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Oxidative Transformation to Naphthodithiophene and Thia[7]helicenes by Intramolecular Scholl Reaction of Substituted 1,2-Bis(2-thienyl)benzene Precursors

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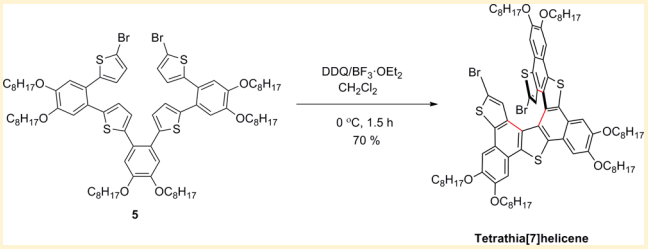
Supporting Information

ABSTRACT: We present here a strategy to synthesize a variety of substituted naphthodithiophene building blocks through DDQ/acid-mediated oxidative cyclizations. The versatility of the Scholl reaction using the DDQ/acid system was demonstrated by the preparation of a novel substituted tetrathia[7]helicene where three new C−C bonds were formed in a one-pot procedure. The new DDQ/acid method was compared to the known strategies such as $FeCl_3$ oxidation and oxidative photocyclization. By protecting the 1,2-bis(2-thienyl)benzene precursors, it is possible to direct the intermediates to controlled cyclization and effectively suppressing the polymerization. The highly reactive α-position of the terminal thiophenes can allow for further functionalization. The efficient preparation of a variety of naphthodithiophene building blocks, the extension to a nonphotochemical synthesis of [n]helicenes, and the ease of isolation of the products are arguments for the use of DDQ/acid system for this Scholl reaction.



INTRODUCTION

During the past several decades, thiophene-based materials have attracted significant interest due to their applications in organic electronics.[1] Incorporation of thiophene rings onto a polycyclic aromatic framework provides aromatic stability while preserving the desirable physical properties such as high conductivity.[2] Thia[n]helicenes,[3] a subclass of heterahelicenes with alternating benzene and thiophene rings, are particularly important. Heterahelicenes combine the electronic properties afforded by their extensive π-conjugated system with the (chiro) optical properties associated to their helical structure.[4] Thiahelicenes are an extremely interesting class of conjugated molecules being investigated for optoelectronic application.[5] The potential of helicenes lies in developing strategies that provide efficient access to a variety of helical frameworks, focusing on efficient routes that are amenable to scale-up and also provide flexibility for functionalization.

Arene cyclizations induced by chemical oxidants have successfully led to the construction of aromatized ring structures,[6] but the study of oxidative carbon−carbon bond formation as a means of constructing discrete thiophene-based materials has been relatively underexplored. In 1996, Larsen et al. synthesized heterahelicenes by oxidative coupling of stilbene-type precursors using $FeCl_3$.[7] Prior to the work of Swager et al.,[8] the highly reactive nature of oxidized thiophene moieties toward polymerization has limited the development of thiophene-centered oxidative cyclizations. Photochemical Mallory-type cyclization[9] using iodine as an oxidant was an important variant of this strategy but has a variety of drawbacks associated with it. Swager et al. described in detail the thienyl−thienyl oxidative cyclization using $FeCl_3$.[2a] The highly reactive α-position of thiophene was selectively substituted, thus protecting the thiophene from polymerization. Later in 2006, Pei and co-workers built on that knowledge and synthesized helical polycyclic thiophene derivatives.[10]

In recent years, the Scholl reaction[11] has gained significant interest due to its potential in the synthesis of several π-conjugated materials. This reaction, first reported in 1910, is an intramolecular oxidative C−C bond formation between two benzenoid rings to produce a biaryl linkage. The Scholl reaction had been extensively utilized for the synthesis of planar polycyclic aromatic compounds. This oxidative cyclodehydrogenation reaction can be accomplished by using a variety of oxidants such as $FeCl_3$ in DCM, $CuCl_2$ or $Cu(OTf)_2$ and $AlCl_3$, $MoCl_5$ in DCM, $Pd(OAc)_4/BF_3{\cdot}Et_2O$ MeCN, and quinones in the presence of strong acid.[12] Rathore et al.[13] have shown that dichlorodicyano-p-benzoquinone (DDQ, E_{red} = +0.60 V vs SCE) in the presence of acid can readily oxidize a variety of aromatic donors with an oxidation potential as high as ∼1.7 V vs SCE to the corresponding cation radicals and can be employed for Scholl reactions.

Herein we report a detailed insight on the oxidative cyclization of 1,2-bis(2-thienyl)benzene precursors. The α-positions of the terminal thiophenes were substituted with a variety of substituents ranging from electron-donating to electron withdrawing groups, thus providing an opportunity to investigate the influence of protecting groups on the

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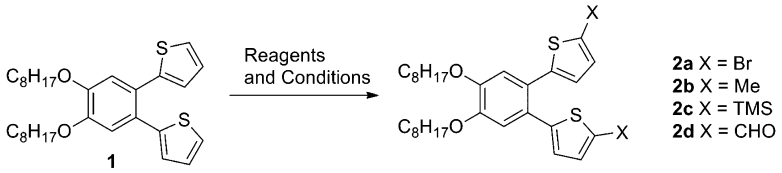
Table 1. Synthesis of α-Substituted Dithienylbenzenes 2a−d



entry	substituent (X)	reagents and conditions	yield (%)
1	Br	**1**, NBS, $CHCl_3$/AcOH (8:2), 0 °C, 2 h	**2a**, 93
2	Me	**1**, *n*-BuLi, MeI, THF −78 °C, 3 h	**2b**, 84
3	TMS	**1**, *n*-BuLi, TMSCl, THF −78 °C, 3 h	**2c**, 93
4	CHO	**1**, *n*-BuLi, DMF, THF −78 °C, 3 h	**2d**, 96

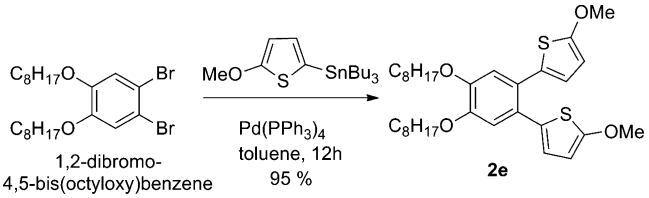
oxidative cyclization. The most suitable reaction conditions were employed to further examine its applicability in the synthesis of thia[*n*]helicenes.

RESULTS AND DISCUSSION

Our approach makes use of 1,2-bis(octyloxy)-4,5-bis(2-thienyl)benzene (**1**)[14] as a versatile building block for further substitution, study of substituent effect on the oxidative cyclization, and finally, synthesis of thia[7]helicene. The choice of the substituents was made, from electron-donating to electron-withdrawing groups (OMe, Me, TMS, Br, CHO), which could provide a possibility of postcyclization functionalization. Substitution of building block **1** with bromine was done using NBS and a $CHCl_3$/AcOH mixture as the solvent at 0 °C to furnish the dibrominated compound **2a** in 93% yield. Further substitution with the methyl, trimethylsilyl, or formyl group was accomplished by lithiation of compound **1** with *n*-BuLi and THF as solvent at −78 °C and subsequently treating the lithiated thiophenes with methyl iodide, trimethylsilyl chloride, and dimethylformamide to furnish the disubstituted compounds **2b**, **2c**, and **2d** in 84%, 93%, and 96% yields, respectively (Table 1).

Substitution with the methoxy group on the building **1** was not straightforward; hence, compound **2e** was prepared by Stille coupling of 1,2-dibromo-4,5-bis(octyloxy)benzene with the in situ prepared stannyl derivative of 2-methoxythiophene, using 10 mol % of $Pd(PPh_3)_4$ and toluene as the solvent (Scheme 1). Compound **2e** was obtained in 95% yield.

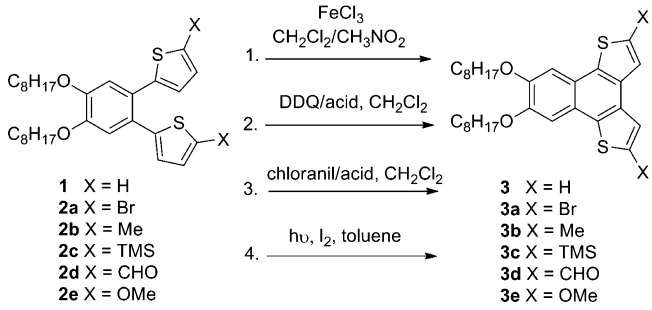
Scheme 1. Synthesis of Dimethoxy-Substituted Dithienylbenzene 2e



The dithienylbenzene derivatives **1** and **2a−e** were subjected to oxidative cyclization to investigate the influence of the α-substituents. The reagents used in the oxidative cyclization reactions are $FeCl_3$ and DDQ/acid as described by Rathore et al.[13] and the chloranil/acid system (Scheme 2). Oxidative photocyclization was also carried out for comparison.

In our previous work,[14] we synthesized the unsubstituted naphthodithiophene building block via oxidative photochemical cyclization of compound **1** to give compound **3** in 82% yield.

Scheme 2. Overview of Oxidative Cyclization toward Naphthodithiophene Building Block



Though the reaction was efficient, scale-up, was limited. To overcome the drawbacks associated with the photochemical cyclization we opted for oxidative cyclization. As a starting point we used the unsubstituted compound **1** to further study the effect of different oxidants. As described by Swager et al., the use of $FeCl_3$ as an oxidant on the unsubstituted thiophene moieties always led to polymerization. Building on that knowledge, we wanted to compare the use of the DDQ/acid system on the unsubstituted benzodithiophene building block **1**. Complete polymerization was observed in the reaction using DDQ/$MeSO_3H$ at 0 °C for 1 h. Changing the acid to $BF_3{\cdot}EtO_2$ did not have a significant effect on the reaction outcome (Table 2).

Table 2. Oxidative Cyclization on Unsubstituted Benzodithiophene Building Block

entry	reagents and conditions	yield of **3** (%)
1[a]	**1**, *hν*, I_2, toluene, 15 h	82
2	**1**, $FeCl_3$[b], CH_2Cl_2/CH_3NO_2[c], 0 °C, 2 h	polymerization
3	**1**, DDQ[d]/$MeSO_3H$[e], CH_2Cl_2, 0 °C, 1 h	polymerization
4	**1**, DDQ[d]/$BF_3{\cdot}Et_2O$[f], CH_2Cl_2, 0 °C, 1 h	polymerization

[a]Previous work. [b]6 equiv $FeCl_3$. [c]CH_2Cl_2/CH_3NO_2 10:1. [d]1.0 equiv of DDQ. [e]CH_2Cl_2/acid 9:1. [f]10 equiv of Lewis acid.

A bromine-substituted benzodithiophene derivative was employed next in the Scholl reaction. Oxidative cyclization of compound **2a** was performed in accordance with the procedure of Pei et al. using $FeCl_3$ (6 equiv per C−C bond) and CH_2Cl_2 as the solvent at room temperature. Complete decomposition was observed owing to the large excess of $FeCl_3$ used. After a series of experiments, oxidative cyclization of compound **2a** with 2.2 equiv of $FeCl_3$ and CH_2Cl_2/CH_3NO_2 (10:1) as solvent at 0 °C for 3 h gave the cyclized compound **3a** in 64% yield and a small amount (8%) of debrominated byproduct (charac-

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terized by NMR, see the Supporting Information for **3a′**). A reaction performed in the absence of CH_3NO_2 also furnished compound **3a** in 50% yield. The use of $Fe(acac)_3$ as an alternative source of iron(III) did not lead to any product formation. We further investigated the quinone/acid systems. Oxidative cyclization of compound **2a** using DDQ/$MeSO_3H$ in CH_2Cl_2 (CH_2Cl_2/acid 9:1) at 0 °C furnished compound **3a** in 65% yield, which was very close to the yield obtained from the $FeCl_3$ reaction. However, at gram scale using a slight excess of DDQ (1.5 equiv)/$MeSO_3H$ compound **3a** was obtained in 85% yield. This drastic increase in yield can be attributed to the explanation given by Rathore et al.[13] that if the oxidation potential of the final product to its radical cation is lower in value than the actual oxidation potential of the starting material further dehydrogenation can be arrested. They proposed to solve this by adding 0.5 equiv of DDQ more. The use of a Lewis acid like $BF_3{\cdot}OEt_2$ proved to be more efficient compared to $MeSO_3H$. The yield of compound **3a** increased to 93%. The other system employed in the study was chloranil/acid. Using similar conditions like DDQ, the chloranil/$MeSO_3H$ combination gave the desired product in 50% yield. The chloranil/$BF_3{\cdot}OEt_2$ combination furnished the compound **3a** in good yields (74%) although the reaction time was substantially increased from 45 min to 20 h (Table 3).

Table 3. Oxidative Cyclization Reactions of Dibromo Substituted Benzodithiophene 2a

entry	reagents and conditions	yield of **3a** (%)
1	**2a**, $FeCl_3$[b], CH_2Cl_2/CH_3NO_2, rt, 1 h	dec
2	**2a**, $FeCl_3$[c], CH_2Cl_2/CH_3NO_2[d], 0 °C, 3 h	64
3[a]	**2a**, $FeCl_3$[c], CH_2Cl_2/CH_3NO_2[d], 0 °C, 3 h	52
4	**2a**, $FeCl_3$[c], CH_2Cl_2, 0 °C, 3 h	50
5	**2a**, $Fe(acac)_3$, CH_2Cl_2/CH_3NO_2, 40 °C, 24 h	no conversion
6	**2a**, DDQ/$MeSO_3H$[g], CH_2Cl_2, 0 °C, 20 min	65
7[a]	**2a**, DDQ[e]/$MeSO_3H$[g], CH_2Cl_2, 0 °C, 20 min	85
8	**2a**, DDQ[e]/$BF_3{\cdot}OEt_2$[f], CH_2Cl_2, 0 °C, 20 min	93
9	**2a**, chloranil[e]/$MeSO_3H$[g], CH_2Cl_2, 0 °C, 45 min	50
10	**2a**, chloranil[e]/ $BF_3{\cdot}OEt_2$[f], CH_2Cl_2, 0 °C, 20 h	74

[a]Reaction on gram scale. [b]6 equiv of $FeCl_3$ per C−C bond. [c]2.2 equiv of $FeCl_3$ per C−C bond. [d]CH_2Cl_2/CH_3NO_2 10:1. [e]1.5 equiv of DDQ or chloranil. [f]10 equiv of Lewis acid. [g]CH_2Cl_2/acid 9:1 in entries 6, 7, and 9.

To conclude, on the basis of the series of experiments (Table 2), $FeCl_3$, CH_2Cl_2/CH_3NO_2, and DDQ/$BF_3{\cdot}OEt_2$ combination proved to be very efficient for the oxidative cyclization of the compound **2a**. These two methods were extended to other substituted benzodithiophene derivatives.

Thus, compound **2b** was subjected to oxidative cyclization using $FeCl_3$ and CH_2Cl_2/CH_3NO_2 at 0 °C for 3 h. Compound **3b** was obtained in a relatively poor 46% yield which was rather unexpected, as the electron-donating methyl group in principle should have a stabilizing effect on the intermediates. The DDQ/acid system gave unexpected results as well. Only 16% of compound **3b** was obtained when DDQ/$BF_3{\cdot}OEt_2$ was used. Variation of the acid from $MeSO_3H$ to acetic acid did not have a significant effect on the reaction, and complete polymerization was observed. The byproducts isolated were unidentified mixtures, and this led us to conclude that highly reactive species, possibly radical in nature, were formed and the methyl group could not be used as an efficient protecting group on thiophenes in oxidative cyclization process. Nevertheless, photochemical cyclization proved to be very efficient, and compound **3b** was obtained in 80% (Table 4).

Table 4. Oxidative Cyclization Reaction of Dimethyldithienylbenzene

entry	reagent and conditions	yield of **3b** (%)
1	**2b**, $FeCl_3$, CH_2Cl_2/CH_3NO_2, 0 °C, 3 h	46
2	**2b**, DDQ/$BF_3{\cdot}OEt_2$, CH_2Cl_2, 0 °C, 20 min	16
3	**2b**, DDQ/$MeSO_3H$, CH_2Cl_2, 0 °C, 3 h	polymerization
4	**2b**, DDQ/CH_3COOH, CH_2Cl_2, 0 °C, 1 h	polymerization
5	**2b**, DDQ, CH_2Cl_2, 0 °C, 2 h	No conversion
6	**2b**, $h\nu$, I_2, toluene, 24 h	80%

Trimethylsilyl-protected benzodithiophene derivative **2c** was subjected to oxidative cyclization under the optimized conditions. The trimethylsilyl group was cleaved under the given reaction conditions furnishing the deprotected compound **1**, but no trace of product was observed. When an additional 2.2 equiv of $FeCl_3$ or 1.5 equiv of DDQ was added, it led to complete polymerization of the starting material. Photochemical cyclization of **2c** led to the formation of the desired product **3c** in 80% yield with no trace of deprotection (Table 5).

Table 5. Oxidative Cyclization of Bis(trimethylsilyl)dithienylbenzene

entry	reagents and conditions	yield of **3c** (%)
1	**2c**, $FeCl_3$, CH_2Cl_2/CH_3NO_2, 0 °C, 30 min	deprotection and polymerization
2	**2c**, DDQ/$BF_3{\cdot}OEt_2$, CH_2Cl_2, 0 °C, 20 min	deprotection and polymerization
3	**2c**, $h\nu$, I_2, toluene, 24 h	80

Methoxy-protected benzodithiophene derivative **2e** was subjected to oxidative cyclization using $FeCl_3$ and CH_2Cl_2/CH_3NO_2 combination at 0 °C for 5 min. Product formation was observed (by TLC), but this product immediately polymerized under the given reaction conditions. The DDQ/acid system also did not lead to product formation. The less reactive chloranil/$BF_3{\cdot}OEt_2$ system was employed and gave compound **3e** in 8% yield and 16% of dimer (confirmed by NMR; see the Supporting Information for **3e′**) was formed. Chloranil with a catalytic amount of Lewis acid proved to be more efficient and gave compound **3e** in 55% yield and only traces of dimer. In the presence of DDQ or chloranil alone, no conversion of starting material **2e** was observed. In comparison, photochemical cyclization gave compound **3e** in 26% yield. This leads us to conclude that although the oxidative cyclization is fast with methoxy-substituted dithienylbenzenes, the product formed is very susceptible to oxidation, which may cause further polymerization in the given reaction conditions (Table 6).

When the methodology for electron-withdrawing dialdehyde derivative was expanded, compound **2d** was subjected to oxidative cyclization using an $FeCl_3$ and DDQ/acid system. The presence of the aldehyde had a significant effect, as there was no conversion observed. This could be attributed to the fact that the oxidation potential of the compound **2d** exceeds 1.7 V vs SCE as described by Rathore et al.[13] The photochemical cyclization also did not lead to any product formation (Table 7).

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Table 6. Oxidative Cyclization of Methoxy-Substituted Dithienylbenzene

entry	reagent and conditions	yield of **3e** (%)
1	**2e**, $FeCl_3$, CH_2Cl_2/CH_3NO_2, 0 °C, 5 min	polymerization
2	**2e**, DDQ/$BF_3{\cdot}OEt_2$, CH_2Cl_2, 0 °C, 5 min	no product trace
3	**2e**, DDQ/$MeSO_3H$, CH_2Cl_2, −10 °C, 5 min	no product trace
4	**2e**, chloranil/$BF_3{\cdot}OEt_2$, CH_2Cl_2, 0 °C, 5 min	8 and 16 dimer
5	**2e**, chloranil/$BF_3{\cdot}OEt_2$ (cat), CH_2Cl_2, −10 °C, 15 min	55
6	**2e**, *hν*, I_2, toluene, 15 h	26

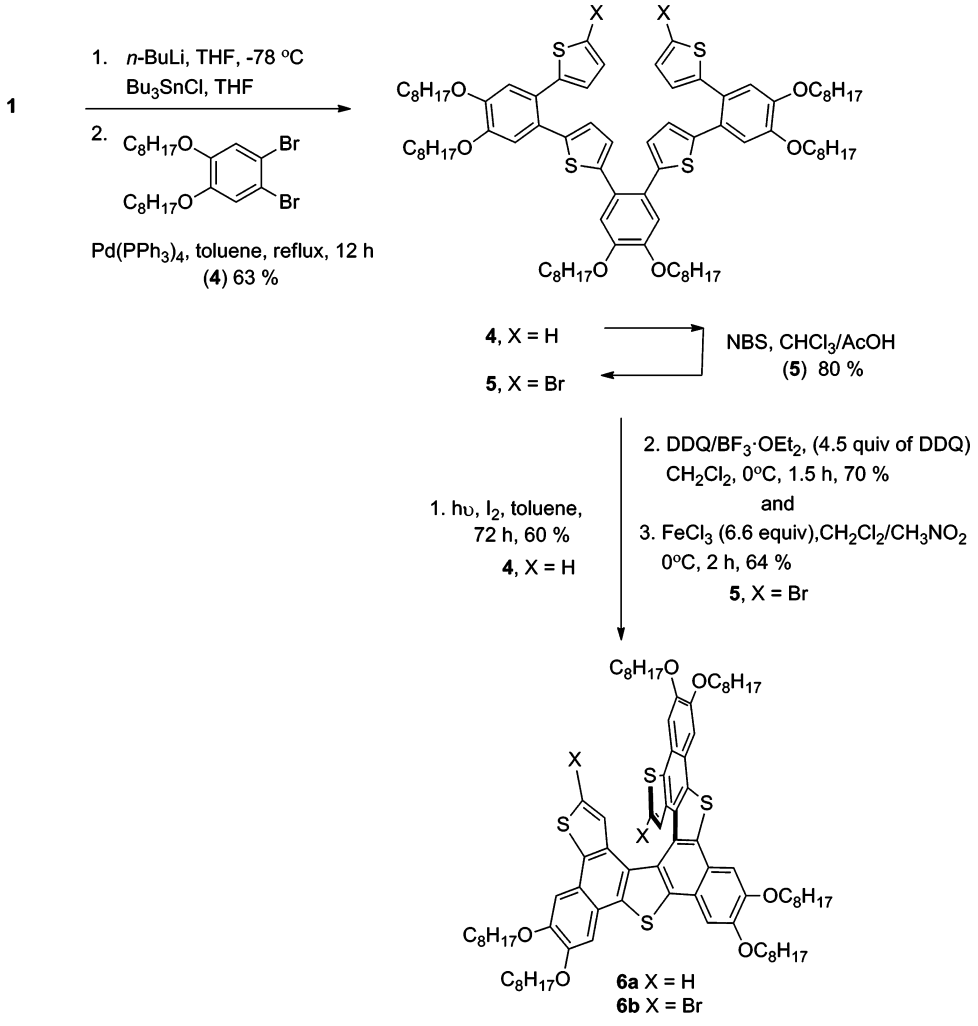
Table 7. Oxidative Cyclization of Aldehyde-Protected Benzodithiophene

entry	reagents and conditions	yield of **3d** (%)
1	**2d**, $FeCl_3$, CH_2Cl_2/CH_3NO_2, 0 °C to rt, 30 h	no conversion
2	**2d**, DDQ/$BF_3{\cdot}OEt_2$, CH_2Cl_2, 0 °C to rt, 30 h	no conversion
3	**2d**, *hν*, I_2, toluene, 72 h	no conversion

From these sets of experiments we could conclude that oxidative conditions may replace the photochemical reaction on a large scale, although the effectiveness of the reagents used in the Scholl reaction is dependent on the substituents present on the α-position of thiophenes.

Expanding on this knowledge, the versatility of the Scholl reaction using the DDQ/acid system was further demonstrated by the preparation of a novel hexaalkoxy-substituted tetrathia[7]helicene where three new C−C bonds were formed in a one-pot procedure. Palladium-mediated coupling between 1,2-dibromo-4,5-bis(octyloxy)benzene and in situ prepared monostannyl derivative of compound **1** gave the highly conjugated helicene precursor **4** in one step. Compound **1** was monolithiated using *n*-BuLi and then treated with tributylstannyl chloride to obtain the monostannyl derivative in quantitative yield. Since protodestannylation was observed during chromatographic purification, the stannyl derivative was used without further purification. Stille coupling of the in situ prepared monostannyl derivative of **1** and 1,2-dibromo-4,5-bis(octyloxy)benzene using 10 mol % of $Pd(PPh_3)_4$ and toluene as the solvent gave the compound **4** in 63% yield. Further bromination of **4** with NBS using $CHCl_3$/AcOH as

Scheme 3. Stille Coupling and Oxidative Cyclization toward the Synthesis of Benzo-Fused Tetrathia[7]helicenes



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solvent at 0 °C gave the dibrominated helicene precursor **5** in 80% yield. Compound **5** was subjected to oxidative cyclization under the optimized conditions used for brominated benzodithiophene **2a** using DDQ/BF_3·OEt_2 (1.5 equiv per C−C bond, 10 equiv of Lewis acid), CH_2Cl_2 as the solvent at 0 °C for 1.5 h. The desired tetrathia[7]helicene was obtained in 70% yield after purification. The reaction was straightforward and confirms the increasing reactivity after each subsequent cyclization. This is in agreement with the studies of Rempala et al.[15] that report that the energy barrier becomes lower with every subsequent intramolecular cyclization; i.e., each cyclization is faster than the preceding one. The driving force given for this phenomenon was the increasing electron delocalization (Scheme 3).

For comparison, oxidative cyclization using an $FeCl_3$/CH_2Cl_2/CH_3NO_2 system (2.2 equiv of $FeCl_3$ per C−C bond) furnished the helicene in 64% yield. Photochemical cyclization on compound **4** using UV light and iodine as the oxidant furnished the helicene (**6a**) in 60% yield. Though the yield was comparable, the reaction time was 72 h, and high dilution conditions were required. The DDQ/acid system proved to be superior in terms of reaction time and purity. Problems such as chlorination can be overcome by using the DDQ/acid system.

CONCLUSION

The optimization of the cyclization reaction leading to the (substituted) naphthodithiophene building block has proved that the Scholl reaction using DDQ/acid can be a good candidate to replace the photochemical cyclization on larger scale or as an alternative to the known $FeCl_3/CH_3NO_2$ method. Furthermore, the substituent on the α-position seems to have a significant influence on the outcome of the oxidative cyclization. The versatility of the DDQ/acid system was shown in the synthesis of tetrathia[7]helicenes.

EXPERIMENTAL SECTION

General Experimental Methods. NMR spectra were acquired on commercial instruments (300 and 400 MHz), and chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (^{1}H) or the internal (NMR) solvent signal (^{13}C). Mass spectra were acquired (EI, 70 eV ionization energy). Exact mass measurements were performed in the EI mode at a resolution of 10000 and also on a quadrupole orthogonal acceleration time-of-flight mass spectrometer. Samples were infused at 3 μL/min, and spectra were obtained in positive (or negative) ionization mode with a resolution of 15000 (fwhm) using leucine enkephalin to lock the mass. Melting points (not corrected) were determined using a Reichert Thermovar apparatus. For column chromatography, 70−230 mesh silica 60 was used as the stationary phase. Chemicals received from commercial sources were used without further purification. K_2CO_3 (anhydrous, granulated) was finely ground (with mortar and pestle) prior to use. All solvents were used as received from commercial sources and not explicitly dried prior to use ($H_2O \leq 0.1\%$). All photochemical reactions were performed in a photochemical reactor equipped with interchangeable light sources (250, 300, 350 nm lamps).

Experimental and Characterization Data. *Synthesis of 1,2-Bis(octyloxy)-4,5-bis(2-thienyl)benzene (**1**).* This compound has been prepared according previously reported literature procedure.[14] Material identity was confirmed by mp, MS, and ^{1}H and ^{13}C NMR.

*Synthesis of 5,5′-(4,5-Bis(octyloxy)-1,2-phenylene)bis(2-bromothiophene) (**2a**).* To a solution of 1,2-bis(octyloxy)-4,5-bis(2-thienyl)-benzene (**1**) (2.0 g, 4.0 mmol) in $CHCl_3$/AcOH (135 mL, 8:2) was added NBS (1.57 g, 8.83 mmol) at 0 °C. The reaction mixture was allowed to stir for an additional 2 h at room temperature. The reaction was quenched with $NaHCO_3$ and subsequently washed with a saturated $NaHCO_3$ solution, H_2O, and brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography using CH_2Cl_2/petroleum ether (20:80) gave compound **2a** (2.45 g, 93%) as a yellow solid: mp 51−53 °C; MS (EI) m/z 656.4, $[MH]^+$; HRMS (EI) calcd for $C_{30}H_{40}Br_2O_2S_2$ 656.0816, found m/z = 657.0894 $[M + H]^+$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (d, J = 3.8 Hz, 2H), 6.89 (s, 2H), 6.62 (d, J = 3.8 Hz, 2H), 4.02 (t, J = 6.6 Hz, 4H), 1.85−1.78 (m, 4H), 1.47 (m, 4H), 1.29 (m, 16H), 0.88 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1, 144.2, 129.9, 127.2, 125.5, 115.9, 112.1, 69.5, 31.9, 29.5, 29.4, 29.3, 26.1, 22.8, 14.3.

*Synthesis of 5,5′-(4,5-Bis(octyloxy)-1,2-phenylene)bis(2-methylthiophene) (**2b**).* To a solution of 1,2-bis(octyloxy)-4,5-bis(2-thienyl)-benzene (**1**) (1.0 g, 2.0 mmol) in dry THF (40 mL), n-BuLi (2.4 mL, 2.5 M, 6 mmol) was added dropwise at −78 °C under argon, and the reaction mixture was allowed to warm to room temperature. After 1.5 h, the reaction was cooled to −78 °C, and MeI (1.25 mL, 20.0 mmol) was added. The solution was quenched with a saturated NH_4Cl solution at 0 °C, extracted with EtOAc, dried over $MgSO_4$, and concentrated. Purification by column chromatography using CH_2Cl_2/petroleum ether (30:70) gave compound **2b** (0.887 g, 84%) as an off-white solid: mp 26−28 °C; MS (EI) m/z 526, $[MH]^+$; HRMS (EI) calcd for $C_{32}H_{46}O_2S_2$ 526.2939, found m/z = 527.3011 $[M + H]^+$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94 (s, 2H), 6.64 (d, J = 3.4 Hz, 2H), 6.59 (dd, J_1 = 3.6 Hz, J_2 = 3.4 Hz, 2H), 4.01 (t, J = 6.6 Hz, 4H), 2.45 (s, 6H), 1.87−1.77 (m, 4H), 1.47−1.5 (m, 4H), 1.28−1.44 (m 16H), 0.89 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4, 140.8, 139.9, 126.5, 125.1, 116.2, 69.4, 31.9, 29.5, 29.4, 29.3, 26.1, 22.8, 15.4, 14.2.

*Synthesis of (5,5′-(4,5-Bis(octyloxy)-1,2-phenylene)bis(thiophene-5,2 diyl))bis(trimethylsilane) (**2c**).* To a solution of 1,2-bis(octyloxy)-4,5-bis(2-thienyl)benzene (**1**) (0.500 g, 1.0 mmol) in THF (20 mL) was added n-BuLi (1.2 mL, 2.5 M, 3.00 mmol) dropwise at −78 °C under argon, and the reaction mixture was allowed to warm to room temperature. After 1 h, trimethylsilyl chloride was added at −78 °C. The reaction mixture was quenched with a saturated solution of NH_4Cl after 30 min and then allowed to come to room temperature. The mixture was extracted with EtOAc, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography using CH_2Cl_2/petroleum ether (20:80) to give compound **2c** (0.596 g, 93%) as a yellow liquid: MS (EI) m/z 643 $[MH]^+$; HRMS (EI) calcd for $C_{36}H_{58}O_2S_2Si_2$ 642.3417, found m/z = 643.3487 $[M + H]$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (d, J = 3.0 Hz, 2H), 6.99 (s, 2H), 6.84 (d, J = 3.0 Hz, 2H), 4.03 (t, J = 6.4 Hz, 4H), 1.85−1.81 (m, 4H), 1.41−1.55 (m, 4H), 1.18−1.40 (m, 16H), 0.89 (s, 6H), 0.28 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 140.4, 133.9, 128.0, 126.4, 116.0, 69.4, 31.9, 29.5, 29.4, 29.4, 26.1, 22.8, 14.2, 0.1.

*Synthesis of 5,5′-(4,5-Bis(octyloxy)-1,2-phenylene)bis(2-carbaldehydethiophene) (**2d**).* To a solution of 1,2-bis(octyloxy)-4,5-bis(2-thienyl)benzene (**1**) (1.0 g, 2.0 mmol) in dry THF (40 mL) was added n-BuLi (2.4 mL, 2.5 M, 6 mmol) dropwise at −78 °C under argon, and the reaction mixture was allowed to warm to room temperature. After 1.5 h, the reaction was cooled to −78 °C and DMF was added (1.54 mL, 20.0 mmol). The reaction was quenched with saturated solution of NH_4Cl, extracted with EtOAc, dried over $MgSO_4$, and concentrated. Column chromatography using EtOAc/petroleum ether (20:80) gave compound **2d** (1.063 g, 96%), as a yellow low melting solid: mp 36−39 °C; MS (EI) m/z 555 $[MH]^+$; HRMS (EI) calcd for $C_{32}H_{42}O_4S_2$ 554.2525, found m/z = 555.2599 $[M + H]$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.84 (s, 2H), 7.59 (d, J = 3.8 Hz, 2H), 6.98 (s, 2H), 6.87 (d, J = 4.0 Hz, 2H), 4.06 (t, J = 6.4 Hz, 4H), 1.87−1.83 (m, 4H), 1.51−1.47 (m, 4H), 1.46−1.31 (m, 16H), 0.89 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.9, 152.6, 149.9, 136.6, 128.4, 125.1, 115.8, 69.6, 31.9, 29.4, 29.4, 29.2, 26.1, 22.8, 14.2.

*Synthesis of 5,5′-(4,5-bis(octyloxy)-1,2-phenylene)bis(2-methoxythiophene) (**2e**).* To a solution of 2-methoxythiophene (0.600 g, 5.20 mmol) in dry THF (30 mL) was added n-BuLi (2.52 mL, 6.31 mmol, 2.5 M in hexanes) at 0 °C under argon, and the mixture was stirred for 1 h. To this was added tributyltin(IV) chloride (2.05 mL, 6.31 mmol) at 0 °C. The reaction mixture was stirred at this temperature for 1 h. The mixture was filtered through a plug of silica gel to remove inorganic salts. The filtrate was concentrated to give the monostannyl

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derivative (02.12 g, quantitative) as a brown oil. This compound was used immediately in the following reaction without further purification. To a solution of monostannyl compound (2.12 g, 5.07 mmol) and 1,2-dibromo-4,5-bis(octyloxy) benzene (1.00 g, 2.03 mmol) in toluene (35 mL) was added $Pd(PPh_3)_4$ (0.242 g, 10 mol %) under argon, and the mixture was refluxed for 12 h. Toluene was removed under reduced pressure, and the crude product was purified by column chromatography using CH_2Cl_2/petroleum ether (30:70) as eluent to give compound **2e** (1.08 g, 95%) as a off-white solid: mp 30−32 °C; MS (EI) m/z 558 $[MH]^+$; HRMS (EI) calcd for $C_{32}H_{45}O_4S_2$ 558.2838, found m/z = 558.2834; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.90 (s, 2H), 6.51 (d, J = 3.9 Hz, 2H), 6.06 (d, J = 3.9 Hz, 2H), 4.01 (t, J = 6.4 Hz, 4H), 3.85 (s, 6H), 1.84−1.77 (m, 4H), 1.48−1.43 (m, 4H), 1.41−1.28 (m, 16H), 0.94−0.88 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 148.4, 129.0, 126.5, 124.1, 116.1, 103.6, 69.5, 60.2, 31.9, 29.5, 29.4, 29.3, 26.1, 22.8, 14.2.

General Experimental Procedures for Thienyl−Thienyl Oxidative Cyclization. *1. Oxidative Cyclization Using $FeCl_3$.* 2.2 equiv of anhydrous $FeCl_3$ was dissolved in CH_3NO_2 and added dropwise to a solution of the substituted 1,2-bis(2-thienyl)benzene building blocks in dry CH_2Cl_2 at 0 °C under argon for 3 or 4 h. After completion, methanol was added, and the reaction mixture was concentrated and purified by column chromatography.

2. Oxidative Cyclization Using DDQ/acid. 1.5 equiv of DDQ was added to a 0.01 M solution of the substituted 1,2-bis(2-thienyl)-benzene building blocks in dry CH_2Cl_2/acid (9:1) (or 10 equiv of Lewis acid) under an argon atmosphere at 0 °C. After completion, the reaction was quenched with $NaHCO_3$. The organic layer was separated, washed with additional $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography.

3. Photochemical Cyclization. To an argon-purged solution of 1,2-bis(2-thienyl)benzene building block in toluene (3 mM), I_2 was added followed by a large excess of 2-methyloxirane. The reaction mixture was irradiated using a photochemical reactor (350 nm). After completion, the reaction mixture was washed with a saturated solution of $Na_2S_2O_3$. The organic layer was separated, washed with brine, dried over $MgSO_4$, and concentrated. Purification was done using column chromatography.

*Synthesis of 8,9-Bis(octyloxy)naphtho[1,2-b:4,3-b′]dithiophene (**3**).* This compound has been prepared according to the previously reported literature procedure[14] starting from 1,2-bis(octyloxy)-4,5-bis(2-thienyl)benzene. Material identity was confirmed by mp, HRMS, and ^{1}H and ^{13}C NMR.

*Synthesis of 2,5-Dibromo-8,9-bis(octyloxy)naphtho[1,2-b:4,3-b′]-dithiophene (**3a**).* Synthesis according to general procedure of oxidative cyclization using the quinone/acid system: Compound **2a** (1.00 g, 1.52 mmol), DDQ (0.517 g, 2.28 mmol), $MeSO_3H$ (14 mL), CH_2Cl_2 (130 mL). Column chromatography using CH_2Cl_2/petroleum ether (20:80) gave compound **3a** (0.847 g, 85%) as pale yellow solid: mp 122−124 °C; MS (EI) m/z 654 $[MH]^+$; HRMS (EI) calcd for $C_{30}H_{38}Br_2S_2O_2$ 652.0680, found m/z = 652.0772; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (s, 2H, 3-Th), 7.16 (s, 2H), 4.16 (t, J = 6.6 Hz, 4H), 1.95−1.90 (m, 4H), 1.25 (m, 20H), 0.89 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 135.9, 130.7, 125.8, 120.9, 112.7, 105.6, 69.4, 31.9, 29.6, 29.5, 29.2, 26.2, 22.8, 14.3.

Compound **2a** (0.200 g, 0.304 mmol), DDQ (0.103 g, 0.46 mmol), $BF_3{\cdot}OEt_2$ (0.82 mL, 3.04 mmol, 48%), and CH_2Cl_2 (30 mL). Compound **3a** (0.185 g, 93%) was obtained as pale yellow solid. Material identity was confirmed by ^{1}H NMR and ^{13}C NMR

Chloranil/acid: Compound **2a** (0.200 g, 0.304 mmol), chloranil (0.075 g, 0.347 mmol), $MeSO_3H$ (3 mL), CH_2Cl_2 (27 mL). Compound **3a** (0.101 g, 50%) was obtained as pale yellow solid. Material identity confirmed by ^{1}H NMR and ^{13}C NMR

Chloranil/acid: Compound **2a** (0.15 g, 0.228 mmol), chloranil (0.084 g, 0.347 mmol), $BF_3{\cdot}OEt_2$ (0.60 mL, 2.28 mmol), CH_2Cl_2 (18 mL). Compound **3a** (0.110 g, 74%) was obtained as pale yellow solid. Material identity was confirmed by ^{1}H NMR and ^{13}C NMR

$FeCl_3$: Compound **2a** (1.0 g, 1.52 mmol), $FeCl_3$ (0.544 g, 3.35 mmol), CH_3NO_2 (17.3 mL), CH_2Cl_2 (173.3 mL). Compound **3a** (0.518 g, 52%) was obtained as pale yellow solid. Material identity was confirmed by ^{1}H NMR and ^{13}C NMR.

*Synthesis of 2,5-Dimethyl-8,9-bis(octyloxy)naphtho[1,2-b:4,3-b′]-dithiophene (**3b**).* Synthesis according to general procedure of oxidative cyclization. $FeCl_3$: Compound **2b** (0.155 g, 0.29 mmol), $FeCl_3$ (105 mg, 0.67 mmol), $MeNO_2$ (3 mL), CH_2Cl_2 (30 mL). Compound **3b** (0.072 g, 46%) was obtained as a pale white solid: mp 114−118 °C; MS (EI) m/z 524 $[MH]^+$; HRMS (EI) calcd for $C_{32}H_{44}O_2S_2$ 524.2783, found m/z = 525.2853 [M + H]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (s, 2H), 7.28 (s, 2H), 4.15 (t, J = 6.6 Hz, 4H), 2.68 (s, 6H), 1.94−1.89 (m, 4H), 1.47−1.56 (m, 4H), 1.21−1.45 (m, 16H), 0.89 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1, 138.7, 133.4, 132.2, 121.4, 121.1, 106.3, 69.4, 31.9, 29.5, 29.4, 29.3, 26.2, 22.8, 16.2, 14.2.

Photochemical cyclization: Compound **2b** (0.20 g, 0.38 mmol), I_2 (0.097 g, 0.38 mmol), propylene oxide (2.2 mL, 38.8 mmol), toluene (125 mL). Column chromatography using EtOAc/petroleum ether (5:95) gave compound **3b** (0.162 g, 81%) as a pale white solid. Material identity was confirmed by ^{1}H NMR and ^{13}C NMR.

DDQ/acid system: Compound **2b** (0.150 g, 0.285 mmol), DDQ (0.097 g, 0.427 mmol), $BF_3{\cdot}OEt_2$ (0.75 mL, 2.85 mmol, 48%), CH_2Cl_2 (30 mL). Column chromatography using EtOAc/petroleum ether (5:95) gave compound **3b** (0.026 g, 16%) as a pale white solid. Material identity was confirmed by ^{1}HNMR and ^{13}CNMR

*Synthesis of (8,9-Bis(octyloxy)naphtho[1,2-b:4,3-b′]dithiophene-2,5-diyl)bis(trimethylsilane) (**3c**).* Synthesis according to the general procedure for oxidative cyclization did not give any product **3c**. Photochemical cyclization: Compound **2c** (0.100 g, 0.155 mmol), I_2 (0.040 g, 0.155 mmol), propylene oxide (1.0 mL, 15.5 mmol), toluene (52 mL). Column chromatography using CH_2Cl_2/petroleum ether (20:80) gave compound **3c** (0. 080 g, 80%) as white solid: mp 53−75 °C; MS (EI) m/z 641 $[MH]^+$; HRMS (EI) calcd for $C_{36}H_{56}O_2S_2Si_2$ 640.3260, found m/z = 641.3362 [M + H]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (s, 2H), 7.47 (s, 2H), 4.18 (t, J = 6.6 Hz, 4H), 1.97−1.89 (m, 4H), 1.35−1.26 (m, 20 H), 0.89−088 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 139.3, 139.3, 133.5, 130.01, 106.5, 69.2, 31.9, 29.5, 29.4, 29.3, 26.2, 22.8, 14.2, 0.1.

*Synthesis of 2,5-Dimethoxy-8,9-bis(octyloxy)naphtho[1,2-b:4,3-b′]dithiophene (**3e**).* Photochemical cyclization: Compound **2e** (0.100 g, 0.179 mmol), I_2 (0.045 g, 0.179 mmol), propylene oxide (1.0 mL, 17.9 mmol), toluene (60 mL). Column chromatography using CH_2Cl_2/petroleum ether (20:80) gave compound **3e** (0. 026 g, 26%) as a white solid: mp 125−127 °C; MS (EI) m/z 556 $[MH]^+$; HRMS (EI) calcd for $C_{32}H_{44}O_4S_2$ 556.2681, found m/z = 557.2748 [M + H]+; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (s, 2H), 6.59 (s, 2H), 4.12 (t, J = 6.6 Hz, 4H), 4.04 (s, 6H), 1.93−1.88 (m, 4H), 1.54−1.51 (m, 4H), 1.38−0.91 (m, 16H), 0.89−0.87 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 148.8, 129.6, 123.9, 120.9, 105.5, 98.6, 69.3, 60.2, 31.9, 29.5, 29.4, 29.3, 26.2, 22.8, 14.2.

Chloranil/Lewis acid system: Compound **2e** (0.100 g, 0.179 mmol), DDQ (0.044 g, 0.179 mmol), $BF_3{\cdot}OEt_2$ (cat), CH_2Cl_2 (30 mL). Column chromatography using EtOAc/petroleum ether (5:95) gave compound **3e** (0.055 g, 55%) as a pale white solid. Material identity was confirmed by ^{1}H NMR and ^{13}C NMR

*Synthesis of 5,5′-(4,5-Bis(octyloxy)-1,2-phenylene)bis(2-(4,5-bis-(octyloxy)-2-(thiophene-2-yl)phenyl)thiophene) (**4**).* To a solution of 1,2-bis(octyloxy)-4,5-bis(2-thienyl)benzene (**1**) (1.50 g, 3.00 mmol) in dry THF (80 mL) was added *n*-BuLi (1.44 mL, 2.5 M, 3.6 mmol) dropwise at −78 °C under argon and the mixture allowed to stir for 1 h. Tributyltin chloride (1.17 mL, 3.60 mmol) was added at −78 °C, and the reaction mixture was filtered over a silica plug, The filtrate was concentrated to give the monostannyl derivative (2.30 g, quantitative) as a brown oil. This compound was used immediately in the following reaction without further purification. To a solution of monostannyl compound (2.30 g, 2.92 mmol) and 1,2-dibromo-4,5-bis(octyloxy)-benzene (0.575 g, 1.16 mmol) in toluene (50 mL) was added $Pd(PPh_3)_4$ (0.134 g, 10 mol %) under argon, and the mixture was refluxed for 12 h. Toluene was removed under reduced pressure, and the crude product was purified by column chromatography using CH_2Cl_2/petroleum ether (30:70) as eluent to give compound **4** (1.10

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g, 63%) as a yellow solid: mp 51−53 °C; MS (EI) m/z 1326 $[MH]^+$; HRMS (EI) calcd for $C_{82}H_{118}O_6S_4$ 1326.7811, found m/z = 1326.7794; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (dd, ^1J = 3.3 Hz, ^2J = 4.7 Hz, 2H), 6.97 (s, 2H), 6.96 (s, 2H), 6.93 (s, 2H), 6.64 (d, J = 3.5 Hz, 2H), 6.60 (d, J = 3.5 Hz, 2H), 4.04−3.98 (m, 12H), 1.84−1.79 (m, 12 H), 1.46−1.44 (m, 12), 1.31−1.28 (m, 48H), 0.90−0.85 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.7, 148.6, 142.9, 142.8, 126.9, 126.7, 126.5, 126.4, 126.3, 125.3, 116.3, 116.1, 69.5, 31.9, 29.5, 29.4, 29.3, 26.1, 22.8, 14.2.

Synthesis of 5,5′-(4,5-Bis(octyloxy)-1,2-phenylene)bis(2-(2-(5-bromothiophene-2-yl)-4,5-bis(octyloxy)phenyl)thiophenes ***5***. To a solution of compound **4** (200 mg, 0.15 mmol) in CH_2Cl_2/AcOH (1:1, 20 mL), NBS (0.059 g, 0.33 mmol) was added under argon at 0 °C. After 1 h, the reaction was quenched with $NaHCO_3$ and subsequently washed with a saturated $NaHCO_3$ solution, H_2O and brine, dried over $MgSO_4$, and concentrated. Purification by column chromatography using CH_2Cl_2/petroleum ether (35:65) gave compound **5** (0.180 g, 80%) as a yellow oil: MS (EI) m/z 1485 $[MH]^+$; HRMS (EI) m/z [M + Na]+ calcd for $C_{82}H_{116}Br_2O_6S_4Na$ 1505.5919, found m/z = 1505.5892 $[M + Na]^+$; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.95 (s, 2H), s (6.94, 2H), 6.70−6.72 (t, J = 4.1 and 4.0 Hz, 4H), 6.69 (d, J = 3.2 Hz, 2H), 6.60 (d, J = 3.2 Hz, 2H), 4.01 (t, J = 6.4 Hz, 12 H), 1.83−1.81 (m, 12H), 1.41−1.49 (m, 12H), 1.21−1.40 (m, 48H), 0.88 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 148.7, 144.7, 143.2, 142.2, 129.6, 127.3, 127.0, 126.9, 126.4, 126.2, 125.6, 116.1, 115.8, 111.8, 69.5, 69.5, 31.9, 29.5, 29.4, 29.3, 26.1, 22.8, 14.2.

*Synthesis of 5,6,10,11,15,16-Hexakis(octyloxy)tribenzotetrathia[7]helicene (**6a**)*. To an argon-purged solution of compound **4** (0.100 g, 0.07 mmol) in toluene (25 mL) was added I_2 (0.059 g, 0.23 mmol) followed by a large excess of 2-methyloxirane. The reaction mixture was irradiated using a photochemical reactor (350 nm). After completion, the reaction mixture was washed with a saturated solution of $Na_2S_2O_3$. The organic layer was separated, washed with brine, dried over $MgSO_4$, and concentrated. Purification was done using column chromatography using CH_2Cl_2/petroleum ether (30:70) as eluent to give compound **6a** (0.060 g, 60%) as a yellow solid: mp 159−161 °C; MS (EI) m/z 1322 $[MH]^+$; HRMS (EI) calcd for $C_{82}H_{112}O_6S_4$ 1343.7239 [M + Na]+, found m/z = 1343.7179 $[M + Na]^+$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (s, 2H), 7.58 (s, 2H), 7.51 (s, 2H), 7.00 (d, J = 5.4 Hz, 2H), 6.79 (d, J = 5.4 Hz, 2H), 4.31−4.22 (m, 12H), 2.00−1.96 (m, 12H), 1.59−1.55 (m, 12H), 1.39−1.33 (m, 48H), 0.93−0.89 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1, 149.7, 135.4, 134.7, 133.3, 129.9, 128.2, 126.6, 122.4, 121.6, 121.3, 106.5, 106.1, 106.0, 69.4, 32.0, 29.5, 29.4, 29.3, 26.3, 22.8, 14.2.

*Synthesis of 2,19-Dibromo-5,6,10,11,15,16-hexakis(octyloxy)-tribenzotetrathia[7]helicene (**6b**)*. To a solution of compound **5** (0.150 g, 0.101 mmol) in dry CH_2Cl_2 (20 mL) was added BF_3.OEt (0.27 mL, 48% solution in Et_2O, 1.01 mmol dropwise under argon at 0 °C. Subsequently, DDQ (107.7 mg, 0.474 mmol) was added, and the reaction was allowed to stir for 1.5 h. The reaction was quenched with a saturated solution of $NaHCO_3$ and subsequently washed with $NaHCO_3$ and brine. The crude product was dried over $MgSO_4$, concentrated, and purified by column chromatography using CH_2Cl_2/petroleum ether (25:75) to give compound **6b** (0.105 g, 70%) as a yellow solid: mp 232−240 °C; MS (EI) m/z 1480 $[MH]^+$; HRMS (EI) calcd for $C_{82}H_{110}Br_2O_6S_4$ 1476.5552, found m/z = 1499.5450 $[M + Na]^+$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 2H), 7.46 (s, 2H), 7.31 (s, 2H), 6.93 (s, 2H), 4.24−4.23 (m, 12H), 1.99−1.95 (m, 12H), 1.59−1.56 (m, 12H), 1.42−1.34 (m, 48H), 0.93−089 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.3, 150.2, 149.9, 135.9, 135.3, 133.6, 132.6, 129.9, 128.2, 127.3, 122.3, 121.9, 121.5, 110.1, 106.2, 105.8, 105.6, 69.4, 32.0, 29.6, 29.5, 29.3, 26.3, 26.2, 22.8, 14.2.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of the novel precursors and tetrathia[7]helicene **6a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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