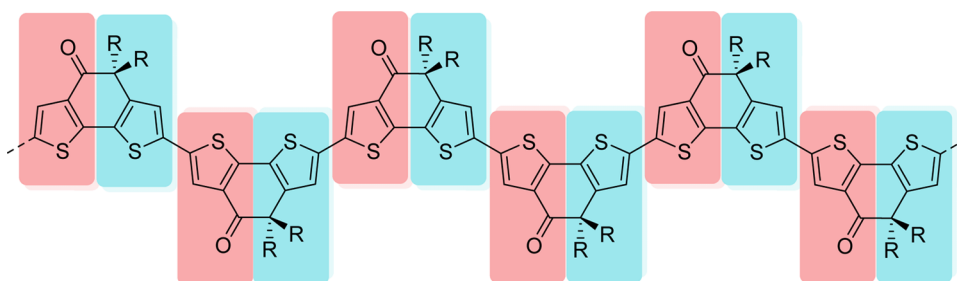

Figure 1. Structure of 5,5-dialkyl-5H-1,8-dithia-as-indacen-4-one DTCH.

The structure differs from that of the more common, all-conjugated benzo[2,1-b;3,4-b']dithiophene already described in the literature of OPV polymers[34−38] and substantially consists of a 2,2'-bithiophene moiety bearing both an electron-accepting group and a site for the straightforward functionalization with orthogonal functionalization chains, in a configuration non-dissimilar to that of other performing fluorene-related building blocks.[39−41] The monomer itself has a donor−acceptor character, due to the presence of both π-excessive bithiophene and the electron-withdrawing ketone residue. This is, to our knowledge, one of the few cases reported in the literature of conjugated monomers with ambipolar character.[42]

In principle, the D−A copolymer class shown in Figure 2 could be prepared by direct homopolymerization of suitable activated DTCH derivatives, for instance, the mono- and/or dibromination products. Naturally, such building blocks could also be combined with other different donors and acceptors, providing access to new molecular and polymeric derivatives.

In this study, we focus on the development of a sustainable access to 5H-dithieno[3,2-b:2',3'-d]cyclohexan-4-one derivatives. We show that the said monomer can be widely functionalized through the elaboration of the corresponding dilithiated species. Finally, we introduce one example of original molecular material prepared by the Suzuki−Miyaura (SM) micellar coupling in water of a commercially available thiophene boronic derivative and a dibromo DTCH unit.
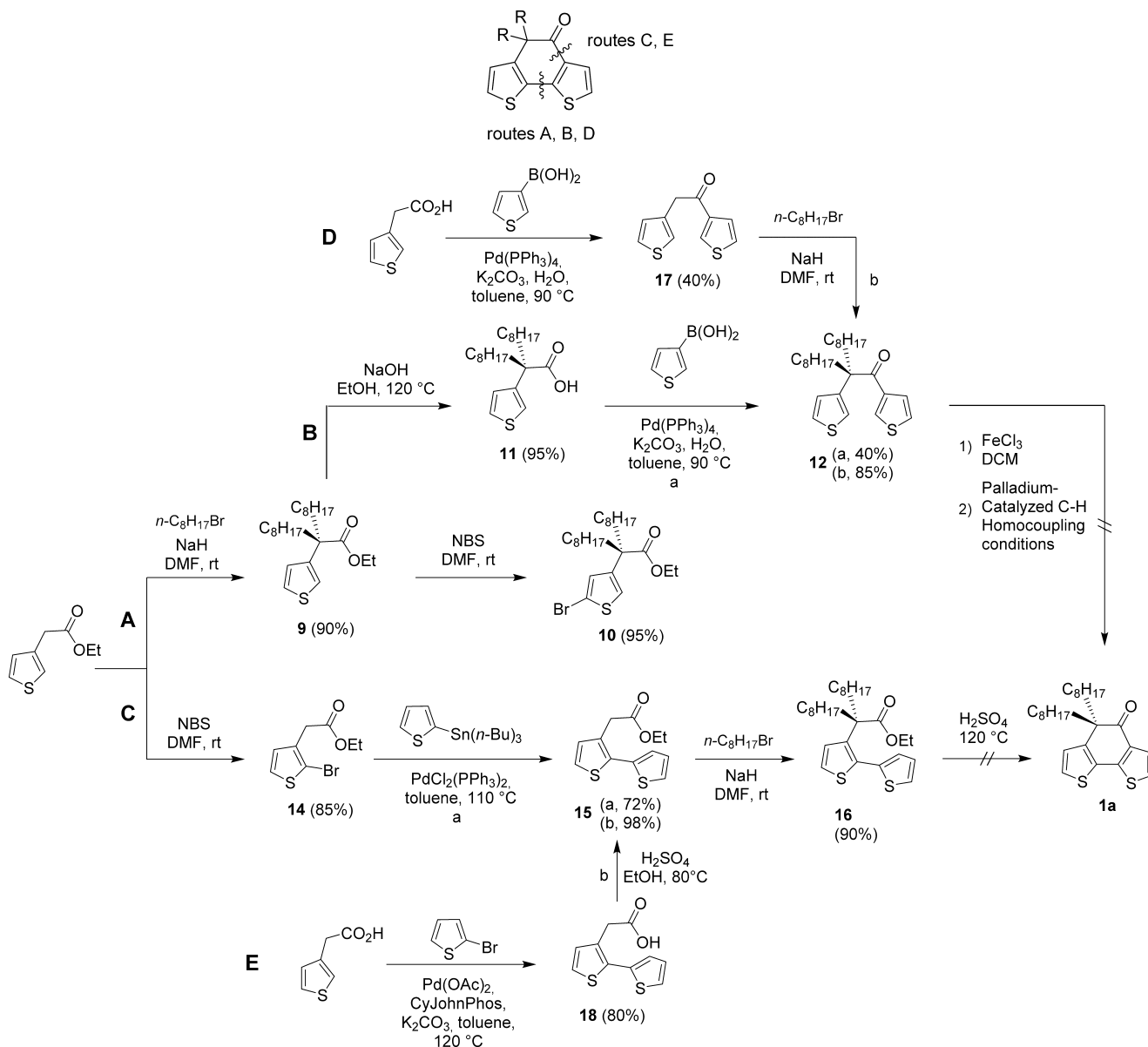
RESULTS AND DISCUSSION

Our first approach on the preparation of DTCH involved the formation of the six-membered ring as the last step. The two possible disconnections coherent with such approaches regard the thiophene−thiophene bond (in principle accessible through oxidative coupling) and the thiophene−ketone bond (accessible through various acylation approaches). The key intermediates for two such scenarios are derivatives **12** and **16**, respectively, as shown in Scheme 1.

All protocols feature the readily available thiophen-3-yl-acetic acid or the corresponding ethyl ester as starting materials. In the pathway A, the alkylation reaction of thiophen-3-yl-acetic acid ethyl ester with an excess of n-octyl bromide in the presence of sodium hydride in N,N-dimethylformamide (DMF) at room temperature for 6 h led to the isolation of ethyl dialkylthienylacetate **9** as the sole reaction product in 90% yield. Unfortunately, the 2-bromo derivative cannot be selectively prepared via direct halogenation reactions (N-bromosuccinimide (NBS)/DMF) and (NBS/CHCl₃). We generally obtained mixtures of mono- and dibromination regioisomers, with the isomer **10** dominating the reaction mixture. Compound **9** (route B) can be readily hydrolyzed with alcoholic potassium hydroxide in a sealed glass tube to give **11** in high yield.[43] Such derivative can be used as the counterpart of thiophene-3-boronic acid in the one-flask acylation/Suzuki[44] reaction leading to the target **12** in moderate yield. The same acylation/Suzuki reaction (route D) enables the preparation of **17** (again with moderate yield), eventually converted in **12** by alkylation with octyl bromide in DMF. In terms of absolute yield, routes D and B are equivalent. Somewhat surprisingly, the oxidative ring closure[45,46] of **12** to give **1a** failed. In particular, we tested both the ring closure in dichloromethane (DCM) with excess FeCl₃ and the new palladium-catalyzed C−H homocoupling recently appeared in the literature.[47−54] Turning to the other possible disconnection, the one requiring an intramolecular Friedel−Crafts acylation,[55,56] we started all over from thiophen-3-yl-acetic acid ethyl ester, in this case successfully brominated in the 2 position to give **14** in good yield. The latter can be converted in the bithiophene derivative **15** by the Stille reaction with 2-tributylstannyl thiophene. However, such Stille coupling should be avoided whenever possible due to the use of toxic organotin compounds. Indeed, **15** can be conveniently prepared (route E) by direct C−H arylation of thiophen-3-yl-acetic acid with 2-bromothiophene, regioregularily in the 2 position and in high yield. Interestingly, the reaction works smoothly even without pivalic acid.[57] Likely, thiophen-3-yl-acetic acid is acting both as the substrate and as the ligand in the same reaction. Alkylation of **15** with bromooctane in the presence of NaH proceeds smoothly to

Figure 2. Structure of poly(5,5-dialkyl-5H-1,8-dithia-as-indacen-4-one) showing the alternation of donor and acceptor units.

**Scheme 1. Unsuccessful Synthetic Routes to DTCH 1a**

give **16** in high yield. Unfortunately, all attempts to cyclize **16** via Friedel–Crafts acylation failed.[55,56]

As the formation of the six-membered ring proved to be the most critical step, we redesigned the synthetic approach to converge on the diketone **3** (Scheme 2), well documented in the literature and thus for sure accessible.

The literature procedure leading to derivative **3** requires the reaction of 3-lithium-thiophene (generated in situ from the corresponding 3-bromo derivative) with oxalyl chloride to give **4**, eventually cyclized by the action of FeCl₃.[58] Aiming at the removal of any harsh reagent, the like of lithium alkanes, we devised two alternative approaches leading to **4** under milder conditions. The first approach starts from cheap and easily available 3-bromothiophene **6**, easily converted via Sonogashira cross-coupling with 3-ethynylthiophene into the 1,2-di-(thiophen-3-yl)ethyne **5** in high yield. The Pd/Cu-catalyzed oxidation reaction of **5** gives the 1,2-di(thiophen-3-yl)ethane-1,2-dione **4** in 90% yield.[59] Derivative **4** can be even more conveniently prepared in two steps, starting from commercially

available aldehyde **8**. The N-heterocyclic carbene-catalyzed benzoin condensation of **8** affords the alcohol **7** in excellent yield and under very mild conditions.[60] The latter can be converted to **4** by MnO_2-promoted heterogeneous-phase oxidation in cyclohexane. Both steps are exceedingly simple and can be readily scaled up to hundreds of grams with minimum amount of organic solvents employed. Up to this point, the overall E factor of the process is 8.6, a remarkably small number compared to the typical synthesis of a functionalized conjugated molecule. Cyclized product benzo-[1,2-*b*:6,5-*b*′]dithiophene-4,5-dione **3** was obtained under oxidative ring-closing conditions via a modification of the method previously reported.[58] In our hands, feeding the oxidant to the reaction mixture as a nitromethane solution, as opposite to adding the open diketone to the suspension of oxidant in CH_2Cl_2, proved to be advantageous[61] when working with over 100 g of starting diketone. Notably, we obtained easier control of reaction temperature and limitation of insoluble byproducts formation (likely due to overoxidation).

Scheme 2. Synthetic Routes to DTCH Derivatives 1
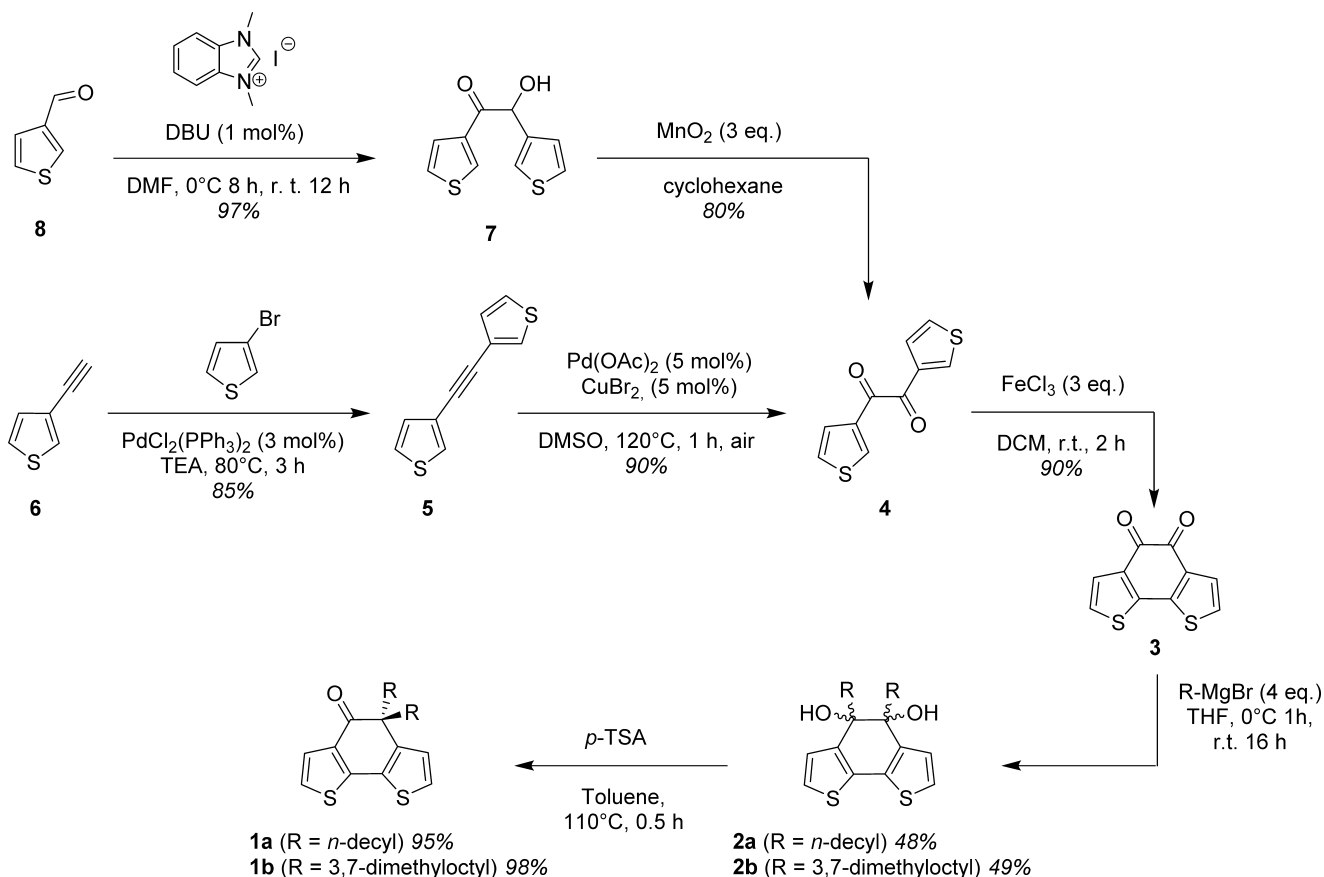
The overall E factor for the preparation of **3** is around 33, a still relatively small number. The fourth step involved a Grignard reaction with a large excess of alkylmagnesium bromide on benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione **3**. The pinacol–pinacolone rearrangement of compound **2** gave the expected compounds **1a** and **1b**. The E factor for the overall process, calculated according to the organic wastes produced in the synthesis of a single 90 g batch, is 363, which would eventually increase to 472 if the bromination step leading to monomers **M1** and **M2** (Scheme 3b) is taken into account as well. This is a remarkably low value when compared to the little available estimates documented in the literature for conjugated compounds produced through a comparable number of steps. Moreover, no harsh reagents are used in the final optimized protocol, thus ensuring a low synthetic complexity alongside the favorable E factor.

Mostly, donor–acceptor polymers are produced via Stille or Suzuki–Miyaura coupling involving alkyltin or boronic derivatives, respectively. From the standpoint of environmental impact, the latter scheme is preferable. Unfortunately, thiophene derivatives do not react efficiently and cleanly under SM protocols and Stille couplings are preferred. Aiming at demonstrating that the DTCH unit could be introduced in polymers requiring Stille coupling, we first challenged **1b** in direct lithiation with lithium tetramethylpiperidine (LTMP), followed by quenching with tributylstannyl chloride. Scheme 3a shows that the reaction is not selective, affording a mixture of three compounds, **T1**, **T1a**, and **T1b**. This can be explained, as outlined in Scheme 3a, by the coordination capabilities of the carbonyl group of DTCH over LTMP. We thus reverted to a

lithium–halogen exchange reaction scheme. Reaction of **M2** *n*-butyllithium followed by quenching with tributylstannyl chloride affords the target stannylated derivative **T1** in 88% yield (Scheme 3b).
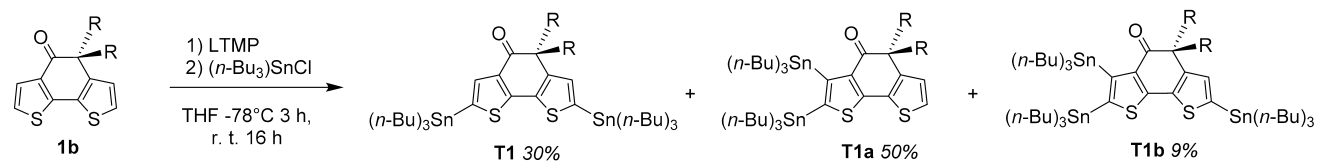
Finally, as a the first exploratory trial of the suitability of DTCH as a sustainable building block for the preparation of organic semiconductors, we prepared derivative **20**. To do so in compliance with our original aim to look for sustainable products, we took advantage of the micellar Suzuki–Miyaura protocol we have recently described, enabling the coupling of aryl bromides and boronic acids and esters in water, at room temperature and under aerobic conditions.[62] Thus, a suspension of **M2**, commercially available 5'-hexyl-2,2'-bithiophene-5-boronic acid pinacol ester **19**, triethylamine, and Pd(dtbf)Cl$_2$ in a 2 wt % solution of Kolliphor EL in deionized water was stirred at room temperature for 3 h under standard laboratory atmosphere, affording **20** in good yield (90%) after a simple silica filtration (Scheme 4).

The spectroscopic features of **20** confirm the mildly accepting nature of the DTCH bridge. The compound displays in fact the typical broad and intense absorption associated with a charge-transfer excitation. The intense, strongly red-shifted fluorescence further contributes in confirming the charge-transfer nature of the excitation (Figure S1 in the Supporting Information). To obtain photovoltaic information of compound **20**, we have fabricated inverted organic solar cells. The performance of photovoltaic devices are summarized in Table S2 in the Supporting Information.
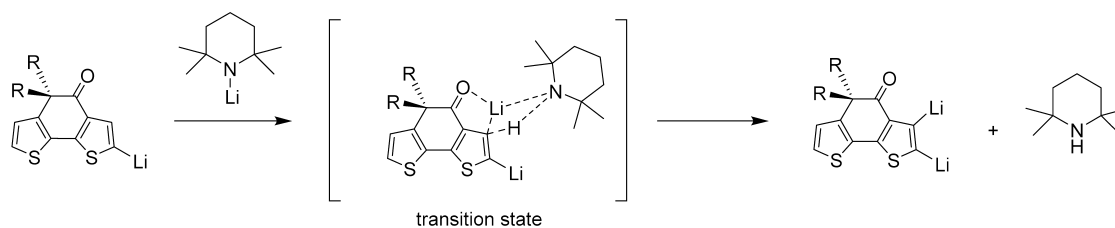
In conclusion, we have synthesized a new building block based on dithienocyclohexanone for conjugated polymers and

Scheme 3. (a) Stannylation Reactions of DTCH According to a Direct Lithiation Approach and (b) Halogenation and Stannylation Reactions of DTCH

(a)

R = 3,7-dimethyloctyl

(b)

1a (R = n-octyl)
1b (R = 3,7-dimethyloctyl)

M1 (R = n-octyl) 95%
M2 (R = 3,7-dimethyloctyl) 96%

M2 (R = 3,7-dimethyloctyl)

T1 (R = 3,7-dimethyloctyl) 88%
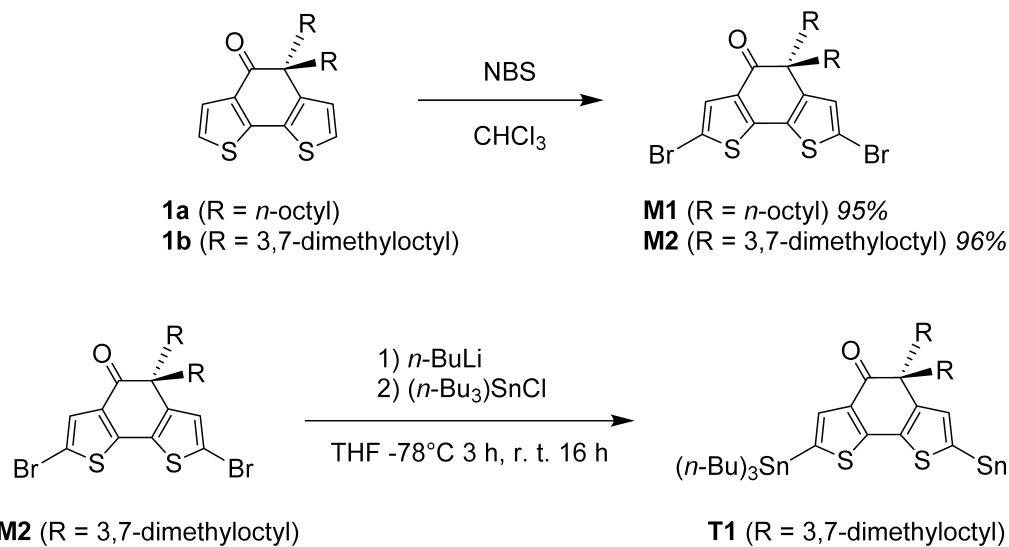
Scheme 4. Difunctionalization of DTCH Derivatives 1 and Synthetic Scheme for New Monomer 20

1a (R = n-decyl)
1b (R = 3,7-dimethyloctyl)

M1 (R = n-decyl) 95%
M2 (R = 3,7-dimethyloctyl) 96%

M2 (R = 3,7-dimethyloctyl)

20 (R = 3,7-dimethyloctyl) 90%
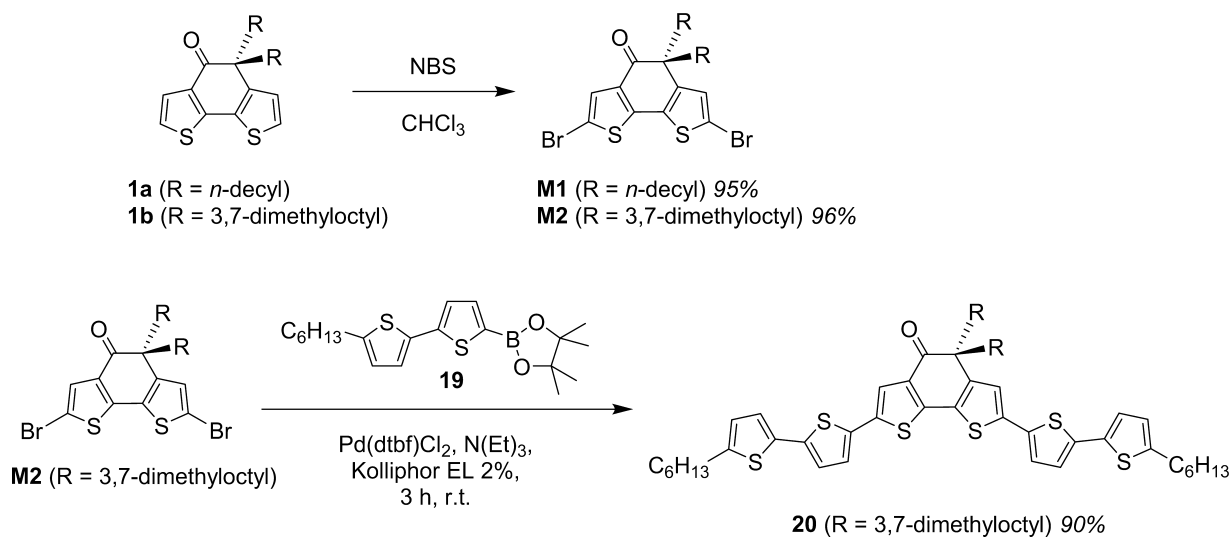
small molecules devising two simple synthetic pathways that uses relatively inexpensive and readily available starting materials. Moreover, these protocols are free from hazardous chemicals like n-butyllithium. This allows a multigram (possibly multikilograms) preparation and makes this process economically viable and environmentally attractive. DTCH can be easily elaborated through its corresponding dibrominated derivative. Moreover, the first example of DTCH-based material we describe, the small-molecule hexathiophene analogue **20**, can be prepared in water at room temperature and without taking care of the reaction environment. Further investigation of this resourceful protocol in polymerization reactions is under way.

A further line of research will involve the functionalization of the carbonyl group, for instance, with malononitrile derivatives, to enhance the acceptor character of the electron-poor portion of DTCH and tune the properties of the final materials.

■ EXPERIMENTAL SECTION

All commercially available starting materials and solvents were purchased from Sigma-Aldrich Chemical Co. and used without further purification. Flash chromatography was performed on silica gel 60 Å (230−400 mesh). Thin-layer chromatography was carried out using Merck silica gel GF254 plates. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer and Bruker Avance 500 (500 MHz) spectrometer, respectively. All of the spectra have been recorded with 90° pulse and a relaxation delay of 1.5 s for ^{1}H NMR and 4 s for ^{13}C NMR spectroscopies. High-resolution mass spectra were recorded using a 7 T Fourier transform ion cyclotron resonance mass spectrometer (LTQ-FT Ultra Thermo Scientific). The instrument ion source used employed was atmospheric pressure chemical ionization (APCI) operated in positive-ion mode using nitrogen as nebulizing gas. Mass spectra were recorded in profile mode with a mass range of 100−1000 m/z and an average resolving power of 400 000 at m/z 400; microscan: 1, maximum injection time: 1000, and automatic gain control on the ion cyclotron resonance cell: 10^6.

■ SYNTHETIC PROCEDURES

1,2-Di(thiophen-3-yl)ethyne (5). A 100 mL flask equipped with condenser was loaded with 3-ethynylthiofene (2.16 g, 20.0 mmol), 30 mL of triethylamine, 3-bromothiophene (3.91 g, 24.0 mmol), copper(I) iodide (0.076 g, 0.40 mmol), and bis(triphenylphosphine)palladium(II) chloride (0.140 g, 0.20 mmol). The reaction mixture was placed at 80 °C for 3 h under inert atmosphere. After cooling to room temperature (25 °C), the reaction mixture was poured in a 0.1 M aqueous solution of HCl (300 mL) and extracted with ethyl acetate (AcOEt, 4 × 50 mL). The organic phase was collected and dried over anhydrous Na$_2$SO$_4$. The residue obtained after solvent evaporation under reduced pressure was further purified by chromatography (SiO$_2$, eluent: heptane/ethyl acetate, 9/1), obtaining **5** as a white solid (1.71 g, yield 90%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ [ppm]: 7.36 (dd, J = 5.1, 1.1 Hz, 2H), 7.30 (dd, J = 3.6, 1.1 Hz, 2H), 7.04 (dd, J = 5.1, 3.6 Hz, 2H). ^{13}C NMR (101 MHz, CD$_2$Cl$_2$) δ [ppm]: 132.8, 128.4, 127.9, 94.0; high-resolution mass spectrometry (HRMS) (APCI+) calcd for C$_{10}$H$_7$S$_2$ [(M + H)$^+$]: 190.9984; found: 190.9981.

2-Hydroxy-(1,2-bis(thiophene-3-yl))ethan-1-one (7). In a 1 L two-necked flask, under inert atmosphere, a solution of 3-thiophenecarboxaldehyde **8** (302.54 g, 2.697 mol),

anhydrous DMF (100 mL), and 1,3-dimethyl-1H-(1,3-benzodiazol-3-ium)iodide (7.330 g, 0.0267 mol) is prepared. The solution is cooled to 0 °C with an ice bath, and 1,8-diazabicyclo[5.4.0]undec-7-ene (4.072 g, 0.0267 mol) is added. The mixture is stirred for 8 h at 0 °C and for 12 h at room temperature. The viscous mixture is poured in 1500 mL of a 0.03 M solution of citric acid. The obtained white precipitate is collected by filtration, washed thoroughly with water, and dried under reduced pressure at 60 °C (293.73 g, 1.311 mol, yield 97.2%).

1,2-Di(thiophen-3-yl)ethane-1,2-dione (4). A mixture of compound **6** (3.04 g, 6.0 mmol), 70 mL of dimethyl sulfoxide, palladium(II) acetate (0.359 g, 1.60 mmol), and copper(II) bromide (0.358 g, 1.60 mmol) was heated at 120 °C for 4 h under nitrogen atmosphere in a 250 mL flask equipped with condenser. After cooling to room temperature (25 °C), the reaction mixture was poured in a saturated aqueous solution of sodium chloride (100 mL) and extracted with diethyl ether (3 × 50 mL). The obtained organic phase was washed with water (3 × 50 mL) and subsequently dried over sodium sulfate and evaporated. The obtained residue was purified by chromatography (SiO$_2$, eluent: heptane/ethyl acetate, 9/1) to give **4** as a yellow solid (1.09 g, yield 82%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ [ppm]: 8.36 (dd, J = 3, 1.2 Hz, 2H), 7.69 (dd, J = 5.1, 1.2 Hz, 2H), 7.44 (dd, J = 5.1, 3 Hz, 2H). ^{13}C NMR (101 MHz, CD$_2$Cl$_2$) δ [ppm]: 186.5, 138.3, 138.0, 128.0, 127.7. HRMS (APCI+) calcd for C$_{10}$H$_6$NaO$_2$S$_2$ [(M + Na)$^+$]: 244.9701; found: 244.9699.

1,2-Di(thiophen-3-yl)ethane-1,2-dione (4) (Alternative Preparation). In a 2 L two-necked flask equipped with Dean−Stark apparatus and condenser, a suspension of derivative **7** (293.73 g, 1.311 mol) in cyclohexane (1500 mL) is prepared. The mixture is heated to reflux, and activated MnO$_2$ (342.17 g, 3.933 mol) is added portionwise. The mixture is refluxed for 5 h removing water through the Dean−Stark trap. The hot mixture is filtered to remove MnO$_2$, and the filtrate is allowed to cool to room temperature. Pure product crystallizes as yellow needles upon cooling and is collected by filtration. The filter containing spent MnO$_2$ is continuously extracted with CH$_2$Cl$_2$ to recover the fraction of adsorbed product, which is later recovered by solvent evaporation under reduced pressure and purified by crystallization from cyclohexane. Residual solvent is evaporated from both fractions under reduced pressure at 50 °C, obtaining pure product as a yellow crystalline solid (234.37 g, 1.055 mmol, yield 80.5%). NMR and HRMS data are consistent with those obtained with the other reported procedure.

Benzo[1,2-b:6,5-b']dithiophene-4,5-dione (3). Anhydrous iron(III) chloride (FeCl$_3$) (343.05 g, 2.115 mol) was suspended in 1 L of dichloromethane. The suspension was cooled at 0 °C, and a solution of compound **4** (156.52 g, 0.706 mol) in 0.4 L of the same solvent was added dropwise. The reaction mixture was left at room temperature for 2 h under inert atmosphere. The solution was poured into 1.2 L of distilled water and gently boiled until all of the organic solvent was evaporated. The obtained residue was collected and washed with distilled water and diethyl ether directly on the filter to give the title compound as a black solid (141.5 g, yield 91%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 38 °C) δ [ppm]: 7.47 (d, 2H, J = 5.2 Hz), 7.26 (d, 2H, J = 5.2 Hz). ^{13}C NMR (101 MHz, CD$_2$Cl$_2$, 38 °C) δ [ppm]: 175.3, 144.5, 135.9, 128.1, 126.5. HRMS (APCI) calcd for C$_{10}$H$_5$O$_2$S$_2$ [(M + H)$^+$] m/z: 220.9726; found 220.9724.

4,5-Dioctyl-4,5-dihydrobenzo[2,1-*b*:3,4-*b*′]-dithiophene-4,5-diol (2a). In a 250 mL three-necked flask equipped with thermometer and solid addition apparatus, a solution of Bu$_4$NBr (2.321 g, 7.20 mmol), 2 M octylmagnesium bromide in diethyl ether (Et$_2$O) (72.0 mmol, 36.0 mL), and anhydrous diglyme (9.661 g, 72.0 mmol) in anhydrous tetrahydrofuran (THF) (100 mL) is prepared under inert atmosphere. The solution is cooled to −15 °C with an ice−salt bath, and derivative **3** (2.640 g, 12.00 mmol) is added portionwise over 1 h. The mixture is stirred at −15 °C for 3 h and then at room temperature for 48 h. The reaction is quenched by addition of 100 mL of 25% NH$_4$Cl solution. Water (50 mL) and Et$_2$O (100 mL) are added, and the mixture is extracted. The organic phase is collected, washed with brine (50 mL), and dried over anhydrous Na$_2$SO$_4$. Solvent is evaporated under reduced pressure, and the obtained oily residue is purified by chromatography (SiO$_2$, eluent: heptane/AcOEt 9/1), obtaining compound **2a** as a pale yellow solid (2.585 g, 5.76 mmol, yield 48%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ [ppm]: 7.11 (AB syst, 4H), 1.75 (m, 4H), 1.55 (m, 4H), 1.40−1.00 (m, 22H), 0.91 (t, J = 7.1 Hz, 3H), 0.86 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, acetone-d_6) δ [ppm]: 142.6, 129.1, 127.6, 122.5, 82.9, 63.5, 34.8, 32.5, 30.7, 30.2, 29.9, 23.3, 14.5. HRMS (APCI+) calcd for C$_{26}$H$_{41}$O$_2$S$_2$ [(M + H)$^+$]: 449.2542; found: 449.2554.

4,5-Di(3,7-dimethyloctyl)-4,5-dihydrobenzo[2,1-*b*:3,4-*b*′]dithiophene-4,5-diol (2b). In a 5000 mL five-necked flanged reactor equipped with thermometer, solid addition apparatus, addition funnel, and mechanical stirrer, a solution of Bu$_4$NBr (21.45 g, 66.5 mmol), 1.25 M 3,7-dimetyloctylmagnesium bromide in Me-THF (665.0 mmol, 533.0 mL), anhydrous diglyme (89.24 g, 665.0 mmol), and anhydrous THF (150 mL) is prepared under inert atmosphere. The solution is cooled to −15 °C with an ice−salt bath, and derivative **3** (40.000 g, 181.8 mmol) is added portionwise over 1 h. The mixture is stirred at −15 °C for 3 h and then at room temperature for 48 h. The reaction is quenched by addition of 500 mL of 25% NH$_4$Cl solution. Water (150 mL) and Et$_2$O (300 mL) are added, and the mixture is filtered on a sintered glass filter to remove insoluble material. The organic phase is collected, and the aqueous phase is further extracted with Et$_2$O (2 × 200 mL). The combined organic phase is washed with brine (3 × 100 mL) and dried over anhydrous Na$_2$SO$_4$. Solvent is evaporated under reduced pressure, and the obtained oily residue is partially purified by chromatography on a short dry silica plug (SiO$_2$, eluent: gradient heptane → toluene), obtaining compound **2b** as an oily mixture of stereoisomers and impurities that can be used for the next step without further purification (44.05 g, 87.26 mmol, yield 49%). The product can be further purified for analytical purpose by chromatography (SiO$_2$, eluent: gradient heptane → heptane/toluene 7/3). ^{1}H NMR (400 MHz, acetone-d_6) δ [ppm]: 7.21 (d, J = 4.9 Hz, 2H), 7.15 (d, J = 4.9 Hz, 2H), 1.93 (m, 2H), 1.71 (m, 2H), 1.45 (m, 2H), 1.23−0.98 (m, 20H), 0.83 (d, J = 6.7 Hz, 6H), 0.73 (d, J = 6.5 Hz, 6H), 0.65 (d, J = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, acetone-d_6) δ [ppm]: 144.2, 128.5, 122.0, 82.6, 60.4, 40.8, 39.8, 38.0, 33.6, 32.4, 31.3, 28.4, 25.2, 22.8, 19.9. HRMS (APCI+) calcd for C$_{30}$H$_{49}$O$_2$S$_2$ [(M + H)$^+$]: 505.3168; found 505.3189.

5,5-Dioctylbenzo[2,1-*b*:3,4-*b*′]dithiophen-4(5*H*)-one (1a). In a 100 mL flask equipped with condenser, a solution of compound **2** (2.24 g, 5.00 mmol) and *p*-toluenesulfonic acid (0.162 g, 0.85 mmol) in 50 mL of toluene is refluxed for 1.5 h

under inert atmosphere. After cooling to room temperature (25 °C), the reaction mixture was poured in 5% aqueous NaHCO$_3$ solution (100 mL) and extracted with diethyl ether (3 × 50 mL). The obtained organic phase was washed to neutral with brine (50 mL) and subsequently dried over sodium sulfate and evaporated. The obtained residue was purified by elution on a chromatographic column of silica gel (eluent: heptane/ethyl acetate, 99/1), obtaining compound **1a** as a pale yellow oil (yield 95%). ^{1}H NMR (400 MHz, acetone-d_6) δ [ppm]: 7.64 (d, J = 5.3 Hz, 1H), 7.40 (d, J = 5.3 Hz, 1H), 7.37 (d, J = 5.1 Hz, 1H), 7.24 (d, J = 5.1 Hz, 1H), 2.13 (m, 2H), 1.86 (m, 2H), 1.21 (m, 4H), 1.20−1.00 (m, 20H), 0.82 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, acetone-d_6) δ [ppm]: 197.8, 147.9, 147.3, 134.4, 128.9, 127.5, 126.9, 125.6, 123.7, 57.5, 43.3, 32.2, 30.4, 30.3, 25.0, 23.0, 14.1. HRMS (APCI+) calcd for C$_{26}$H$_{39}$OS$_2$ [(M + H)$^+$]: 431.2441; found: 431.2437.

5,5-Di(3,7-dimethyloctyl)benzo[2,1-*b*:3,4-*b*′]-dithiophen-4(5*H*)-one (1b). In a 1 L flask equipped with Dean−Stark trap and condenser, a solution of crude **2b** (44.05 g, 87.26 mmol) and *p*-toluenesulfonic acid monohydrate (500 mg, 2.62 mmol) in toluene (500 mL) is heated to reflux for 1 h. The mixture is cooled to room temperature and poured in 5% aqueous NaHCO$_3$ solution (400 mL). The organic phase is collected, washed with brine (100 mL), and dried over anhydrous MgSO$_4$. To remove coeluting impurities, the crude product obtained after solvent removal under reduced pressure is dissolved in 400 mL of *n*-heptane in a 3 L beaker. A water solution of oxone (140 g, 228 mmol in 600 mL of water) is added, and the biphasic mixture is vigorously stirred. An aqueous solution of NaI (14 g, 93 mmol) is added dropwise over 1 h. The formation of a red precipitate (compound **3**) is observed. The mixture is filtered over celite and washing with toluene. The organic phase is collected, washed with a 5% NaHCO$_3$ aqueous solution, and dried over MgSO$_4$. Solvent is evaporated under reduced pressure, obtaining a pale yellow oil (41.38 g, 85.01 mmol, yield 98%). ^{1}H NMR (400 MHz, acetone-d_6) δ [ppm]: 7.64 (d, J = 5.2 Hz, 1H), 7.40 (d, J = 5.2 Hz, 1H), 7.37 (d, J = 5.1 Hz, 1H), 7.26 (d, J = 5.0 Hz, 1H), 2.15 (m, 2H), 1.89 (m, 2H), 1.45 (m, 2H), 1.25−1.00 (m, 18H), 0.82 (d, J = 6.4 Hz, 6H), 0.72 (d, J = 6.4 Hz, 6H), 0.71 (d, J = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, acetone-d_6) δ [ppm]: 197.8, 148.0, 147.3, 134.5, 129.0, 127.5, 126.9, 125.5, 123.7, 57.4, 41.0, 39.6, 37.2, 33.4, 31.7, 29.6, 28.4, 25.1, 23.2, 14.4. HRMS (APCI+) calcd for C$_{30}$H$_{47}$OS$_2$ [(M + H)$^+$]: 487.3063; found: 487.3065.

2,7-Dibromo-5,5-dioctylbenzo[2,1-*b*:3,4-*b*′]-dithiophen-4(5*H*)-one (M1). A 100 mL flask equipped with a reflux condenser was loaded with compound **1a** (2.00 g, 4.65 mmol), 40 mL of chloroform, and *N*-bromosuccinimide (1.67 g, 9.40 mmol). The reaction mixture was protected from light and left at room temperature for 16 h under inert atmosphere. The reaction mixture was washed with a 0.1 M solution of sodium thiosulfate (100 mL). Aqueous phase was extracted with dichloromethane (3 × 50 mL). The combined organic phase was washed to neutral with water (3 × 50 mL) and subsequently dried over sodium sulfate and evaporated. The obtained residue was purified by chromatography on silica gel (eluent: heptane/ethyl acetate, 99/1) to give **M1** as a pale yellow solid (2.98 g, yield 98%). ^{1}H NMR (400 MHz, acetone-d_6) δ [ppm]: 7.44 (s, 1H), 7.41 (s, 1H), 2.10 (m, 2H), 1.87 (m, 2H), 1.22 (m, 4H), 1.20−1.00 (m, 20H), 0.83 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, acetone-d_6) δ [ppm]: 195.8, 148.8, 146.9, 134.6, 129.4, 131.0, 128.3, 114.7, 111.2, 57.8, 43.2, 32.2,

29.6, 25.0, 23.0, 14.1. HRMS (APCI+) calcd for $C_{26}H_{37}Br_2OS_2$ [(M + H)$^+$]: 587.0647; found 587.0663.

2,7-Dibromo-5,5-bis(3,7-dimethyloctyl)benzo[2,1-b:3,4-b']dithiophen-4(5H)-one (M2). In a 500 mL flask, a solution of compound **1b** (29.56 g, 60.72 mmol) in anhydrous DMF (250 mL) is prepared under inert atmosphere. NBS (22.696 g, 127.51 mmol) is added portionwise at room temperature. The mixture is stirred for 24 h and poured in 600 mL of water containing NaCl (30 g) and $Na_2S_2O_3$ (5 g). The mixture is extracted with 4 × 200 mL of petroleum ether (ETP)/Et$_2$O mixture. The organic phase is washed with 3 × 100 mL of brine and dried over anhydrous Na_2SO_4. Solvent is evaporated under reduced pressure, and the obtained oil is further purified by filtration through a silica plug (SiO$_2$, eluent: heptane → heptane/AcOEt 98/2), obtaining product as a yellow oil that slowly crystallizes over few days (37.58 g, 58.29 mmol, yield 96%). ^{1}H NMR (400 MHz, acetone-d_6) δ [ppm]: 7.44 (s, 2H), 2.13 (m, 2H), 1.90 (m, 2H), 1.46 (m, 2H), 1.26–0.85 (m, 18 H), 0.83 (d, J = 6.3 Hz, 6H), 0.74 (d, J = 6.6, 6H), 0.73 (d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, acetone-d_6) δ [ppm]: 195.9, 148.9, 146.9, 134.8, 129.5, 131.0, 128.3, 114.7, 111.2, 57.7, 40.8, 40.5, 39.6, 37.1, 37.0, 33.4, 33.2, 31.6, 28.4, 25.1, 24.9, 22.7. HRMS (APCI+) calcd for $C_{30}H_{45}Br_2OS_2$ [(M + H)$^+$]: 643.1273; found 643.1290.

5,5-Bis(3,7-dimethyloctyl)-2,7-bis(tributylstannyl)-benzo[2,1-b:3,4-b']dithiophen-4(5H)-one (T1). A 100 mL two-necked round-bottom flask was loaded with compound **M2** (0.77 g, 1.2 mmol) and THF (25 mL) under argon protection. The solution was kept at −78 °C and 1.7 mL (2.7 mmol) of *n*-butyllithium (1.6 M solution in hexane) was dropped slowly. The solution was stirred at −78 °C for 3 h. Then, 0.92 mL of tributyltin chloride (3.4 mmol) was added at −78 °C in one portion. Stirring was maintained at room temperature for 16 h and then 30 mL of water was added to quench the reaction. Diethyl ether (30 mL) was added to extract the organic part, and the solvent was removed under vacuum. The product was purified by silica gel column with heptane as eluent. (In advance, the silica gel was dipped into heptane containing 10% triethylamine for 1 h and flushed out with heptane.) After removing the solvent, **T1** was obtained as an yellowish oil (yield 88%). ^{1}H NMR (400 MHz, THF-d_8) δ [ppm]: 7.48 (s, 1H), 7.14 (s, 1H), 2.17 (m, 2H), 1.85 (m, 2H), 1.65 (m, 12H), 1,40 (m, 12H), 1,21 (m, 12H), 1.55–1.05 (m, 18 H), 0.93 (t, J = 6.3 Hz, 18H), 0.86 (d, J = 6.9 Hz, 6H), 0.85 (d, J = 6.8 Hz, 6H), 0.73 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, THF-d_8) δ [ppm]: 195.4, 150.3, 146.3, 136.4, 136.4, 133.4, 133.0, 132.9, 132.3, 55.4, 39.0 (2C), 38.0, 37.9, 35.6, 35.3, 31.8, 31.8, 30.1, 29.9, 27.7 (2C), 26.6 (2C), 25.9 (2C), 20.9, 20.8, 17.8, 17.6, 11.8 (2C), 9.4 (2C). HRMS (APCI+) calcd for $C_{54}H_{98}OS_2Sn_2$: 1065.5109; found 1065.5105.

5,5-Bis(3,7-dimethyloctyl)-2,7-bis(5-hexyl-2,2'-bithiophene)benzo[2,1-b:3,4-b']dithiophen-4(5H)-one (20). In a 10 mL test tube equipped with magnetic stirrer, bromide **M2** (0.5 mmol, 322 mg) and 5-hexyl-2,2-bithiophene-5 boronic acid pinacol ester (565 mg, 1.5 mmol) were suspended in 1.5 mL of Kolliphor EL 2% solution. Pd(dtbpf)-Cl$_2$ (15 mg) and N(Et)$_3$ (303 mg, 3 mmol) were added under stirring at room temperature. The viscous reaction mixture was vigorously stirred for 3 h, observing a gradual color change from yellow to deep red. The mixture was diluted with 10 mL of CH$_2$Cl$_2$ and filtered through a pad of silica. The filtrated was evaporated under reduced pressure and purified by chromatography (SiO$_2$ CH$_2$Cl$_2$/heptane 1/1) to give the pure title

compound as a red powder (0.45 mmol, 443 mg, yield 90%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ [ppm]: 7.46 (s, 1H), 7.17 (d, J = 3.8 Hz, 1H), 7.13 (d, J = 3.7 Hz, 1H), 7.09 (s, 1H), 7.06 (d, J = 3.7 Hz, 1H), 7.04 (d, J = 3.6 Hz, 2H), 7.04 (d, J = 3,7, 1H), 6.73 (m, 2H), 2.82 (t, J = 7.6 Hz, 4H), 2.19 (m, 2H), 1.79 (m, 2H), 1.70 (m, 4H), 1.41 (m, 8H), 1,34 (m, 8H), 1.29–1.00 (m, 16 H), 0.91 (t, J = 6.3 Hz, 6H), 0.81 (d, J = 6.9 Hz, 6H), 0.80 (d, J = 6.8, 6H), 0.75 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, CD$_2$Cl$_2$) δ [ppm]: 197.9, 149.5, 147.0, 145.7, 138.5, 135.3, 135.1, 134.7, 127.7, 125.7, 124,4, 123.0, 121.1, 57.8, 41.4, 41.1, 39.8, 37.2, 33.7, 33.5, 31.9, 30.8, 29.4, 28.6, 25.4, 25.1, 23.2, 23.0, 19.9, 14.5. HRMS (APCI+) calcd for $C_{58}H_{79}Br_2OS_6$ [(M + H)$^+$]: 983.4450; found 983.4356.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00987.

> Additional experiments for cyclization of compound **12**; device fabrication and characterization; UV–vis spectra of compound **20**; and ^{1}H NMR and ^{13}C NMR spectra of compounds **9−12**, **16**, **17**, and **20** (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: gabriele.bianchi1@eni.com.

ORCID Ⓞ

Gabriele Bianchi: 0000-0002-7448-7363

Riccardo Po: 0000-0002-8374-195X

Mauro Sassi: 0000-0002-5529-6449

Luca Beverina: 0000-0002-6450-545X

Notes

The authors declare no competing financial interest.

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