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FULL PAPER

Synthesis of Sulfur-Hybridized Pyracylene and the Unexpected Phenyl Shift Mediated Rearrangement of Scholl Reaction

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Abstract: We present here a strategy towards the straightforward synthesis of a novel sulphur-hybridized pyracylene, tetraceno[5,6-bc:11,12-b'c']dithiophene (TDT) derivatives, via 2-fold $FeCl_3$-mediated Scholl reaction. Surprisingly, the substituents on the precursors will guide the synthetic route where quantitatively debromination *vs* phenyl ring shift mediated rearrangement were observed and the rearrangement products were identified by the HR-MALDI-TOF and 2D NMR analyses. Additionally, a retrosynthetic method was adopted to confirm the unexpected reaction results in rearrangement of Scholl reaction.

Introduction

The design and synthesis of fused ring aromatics have attracted considerable interests owing to their potentials in organic electronics applications,[1] such as field-effect transistors,[2] organic light-emitting diodes,[3] and solar cells.[4] One efficient approach toward the development of new oligomers and/or conjugated polymers for particular properties and applications is to integrate the parent structures of fused ring aromatics into conjugated systems.[5] Works are mainly focused on obtaining the end products; however, few efforts have been devoted into the discovery of building-blocks with widespread usages. As the field aims is to products the materials with tunable properties, it is necessary to emphasize the design and synthesis of novel fused ring aromatics. Over the past decade, the synthetic methodologies mainly include cross-coupling reaction, Diels-Alder reaction, alkyne cyclization, photo-cyclization that can serve this purpose.[5,6] Among the acene-based polycyclic aromatic hydrocarbons (PAHs), tetracene and its derivatives which containing heteroatoms such as N, S, O in their aromatic skeletons exhibit unprecedented chemical and physical properties.[7] They have attracted increasing interests owing to their potentially interesting properties that might qualify them as new opto-electronic materials for various applications.[8]

With very few exceptions, most reported tetracene derivatives to date have been constructed by combining functional groups onto tetracene motif to tune their energy levels and solubility.[9] Many innovative bottom-up synthetic strategies have been developed to tetracene based PAHs.[10] For example, the Scholl reaction, that is, oxidized dehydrogeneration cyclization reaction conducted with acidic oxidants such as $FeCl_3$ or DDQ/$MeSO_3H$ is usually preferred.[11,12] Müllen and coworkers synthesize numbers of excellent PAHs molecules by Scholl reaction and have made great contributions to explore the mechanism of Scholl reaction.[13] Very recently, Murata et al. reported the synthesis of dithieno-fused PAH and tetrabenzo-fused pyracylene with a pyracylene moiety starting with 5,11-dibromo-tetracene via a 2-fold Scholl reaction.[14] Whatever the global synthetic strategy were adopted, in most cases the last step is similar, a highly conjugated but flexible molecules has to be fused, that is, transformed into rigid, polycyclic, aromatic plate by the formation of several C-C bonds between adjacent aromatic rings.[6d,15]

On the other hand, by introducing heteroatoms into PAHs will smartly tune their HOMO/LUMO levels, bandgaps, and the crystalline phase via supramolecular interactions.[16] It will be very interesting to introduce heteroatoms into the antiaromatic cyclopentafused PAHs so as to discover interesting physical and chemical properties.[17] Note that despite all of these attracting properties and promising applications, the π-conjugation of naphtho[1,2-b:5,6-b']dithiophene (NDT)[18] was seldom developed to extend their π-delocalization skeletons deeply due to the lack of suitable design principle and synthetic strategy. Herein, we report the design and synthesis of novel tetraceno[5,6-bc:11,12-b'c']dithiophene (TDT) derivatives starting from several 3,3-bisthiophene derivatives (shown in Scheme 1 and 2). Yet, only the bilateral ring fused 2-bromotetraceno[5,6-*bc*:11,12-*b'c'*]dithiophene (**2-BrTDT**, noted as **1**) with debromination was exclusively observed when we adopted the $FeCl_3$-mediated Scholl reaction to synthesize 2,8-dibromotetraceno[5,6-bc:11,12-b'c']dithiophene (2,8-DBrTDT, noted as **7**) (Scheme 2). Furtherly, compound **8** was developed by replacing two bromine atoms in compound **6** with phenyl, 4-methyloxyl-phenyl and 4-methylphenyl groups (Scheme 2). Surprisingly, instead of the bilateral ring fusion products, very complicated reactions took place on **8** under the same Scholl conditions. We are extremely intrigued with these unusual observations associated with the synthesis of S-cyclopenta fused tetracenes. We would like to report our preliminary investigations on these reactions and the corresponding products including, 1) The unexpected products obtained through the rearrangement of Scholl reaction were confirmed with a designed retrosynthetic route, 2) The possible reaction mechanisms were proposed.

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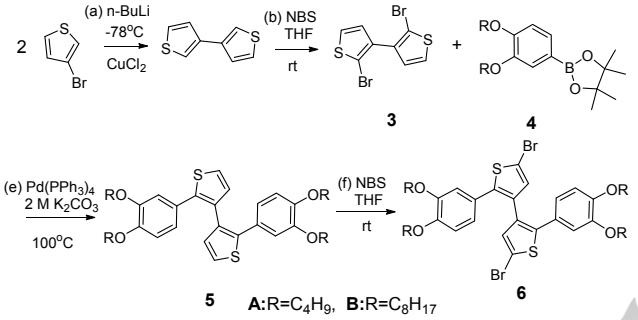
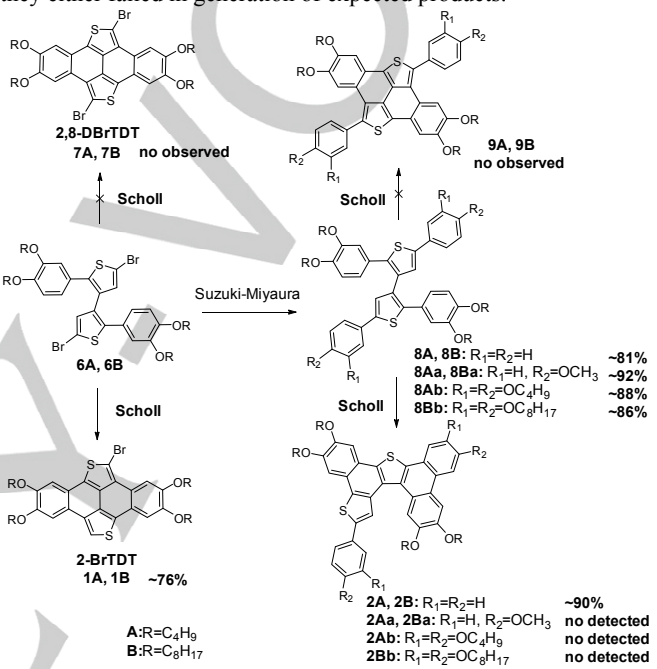
Results and Discussion

As shown in Scheme 1, starting from catechol, **4** was prepared following the reported procedures with optimization in excellent yields.[19] The lithium exchange of 3-bromo-thiophene by addition of *n*-butyl lithium in anhydrous tetrahedronfuran (THF) was followed by a copper-catalyzed coupling reaction to give 3,3'-bisthiophene in a yield of 60%.[20] The bromination with 3,3'-bisthiophene using NBS in THF furnished compound **3**, quantitatively. 3,3'-Bisthiophene-2,2'-bisphenyl (**5**) was obtained via Suzuki-Miyaura coupling reaction starting from compound **3** and **4**. Then, **5** was subjected to NBS mediated bromination to afford the key intermediates of **6**. Interestingly, although very electron-rich, no bromination on the two bisalkyloxylphenyl rings was observed, indicating the electrophilicity of α-thiophene is superior to bisalkyloxylphenyl ring.



Scheme 1. Synthesis of the key intermediate of **6**.

The $FeCl_3$-mediated Scholl reaction has been successfully used for the synthesis of various benzenoid PAHs,[11] PAHs with a pyracylene moiety and other π-extended systems. Given the electron-rich characteristics of **6**, we hypothesized that the 2,2'-alkyloxylphenyl substituted 3,3'-bisthiophene compounds can undergo similar oxidative cyclization reactions to form thiophene rings fused tetracene along the peri-position. To test this idea, a series derivatives of **8** were first prepared from **6** by using a standard Suzuki-Miyaura protocol (Scheme 2). It was also expected that the $FeCl_3$-mediated oxidative cyclodehydrogeneration reaction on **6** can afford compounds **7**, which contains two bromine atoms will be priority to be used as versatile building blocks to develop oligomers or polymers. Surprisingly, the $FeCl_3$ mediated Scholl reaction of **6** and **8** gave very different results. For example, upon 2-fold cyclization of compound **6**, the debrominated products of **1** were isolated in high yields, and no compounds **7** were observed. As well known, the loss of perssad phenomenon is common for the typical Scholl reaction,[21] however, it is rare to observe this kind of quantitative debromination process. To confirm this result, we lowered the ratio of $FeCl_3$ to **6** from 2.2:1 to 1.1:1. Interestingly, only compound **1** and **6** were collected, with no single fused intermediate detected, indicating the $FeCl_3$ mediated oxidization cyclization step run in a cascade fashion leading to a bilateral fusion product.[22] Considering the C-Br bond energy is lower than C-C band[23] and the cleavage of aromatic ring from a conjugated system is difficult, Scholl reaction on compound **8** was conducted with the similar conditions as those for **6**. It was found that the electron-donating property of benzene rings, 4-methoxylbenzene and 3,4-dimethyloxylbenzene rings imparted significant influence on the products of Scholl reaction upon **8**. The $FeCl_3$-mediated Scholl reaction was performed on **8A**/**8B**, which produced an unusual double fused product of **2A**/**2B** in yields around 90% instead of the expected compound **9**. The dehedrogeneration and success in ring-fusion steps of **8A**/**8B** to generate **2A**/**2B** were identified by the HR-MS and 2D NMR analyses. However, when the same Scholl reactions were attempted upon **8Aa/8Ba/8Ab/8Bb**, there was no expected ring fusion products observed. Considering the strong electron donating characteristics of 4-methoxylbenzene and 3,4-dimethyloxylbenzene rings, this is common for **8Aa/8Ba/8Ab/8Bb** under the $FeCl_3$-mediated Scholl reaction, because the mechanism of Scholl reaction involved a cationic generation process.[24] When other Lewis acids, such as Scannium triflates and DDQ/trifluoromethylsufuric acid, for Scholl reaction were used, they either failed in generation of expected products.[12,13,25]



Scheme 2. The ring-fusion toward bithiophene-fused tetracene.

The chemical structure of **1** is unambiguously determined by NMR and HR-MS measurements. As shown in Figure 1, the ^1H NMR spectra of **1A** at low field display five distinct proton signals, indicating the double-fold ring-fusion of compound **6A**. Particularly, when the concentrations of **1A** in $CDCl_3$ increase from 2.0 mg/mL to 60.0 mg/mL, each of these peaks shift to high field, suggesting the existing of strong π-π interaction. This result agrees well with its theoretically simulated planar molecular structure. As seen in Figure S1b, compound **1** displays a planar molecular configuration. In contrast to compound **1**, the ^1H NMR spectra of **2A**/**2B** exhibit very complicated features (see ESI), which suggests the molecular symmetricity of **2A**/**2B** has been disrupted. This notion is consistent with the chemical structure shown in Scheme 2. Fortunately, the chemical structures of **2A**/**2B** can be confirmed with the COSY and NOESY analyses, and the integrations in ^1H NMR spectrum agree well with their chemical structures. As shown in Figure 2 (also see Figure S2), the duplet peaks of H*a*/H*d* and multiplet peaks of H*b*/H*c* can be assigned accordingly, thus, the left duplet peak (at 7.74 ppm) is assigned to proton H*j* according to the *J* values and the COSY analysis deduced from the aromatic regime, proton H*i* is also confirmed. Other singlet peaks are assigned unambiguously according to the NOESY spectrum shown in Figure 3. For instance, H*f* at 8.31 ppm is close to H*g* at 8.51 ppm. Proton H*d* at 8.57 ppm is spatially close to proton H*e* at 8.11 ppm. And the other protons in

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compound **2A** could be assigned accordingly. Thus, the assignment of all protons in compound **2A** can definitely define the chemical structure of compound **2A/2B**.

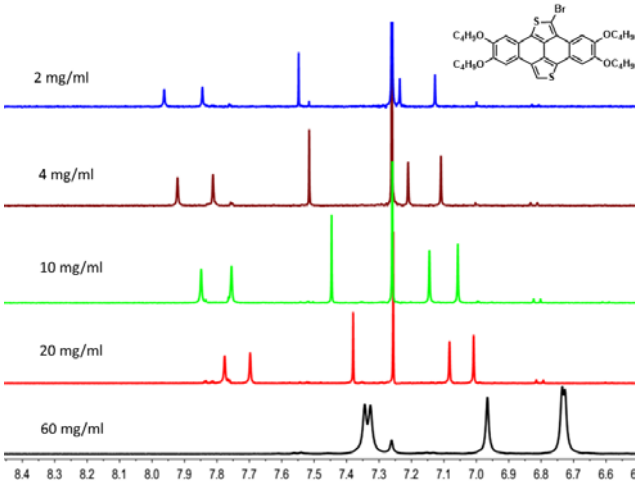


Figure 1. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **1A** at different concentrations for aromatic regime.

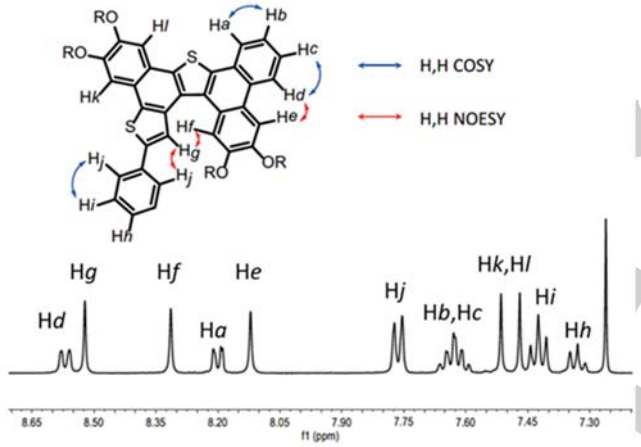
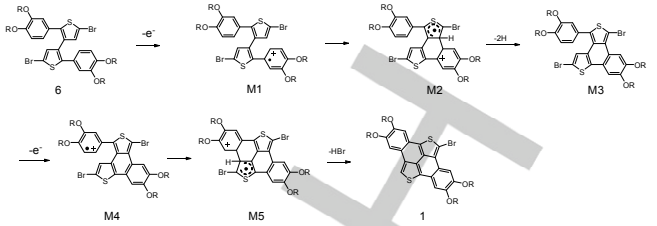
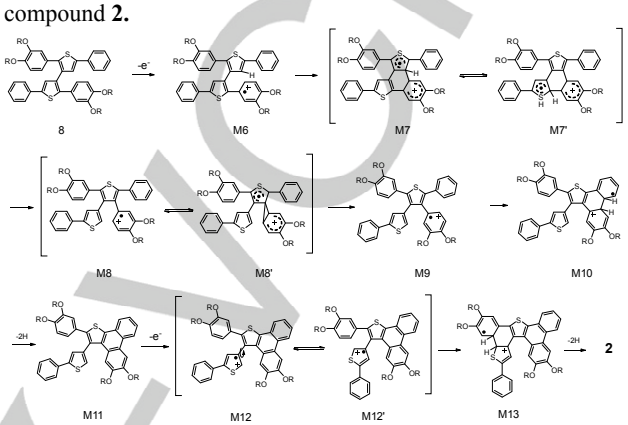


Figure 2. 2D NMR / ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **2A** and the assignment of the corresponding proton signals.

The reactivity and regioselectivity of intramolecular Scholl reactions remain only partially predictable. Not every polyphenylene configuration can be fused to produce PAHs with designed chemical structures, mainly because of incomplete reactions or the unexpected rearrangements.[12,14b] In addition, some experimentally determined regioselectivity remains unexplained.[14c] In this study, both the quantitative debromination in the 2-fold fusion step from **6** to **1** and the aromatic system rearrangement in that from **8A/8B** to **2** are unexpected. Empirically, the debromination could be accounted for the localization of cationic ion on the thiophene motif in compound **6**, which underwent a process as the mechanism shown in Scheme 3. The Scholl reaction of compound **6** likely proceeds by oxidization (**M1**), electrophilic attack (**M2**), deprotonation and subsequently oxidized dehydrogenation to obtain **M3**.[14c] In the second ring-fusion step, **M5** is formed through the same protonation and electrophilic attack process. But, the deprotonation and oxidation process involve the split of HBr, which leads the debrominated products **1** in high yields. We speculate that the split of HBr is caused by more electron rich of the intermediate **M5**.

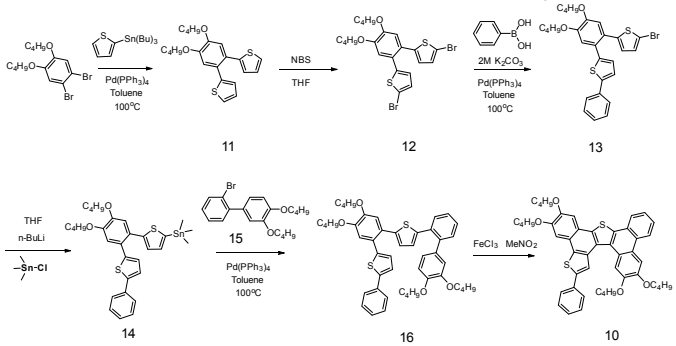


Scheme 3. Possible mechanisms of the Scholl reaction to get compound **2.**



Scheme 4. Possible mechanisms of the Scholl reaction to get compound **2.**

According to the study of rearrangements in the Scholl oxidation reported by King and coworkers,[12,26] the formation of **2** seems reasonable. Scheme 4 depicts the first oxidization step to convert precursor **8A/8B** into radical cation **M6**. Radical cation **M6** can potentially undergo 1,4-shift of the 3,4-dimethyloxylbenzene group to generate radical cation **M8**, through the radical cations **M7** and **M7'** containing a six-member ring as the transition state. Then, **M8** can potentially undergo1,2-shift of the 3,4-dimethyloxylbenzene group to afford radical cation **M9**. After the oxidization dehydrogenation step, **M11** is formed. **M11** can occur the same protonation.Then, the thienyl ring in the radical cation **M12** rotates to **M12'** as the transition state. Subsequently, compound **2** is formed after the deproton step. Obviously, during the first Scholl oxidation stage for compound **8A/8B**, a phenyl migration occurs to convert **M8** into **M8'**. This mechanism speculated by us, which involves a possible cleave of phenyl ring followed by intramolecular migration to form a rearrangement ring-fusion product, has never been reported before. Furthermore, we attempt to propose a retrosynthetic strategy to confirm the chemical structure of compound **2A**, instead of the indirect evidences of the COSY and NOESY analyses.



Scheme 5. Retrosynthesis of compound **10** for identification of its chemical structure.

As shown in Scheme 5, compound **10** can be obtained starting from **11**, where short alkyl chains were used for simplifying the NMR spectrum. Obviously, the two key intermediates, **13** and **16**, can be obtained via common coupling reactions with designed building blocks. Finally, compound **16** undergoes a two-fold Scholl reaction to give compound **10**.[27] As shown in Figure S4, all intermediates mentioned in this retrosynthetic route were unambiguously identified. Since the only reactive site in compound **16** is designed. the chemical structure of compound **10** can be deduced by the conventional consideration of Scholl reaction. Excitingly, the proton peaks shown in aromatic regime of compound **2A** and compound **10** agree very well at the same molar concentration in $CDCl_3$. In addition, their ^{13}C NMR spectra are also the same at the low field (see ESI, Figure S3 and S4). As a result, we exclusively confirmed the phenyl ring migration mediated rearrangement of the Scholl reaction in converting **8A** to **2A**.

With **1** and **2** in hand, their absorption spectra and cyclic voltammograms were measured to elucidate their electronic properties, and the data were summarized in Table 1. Figure 3 shows the UV-vis absorption spectra of **6A** and **1A**. After the ring fusion, the absorption maximum of **1A** (at 356 nm) shows a red shift in comparison with that of **6A** (at 310 nm). Similarly, as to **2A** and **8A**, the absorption maximum of **2A** red-shifted about 36 nm in comparison with that of **8A**, indicating **2A** has a lower band-gap and more extended π-conjugation system. The HOMO/LUMO energy levels were determined to be -5.50/-3.50 eV for **6A**, -5.12/-3.48 eV for **1A**. Meanwhile, -5.40/-3.51 eV for **8A** and -5.38/-3.53 eV for **2A** from their onsets of the first oxidation/reduction waves. The corresponding electrochemical energy gaps were then estimated to be 2.00 (**6A**), 1.64 (**1A**) and 1.89 (**8A**) and 1.85 eV (**2A**). The calculations on HOMO-LUMO energy levels for **1** and **2** also predicted a significant decrease of band gaps, which is consistent with the experiment data.

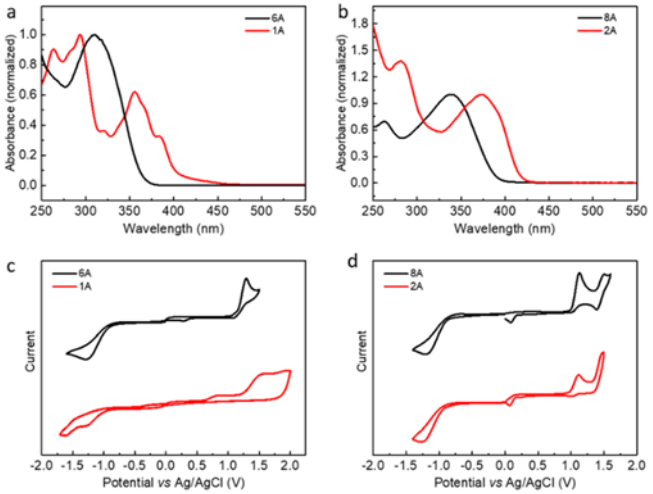


Figure 3. (a, b) UV-vis absorption spectra of **6A/1A** and **8A/2A**; (c, d) cyclic voltammograms of **6A/1A** and **8A/2A** in dry dichloromethane.

Table 1 Summary of Photophysical properties and Electrochemical Data of compound **6**, **8**, **1** and **2**.

Compound	λ_{ab}^{max} (nm)	E_{ox}^{onset} [a] (V)	E_{red}^{onset} [a] (V)	HOMO [b] (eV)	LUMO [c] (eV)	E_g [d] (eV)	HOMO [e] (eV)	LUMO [e] (eV)
6A,6B	310	1.10	–0.90	–5.50	–3.50	2.00	–4.74	–1.17
8A, 8B	263,339	1.00	–0.89	–5.40	–3.51	1.89	–4.88	–1.19
1A,1B	263, 294,356	0.72	–0.92	–5.12	–3.48	1.64	–4.83	–1.43
2A,2B	282,375	0.98	–0.87	–5.38	–3.53	2.05	–5.00	–1.37

[a] $E_{ox}^{onset}$is the onset potential of the first oxidation wave relative to Fc^+/Fc. Fc^+/Fc was used as internal reference for the measurements, $E_{1/2}$ = 0.40 V for Fc^+/Fc *vs* Ag/AgCl. [b] HOMO = − (4.40 + E_{ox}^{onset}). [c] LUMO = − (4.40 + E_{red}^{onset}) [d] E_g = LUMO – HOMO [e] values obtained by theoretical simulation.

Conclusion

In summary, we have synthesized a family of sulfur-hybridized pyracylene (**1A**/**1B**) via 2-fold Scholl cyclization with quantitatively single debromination. The same Scholl reaction conducted on derivatives of **8** delivered very different results. An unusual phenyl-shift mediated rearrangement Scholl reaction was observed and afforded 2-fold fused product of **2**. According to the ^1H NMR, ^{13}C NMR, HR-MALDI-TOF, 2D NMR analyses and retrosynthetic strategy, the chemical structures of **1A**/**1B** and **2A**/**2B** are determined unambiguously. A possible mechanism for debromination and phenyl-migration mediated rearrangement both were proposed. For the first time, the retrosynthesis of PAHs was realized and used to confirm an unusual rearrangement. Further studies on sulfur hybridized pyracylene for applications in low-band gap materials or other organic electronic applications are currently in progress in our laboratory and will be reported in due course.

Experimental Section

General: All reagents were commercially supplied and used as received without any further treatment. Anhydrous DCM and N,N-dimethylformaldehyde (DMF) were freshly distilled from CaH_2. Toluene and THF were distilled from sodium benzophenone immediately prior to use. The ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on NMR spectrometer with tetramethylsilane (TMS) as the standard. The chemical shift was recorded in ppm, and the following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. MALDI-TOF mass spectra were measured by using *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as a matrix. UV-vis absorption and fluorescence spectra were recorded in HPLC pure solvents. The electrochemical measurements were carried out in anhydrous DCM with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte at a scan rate of 0.02 V/s at room temperature under the protection of nitrogen. A gold disk was used as working electrode, platinum wire was used as counting electrode, and Ag/AgCl (3 M KCl solution) was used as reference electrode. Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCI MS) measurements were performed on a Finnigan TSQ 7000 triple stage quadrupole mass spectrometer.

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2-(3,4-dibutoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4A). To a 50 mL dry two-necked flask containing 4-bromo-1,2-dibutoxybenzene (4.21 g, 13.99 mmol), 40 mL of THF was added dropwise 9.62 mL (15.39 mmol) of 1.6 M n-BuLi at -78°C under N_2. After stirring at -78°C for 3 hr, then isopropoxyboronic acid pinacol ester (2.86 g, 15.39 mmol) was added. The resulting solution was allowed to warm up to room temperature and stirred overnight. The resulting was poured into water and the product was extracted with ethyl acetate (3×100 mL). The organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel, ethyl acetate/petroleum ether, 1:10) to give a canary yellow oily liquid (4.23 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.39 (m, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 1.4 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 4.03 (m, *J* = 6.6 Hz, 4H), 1.84 – 1.77 (m, 4H), 1.51 (m, *J* = 7.5 Hz, 4H), 1.33 (s, 12H), 0.98 (m, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 152.07, 148.59, 128.72, 119.67, 112.84, 83.51, 68.99, 68.58, 31.52, 31.29, 24.86, 19.28, 19.23, 13.90, 13.85.

(4B) Apart from the formation of **4A** using the conditions mentioned above, **4B** can be separated as a canary yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.41 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.32 (d, *J* = 1.4 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 4.03 (dt, *J* = 10.9, 6.6 Hz, 4H), 1.87 – 1.80 (m, 4H), 1.48 (br, 4H), 1.38 – 1.27 (m, 28H), 0.90 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 151.99, 148.52, 128.69, 119.45, 112.66, 83.50, 69.21, 68.82, 31.88, 31.86, 29.44, 29.41, 29.34, 29.32, 29.24, 26.11, 26.05, 24.86, 22.72, 22.71, 14.13.

2,2'-bis(3,4-dibutoxyphenyl)-3,3'-bithiophene (5A). To a 50 mL flask was added 2-(3,4-dibutoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.77 g, 2.23 mmol), 2,2'-dibromo-3,3'-bithiophene (0.30 g, 0.93 mmol), $Pd(PPh_3)_4$ (15 mg), toluene (15 mL) and 2 M K_2CO_3 (6.0 mL). The solution mixture was heated to 110°C overnight under N_2 in the dark. After cooling to room temperature, the reaction mixture was poured into water and extracted with dichloromethane (3 × 20 mL). The organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel, DCM/petroleum ether, 1:4) to give a white solid (0.42 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.16 (d, *J* = 5.2 Hz, 2H), 6.87 (d, *J* = 5.2 Hz, 2H), 6.76 (m, 2H), 6.70 (m, 4H), 3.96 (t, *J* = 6.7 Hz, 4H), 3.70 (t, *J* = 6.7 Hz, 4H), 1.82 – 1.75 (m, 4H), 1.70 – 1.63 (m, 4H), 1.52 – 1.45 (m, 4H), 1.45 – 1.37 (m, 4H), 0.95 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 148.65, 148.36, 140.10, 132.36, 130.78, 127.11, 122.89, 120.78, 113.53, 113.48, 68.93, 68.50, 31.33, 31.14, 19.23, 19.17, 13.89, 13.85. MS (Maldi-TOF, positive mode, DCTB in chloroform) Calcd for $C_{36}H_{46}O_4S_2$: 606.28; found: 606.33. Elemental Analysis: calcd for C, 71.25; H, 7.64. Found C, 71.28; H, 7.62.

(5B). Apart from the formation of **5A** using the conditions mentioned above, **5B** can be separated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.15 (d, *J* = 5.2 Hz, 2H), 6.86 (d, *J* = 5.2 Hz, 2H), 6.75 (dd, *J* = 8.3, 2.0 Hz, 2H), 6.69 (dd, *J* = 5.2, 3.1 Hz, 4H), 3.94 (t, *J* = 6.7 Hz, 4H), 3.68 (t, *J* = 6.7 Hz, 4H), 1.83 – 1.74 (m, 4H), 1.67 (m, 4H), 1.43 (m, 4H), 1.33 – 1.23 (br, 36H), 0.88 (t, *J* = 6.9 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 148.89, 148.78, 142.26, 132.76, 131.33, 125.67, 120.66, 113.43, 113.15, 109.71, 69.21, 68.98, 31.85, 31.83, 29.40, 29.38, 29.33, 29.28, 29.25, 26.02, 25.99, 22.70, 22.68, 14.12, 14.10. MS (Maldi-TOF, positive mode, DCTB in chloroform) Calcd for $C_{52}H_{78}O_4S_2$: 830.53. found: 830.25. Elemental Analysis: calcd for C, 75.13; H, 9.46; found C, 75.15; H, 9.43.

5,5'-dibromo-2,2'-bis(3,4-dibutoxyphenyl)-3,3'-bithiophene (6A). **5** (133 mg, 0.22 mmol), N-bromosuccinimid (78 mg, 0.44 mmol) were dissolved in THF (10 ml). The mixture was stirred in the dark for 3 h. The resulting was poured into water and the product was extracted with dichloromethane (3×10 mL). The organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The product was collected by filtration and rinsed with methanol, and recrystallization from 1:1 dichloroethane/methanol affording the title product as a white solid (151 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 6.82 (s, 2H), 6.70 (d, *J* = 8.3 Hz, 2H), 6.68 – 6.64 (m, 2H), 6.62 (d, *J* = 2.0 Hz, 2H), 3.96 (t, *J* = 6.7 Hz, 4H), 3.73 (t, *J* = 6.7 Hz, 4H), 1.82 – 1.75 (m, 4H), 1.74 – 1.66 (m, 4H), 1.54 – 1.40 (m, 8H), 0.96 (dt, *J* = 10.2, 7.4 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm):148.91, 148.79, 142.26, 132.76, 131.32, 125.69, 120.70, 113.47, 113.20, 109.74, 68.91, 68.70, 31.27, 31.14, 19.22, 13.88. MS (Maldi-TOF, positive mode, DCTB in chloroform) Calcd for $C_{36}H_{44}Br_2O_4S_2$: 762.10; found: 762.66.

(6B). Apart from the formation of **6A** using the conditions mentioned above, **6B** can be separated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 6.81 (s, 2H), 6.70 (t, *J* = 8.3 Hz, 2H), 6.67 – 6.61 (m, 4H), 3.95 (t, *J* = 6.7 Hz, 4H), 3.71 (t, *J* = 6.8 Hz, 4H), 1.79 (m, 4H), 1.70 (m, 4H), 1.42 (m, 8H), 1.28 (m, 32H), 0.88 (t, *J* = 6.9 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm) 148.88, 148.78, 142.26, 132.76, 131.32, 125.66, 120.66, 113.42, 113.14, 109.71, 69.20, 68.97, 31.85, 31.84, 29.41, 29.38, 29.33, 29.29, 29.25, 26.03, 25.99, 22.71, 22.68, 14.13, 14.11. MS (Maldi-TOF, positive mode, DCTB in chloroform) Calcd for $C_{64}H_{76}Br_2O_4S_2$: 986.36; found: 986.65.

2-bromo-4,5,10,11-tetrabutoxytetraceno[5,6-bc:11,12-b'c']dithiophene (1A). To a solution of **6A** (114 mg, 0.15 mmol) in 50 mL dry dichloroethane was added dropwise a solution of iron(III) chloride (96 mg, 0.60 mmol) in 2 mL of nitromethane. After complete addition, the reaction mixture was allowed to stir for 5min. Methanol (50 mL) was added and then the reaction mixture was stirred for 10 min. the reaction mixture was poured into water and extracted with dichlorome. The organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel, DCM/petroleum ether, 1:3) to give a brick-red solid (78 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.67 (s, 1H), 7.62 (s, 1H), 7.28 (s, 1H), 7.00 (s, 1H), 6.95 (s, 1H), 4.19 – 4.07 (m, 8H), 1.89 (d, *J* = 6.3 Hz, 8H), 1.59 (dd, *J* = 9.8, 5.2 Hz, 8H), 1.08 – 1.02 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm):148.69, 148.58, 148.40, 147.69, 135.75, 132.49, 130.19, 124.40, 122.01, 111.87, 109.93, 108.22, 105.19, 104.61, 87.81, 69.46, 68.89, 68.37, 68.29, 31.70, 31.58, 31.34, 19.42, 19.41, 14.12, 14.09. HR-Mass (APCI) (m/z): $[M+H]^+$ Calcd for $C_{36}H_{42}BrO_4S_2$, 681.1715; Found $C_{36}H_{42}BrO_4S_2$, 681.1702.

(1B). Apart from the formation of **1A** using the conditions mentioned above, **1B** can be separated as a brick-red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.88 (s, 1H), 7.78 (s, 1H), 7.47 (s, 1H), 7.17 (s, 1H), 7.07 (s, 1H), 4.22 – 4.08 (m, 8H), 1.99 – 1.87 (m, 8H), 1.55 (m, 8H), 1.30 (m, 32H), 0.91 – 0.85 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 148.81, 148.68, 148.49, 147.72, 135.82, 132.58, 130.14, 128.33, 124.74, 124.49, 124.43, 123.01, 122.09, 112.01, 109.87, 108.41, 105.26, 104.73, 87.83, 69.74, 69.29, 68.73, 68.63, 32.00, 31.96, 31.95, 29.70, 29.49, 29.44, 29.42, 26.23, 22.78, 14.48, 14.17, 14.16. HR-Mass (APCI) (m/z): $[M+H]^+$ Calcd for $C_{52}H_{74}BrO_4S_2$, 905.4223; Found $C_{52}H_{74}BrO_4S_2$, 905.4206.

(8A). To a 25 mL two-neck round-bottom flask was added **6A** (0.30 g, 0.39 mmol), phenylboronic acid (0.11 g, 0.94 mmol), $Pd(PPh_3)_4$ (15 mg), THF (10 mL) and 2 M K_2CO_3 (5.0 mL). The solution

mixture was heated to 70°C overnight under N_2 in the dark. After cooling to room temperature, the reaction mixture was poured into water and extracted with dichloromethane (3 × 20 mL). The organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel, DCM/Petroleum ether, 1:2) to give a yellow solid (0.24 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.56 (d, *J* = 7.5 Hz, 4H), 7.36 (t, *J* = 7.6 Hz, 4H), 7.28 (d, *J* = 7.4 Hz, 2H), 7.25 (s, 1H), 7.19 (s, 2H), 6.88 – 6.82 (m, 4H), 6.72 (d, *J* = 8.2 Hz, 2H), 3.96 (t, *J* = 6.7 Hz, 4H), 3.70 (t, *J* = 6.7 Hz, 4H), 1.78 (s, 4H), 1.63 (s, 4H), 1.47 (d, *J* = 7.5 Hz, 4H), 1.32 (d, *J* = 7.5 Hz, 4H), 0.96 (t, *J* = 7.4 Hz, 6H), 0.84 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ(ppm):148.73, 148.46, 141.31, 139.72, 134.10, 133.24, 128.92, 127.49, 126.92, 125.42, 120.47, 113.54, 113.07, 69.26, 68.85, 31.86, 31.84, 29.43, 29.36, 29.31, 29.29, 29.13, 26.04, 25.91, 22.72, 22.70, 14.15, 14.12. MS (Maldi-TOF, positive mode, DCTB in chloroform) Calcd for $C_{48}H_{54}O_4S_2$: 758.35; found: 758.09. Elemental Analysis: calcd for C, 75.95; H, 7.17. found C, 75.98; H, 7.16.

(8B). Apart from the formation of **8A** using the conditions mentioned above, **8B** can be separated as a yellow solid solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.58 – 7.54 (m, 4H), 7.36 (t, *J* = 7.6 Hz, 4H), 7.28 – 7.25 (m, 2H), 7.18 (s, 2H), 6.85 (m, 4H), 6.71 (d, *J* = 8.2 Hz, 2H), 3.94 (t, *J* = 6.7 Hz, 4H), 3.68 (t, *J* = 6.8 Hz, 4H), 1.83 – 1.74 (m, 4H), 1.67 – 1.59 (m, 4H), 1.47 – 1.38 (m, 4H), 1.32 – 1.17 (m, 36H), 0.88 (t, *J* = 7.0 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 148.73, 148.46, 141.31, 139.72, 134.10, 133.24, 128.92, 127.49, 126.92, 126.65, 125.42, 120.47, 113.54, 113.07, 69.26, 68.85, 31.86, 31.84, 29.43, 29.36, 29.31, 29.29, 29.13, 26.04, 25.91, 22.72, 22.70, 14.15, 14.12. MS (Maldi-TOF, positive mode, DCTB in chloroform) MS (Maldi-TOF, positive mode, DCTB in chloroform) Calcd for $C_{64}H_{86}O_4S_2$: 982.60, found: 982.87. Elemental Analysis: calcd for C, 78.16; H, 8.81. found C, 78.20; H, 8.77.

(2A). To a solution of **8A** (103 mg, 0.13 mmol) in 50 mL dry dichloroethane was added dropwise a solution of iron(III) chloride (96 mg, 0.60 mmol) in 2 mL of nitromethane. After complete addition, the reaction mixture was allowed to stir for 5min. Methanol (50 mL) was added and then the reaction mixture was stirred for 10 min. the reaction mixture was poured into water and extracted with dichlorome. The organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel, DCM/Petroleum ether, 1:1) to give a yellow solid (91 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.50 – 7.46 (m, 4H), 7.06 (s, 2H), 6.91 – 6.84 (m, 8H), 6.71 (d, *J* = 8.7 Hz, 2H), 3.95 (t, *J* = 6.7 Hz, 4H), 3.83 (s, 6H), 3.70 (t, *J* = 6.7 Hz, 4H), 1.80 – 1.74 (m, 4H), 1.65 – 1.59 (m, 4H), 1.47 (d, *J* = 7.5 Hz, 4H), 1.32 (d, *J* = 7.5 Hz, 4H), 0.95 (d, *J* = 7.4 Hz, 6H), 0.84 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ(ppm): 149.91, 149.61, 148.30, 148.14, 140.21, 135.77,134.99, 134.53, 134.31, 132.49, 130.75, 129.11, 129.02, 127.84, 127.40, 126.26, 126.15, 125.81, 124.64,124.43, 124.01, 122.90, 122.33, 122.28, 121.60, 109.64, 106.03, 69.02, 68.83, 31.50, 31.30, 31.27, 31.20, 19.44, 19.41, 19.01, 14.08, 14.06, 13.75. MS (Maldi-TOF, positive mode, DCTB in chloroform) Calcd for $C_{48}H_{50}O_4S_2$: 754.32; found: 753.84. Elemental Analysis: calcd for C, 76.36; H, 6.68. found C, 76.39; H, 6.66.

(2B). Apart from the formation of **8A** using the conditions mentioned above, **8B** can be separated as a yellow solid solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.57 (d, *J* = 7.5 Hz, 1H), 8.52 (s, 1H), 8.31 (s, 1H), 8.22 – 8.18 (m, 1H), 8.12 (s, 1H), 7.76 (d, *J* = 7.4 Hz, 2H), 7.67 – 7.58 (m, 2H), 7.51 (s, 1H), 7.47 (s, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 4.33 – 4.20 (m, 6H), 4.02 (t, *J* = 6.8 Hz, 2H), 2.00 (m, *J* = 14.7, 7.4 Hz, 6H), 1.70 (br, 2H), 1.58 (br, 6H), 1.27 (m, 34H), 0.95 – 0.85 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 149.83, 149.54, 148.24, 148.07, 140.05, 135.73, 134.97, 134.48, 134.31, 132.40, 130.72, 129.08, 129.01, 128.38, 127.80, 127.38, 126.19, 126.07, 125.75, 124.62, 124.39, 123.97, 122.87, 122.31, 122.20, 121.56, 109.62, 106.65, 105.94, 105.35, 69.28, 69.17, 69.13, 31.97, 31.96, 31.82, 29.76, 29.60, 29.57, 29.47, 29.44, 29.43, 29.36, 29.30, 29.25, 26.26, 26.20, 26.19, 25.80, 22.80, 22.79, 22.78, 22.74, 14.21, 14.18. HR-Mass (APCI) (m/z): $[M+H]^+$ Calcd for $C_{64}H_{83}O_4S_2$, 979.5720; Found $C_{64}H_{83}O_4S_2$, 979.5727.

(8Aa). To a 25 mL two-neck round-bottom flask was added **6A** (0.30 g, 0.39 mmol), 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.22 g, 0.94 mmol), $Pd(PPh_3)_4$ (15 mg),THF (10 mL) and 2 M K_2CO_3 (5.0 mL). The solution mixture was heated to 70°C overnight under N_2 in the dark. After cooling to room temperature, the reaction mixture was poured into water and extracted with dichloromethane (3 × 20 mL). The organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel, DCM/Petroleum ether, 2:3) to give a yellow solid (0.30 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.50 – 7.46 (m, 4H), 7.06 (s, 2H), 6.91 – 6.84 (m, 8H), 6.71 (d, *J* = 8.7 Hz, 2H), 3.95 (t, *J* = 6.7 Hz, 4H), 3.83 (s, 6H), 3.70 (t, *J* = 6.7 Hz, 4H), 1.80 – 1.74 (m, 4H), 1.65 – 1.59 (m, 4H), 1.47 (d, *J* = 7.5 Hz, 4H), 1.32 (d, *J* = 7.5 Hz, 4H), 0.95 (d, *J* = 7.4 Hz, 6H), 0.84 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ(ppm): 159.21, 148.67, 148.28, 141.21, 138.54, 133.26, 127.09, 126.70, 125.63, 120.36, 114.30, 113.51, 113.01, 68.93, 68.49, 55.39, 31.30, 31.11, 19.23, 19.10, 13.91, 13.82. MS (Maldi-TOF, positive mode, DCTB in chloroform) Calcd for $C_{50}H_{58}O_6S_2$: 818.37; found: 817.90. Elemental Analysis: calcd for C, 73.32; H, 7.14. found C, 73.33; H, 7.12.

(8Ba). Apart from the formation of **8Aa** using the conditions mentioned above, **8Ba** can be separated as a yellow solid solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) 7.50 – 7.46 (m, 4H), 7.06 (s, 2H), 6.92 – 6.87 (m, 4H), 6.87 – 6.82 (m, 4H), 6.70 (d, *J* = 8.0 Hz, 2H), 3.94 (t, *J* = 6.7 Hz, 4H), 3.83 (s, 6H), 3.68 (t, *J* = 6.8 Hz, 4H), 1.82 – 1.74 (m, 4H), 1.62 (m, 4H), 1.43 (m, 4H), 1.27 (m, 32H), 0.88 (t, *J* = 7.0 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 159.20, 148.60, 148.21, 141.20, 138.54, 133.27, 127.04, 126.97, 126.70, 125.62, 120.29, 114.29, 113.39, 112.85, 77.38, 77.07, 76.75, 69.20, 68.75, 55.36, 31.86, 29.44, 29.38, 29.35, 29.32, 26.04, 25.92, 22.74, 22.71, 14.17, 14.15. MS (Maldi-TOF, positive mode, DCTB in chloroform) Calcd for $C_{66}H_{90}O_6S_2$: 1142.62; found: 1042.83. Elemental Analysis: calcd for C, 75.96; H, 8.69. found C, 75.97; H, 8.67.

(8Ab). To a 25 mL two-neck round-bottom flask was added **6A** (0.30 g, 0.39 mmol), 2-(3,4-dibutoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(0.33 g, 0.94 mmol), $Pd(PPh_3)_4$ (15 mg), THF (10 mL) and 2 M K_2CO_3 (5.0 mL). The solution mixture was heated to 70°C overnight under N_2 in the dark. After cooling to room temperature, the reaction mixture was poured into water and extracted with dichloromethane (3 × 20 mL). The organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel, DCM/Petroleum ether, 1:4) to give a yellow solid (0.35 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.12 – 7.05 (m, 6H), 6.88 – 6.80 (m, 6H), 6.70 (d, *J* = 8.5 Hz, 2H), 4.03 (td, *J* = 6.6, 2.7 Hz, 8H), 3.94 (t, *J* = 6.7 Hz, 4H), 3.69 (t, *J* = 6.7 Hz, 4H), 1.91 – 1.68 (m, 12H), 1.66 – 1.39 (m, 4H), 1.35 – 1.06 (m, 16H), 1.07 – 0.78 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$)

δ(ppm):149.36, 149.00, 148.66, 148.26, 141.49, 138.58, 133.24, 127.30, 125.71, 120.29, 118.24, 114.07, 113.47, 112.90, 111.35, 69.10, 68.92, 68.46, 31.38, 31.33, 31.30, 31.13, 19.27, 19.25, 19.22, 19.11, 13.93, 13.01. MS (Maldi-TOF, positive mode, DCTB in chloroform) Calcd for $C_{64}H_{86}O_8S_2$: 1046.58; found: 1046.10. Elemental Analysis: calcd for C, 73.38; H, 8.28. found C, 73.40; H, 8.27.

(8Bb). Apart from the formation of **8Ab** using the conditions mentioned above, **8Bb** can be separated as a yellow solid solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.08 (dt, *J* = 7.3, 2.7 Hz, 6H), 6.87 – 6.80 (m, 6H), 6.69 (d, *J* = 8.1 Hz, 2H), 4.01 (td, *J* = 6.6, 3.7 Hz, 8H), 3.93 (t, *J* = 6.7 Hz, 4H), 3.67 (t, *J* = 6.7 Hz, 4H), 1.85 – 1.63 (m, 16H), 1.52 – 1.38 (m, 16H), 1.25 (m, 64H), 0.87 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 149.36, 148.99, 148.63, 148.22, 125.69, 120.24, 118.22, 113.99, 113.43, 112.84, 111.29, 69.38, 69.23, 68.76, 31.85, 29.43, 29.39, 29.35, 29.32, 29.28, 29.12, 26.08, 26.05, 26.03, 25.94, 22.70, 14.13. MS (Maldi-TOF, positive mode, DCTB in chloroform) Calcd for $C_{96}H_{150}O_8S_2$: 1495.08; found: 1495.23. Elemental Analysis: calcd for C, 77.06; H, 10.10. found C, 77.08; H, 10.09.

2,2'-(4,5-dibutoxy-1,2-phenylene)dithiophene (11) To a 25 mL two-neck round-bottom flask was added 1,2-dibromo-4,5-dibutoxybenzene (2.00 g, 5.26 mmol), 2-(tributylstannyl)thiophene (4.32 g, 11.58 mmol), $Pd(PPh_3)_4$ (15 mg), toluene (20 mL). The solution mixture was heated to 100°C overnight under N_2 in the dark. After cooling to room temperature, the reaction mixture was poured into water and extracted with dichloromethane (3 × 20 mL). The organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel, DCM/Petroleum ether, 1:8) to give a yellow solid (1.72 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.23 (dd, *J* = 5.1, 1.1 Hz, 2H), 7.00 (s, 2H), 6.94 (dd, *J* = 5.1, 3.5 Hz, 2H), 6.84 (dd, *J* = 3.5, 0.7 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 4H), 1.86 – 1.79 (m, 4H), 1.52 (m, 4H), 0.99 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 148.67, 142.96, 126.84, 126.73, 126.38, 125.47, 116.24, 69.13, 31.33, 19.28, 13.93.

5,5'-(4,5-dibutoxy-1,2-phenylene)bis(2-bromothiophene) (12) Compound **11** (1.50 g, 3.89 mmol), N-bromosuccinimid (1.38 g, 7.77 mmol) were dissolved in THF (15 ml). The mixture was stirred in the dark for 3 h. The resulting was poured into water and the product was extracted with dichloromethane (3×10 mL). The organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The product was collected by filtration and rinsed with methanol, and recrystallization from 1:1 dichloroethane/methanol affording the title product as a white solid (2.07 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 6.91 (d, *J* = 3.9 Hz, 4H), 6.61 (d, *J* = 3.8 Hz, 2H), 4.03 (t, *J* = 6.6 Hz, 4H), 1.86 – 1.79 (m, 4H), 1.51 (m, 4H), 0.98 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 149.01, 144.03, 129.84, 127.14, 125.38, 115.84, 112.03, 69.12, 31.24, 19.24, 13.90.

2-bromo-5-(4,5-dibutoxy-2-(5-phenylthiophen-2-yl)phenyl)thiophene (13) To a 25 mL two-neck round-bottom flask was added compound **12** (1.50 g, 2.76 mmol), phenylboronic acid (0.36 g, 2.76 mmol), $Pd(PPh_3)_4$ (15 mg), THF (10 mL) and 2 M K_2CO_3 (5.0 mL). The solution mixture was heated to 70°C overnight under N_2 in the dark. After cooling to room temperature, the reaction mixture was poured into water and extracted with dichloromethane (3 × 20 mL). The organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel, DCM/Petroleum ether, 1:8) to give a yellow solid (0.46 g, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.59 – 7.56 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.28 (s, 1H), 7.24 (s, 1H), 7.17 (d, *J* = 3.7 Hz, 1H), 7.01 (s, 1H), 6.93 (s, 1H), 6.90 (d, *J* = 3.8 Hz, 1H), 6.80 (d, *J* = 3.7 Hz, 1H), 6.66 (d, *J* = 3.8 Hz, 1H), 4.05 (dd, *J* = 12.3, 6.5 Hz, 4H), 1.87 – 1.80 (m, 4H), 1.52 (m, 4H), 0.99 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 149.02, 148.76, 144.51, 144.37, 141.79, 134.32, 129.81, 129.80, 128.90, 127.97, 127.43, 126.99, 126.24, 125.63, 125.31, 123.10, 115.97, 111.80, 69.16, 69.10, 31.28, 19.27, 13.92.

(5-(4,5-dibutoxy-2-(5-phenylthiophen-2-yl)phenyl)thiophen-2-yl)trimethylstannane (14) To a solution of compound **13** (0.40 g, 0.74 mmol) in dry THF (10 mL), n-BuLi (0.50 mL, 1.6 M in hexanes) was added via syringe at -78°C under N_2. The mixture was kept at -78°C for 2 hr before trimethyltin chloride (0.75 mL, 1 M in THF) was added. The reaction mixture was extracted with PE (3 × 20 mL) and the combined organic phase was dried over Na_2SO_4. The solwent was removed under vacuum to give compound **14** quantitatively (0.46 g) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.58 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 3.7 Hz, 1H), 7.06 (s, 1H), 7.05 (d, *J* = 3.3 Hz, 1H), 7.03 (s, 1H), 6.99 (d, *J* = 3.3 Hz, 1H), 6.78 (d, *J* = 3.7 Hz, 1H), 4.11 – 4.06 (m, 4H), 1.88 – 1.82 (m, 4H), 1.57 – 1.50 (m, 4H), 1.01 (m, 6H), 0.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 148.63, 148.56, 148.48, 143.86, 142.63, 137.70, 135.24, 134.54, 128.82, 128.15, 127.56, 127.22, 126.54, 125.90, 125.58, 122.98, 116.18, 115.93, 69.14, 69.04, 31.33, 31.30, 19.26, 13.91, 13.90.

2-(4,5-dibutoxy-2-(5-(3',4'-dibutoxy-[1,1'-biphenyl]-2-yl)thiophen-2-yl)phenyl)-5-phenylthiophene (16) To a 25 mL two-neck round-bottom flask was added compound **14** (0.40 g, 0.64 mmol), compound **15** (0.27 g, 0.70 mmol), $Pd(PPh_3)_4$ (10 mg), dry toluene (10 mL). The reaction mixture was heated to 100°C overnight under N_2 in the dark. After cooling to room temperature, the reaction mixture was poured into water and extracted with dichloromethane (3 × 20 mL). The organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel, DCM/Petroleum ether, 1:4) to give a yellow solid (0.36 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.60 (d, *J* = 7.2 Hz, 2H), 7.54 – 7.51 (m, 1H), 7.39 – 7.33 (m, 5H), 7.27 (s, 1H), 7.18 (d, *J* = 3.7 Hz, 1H), 7.03 (s, 1H), 6.96 (s, 1H), 6.82 – 6.79 (m, 2H), 6.78 – 6.74 (m, 2H), 6.66 (d, *J* = 3.7 Hz, 1H), 6.54 (d, *J* = 3.7 Hz, 1H), 4.10 – 4.04 (m, 4H), 3.95 (t, *J* = 6.6 Hz, 2H), 3.89 (t, *J* = 6.6 Hz, 2H), 1.87 – 1.72 (m, 8H), 1.53 (m, 8H), 1.03 – 0.92 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 148.66, 148.57, 148.37, 143.92, 143.29, 142.60, 142.37, 140.63, 134.51, 134.17, 133.22, 130.77, 130.29, 128.87, 127.74, 127.55, 127.29, 127.21, 126.99, 126.91, 126.21, 126.11, 125.57, 123.05, 122.11, 116.12, 116.06, 115.72, 113.30, 69.16, 69.11, 68.92, 68.86, 31.46, 31.34, 31.32, 19.31, 19.28, 13.97, 13.91. MS (Maldi-TOF, positive mode, DCTB in chloroform) Calcd for $C_{48}H_{54}O_4S_2$: 758.35; found: 758.20. Elemental Analysis: calcd for C, 75.95; H, 7.17. found C, 75.97; H, 7.15.

(10) To a solution of **16** (100 mg, 0.13 mmol) in 50 mL dry dichloroethane was added dropwise a solution of iron(III) chloride (96 mg, 0.60 mmol) in 2 mL of nitromethane. After complete addition, the reaction mixture was allowed to stir for 5min. Methanol (50 mL) was added and then the reaction mixture was stirred for 10 min. the reaction mixture was poured into water and extracted with dichlorome. The organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography

(silica gel, DCM/Petroleum ether, 1:1) to give a yellow solid (75 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.59 (d, *J* = 7.9 Hz, 1H), 8.54 (s, 1H), 8.34 (s, 1H), 8.22 (d, *J* = 7.3 Hz, 1H), 8.15 (s, 1H), 7.78 (d, *J* = 7.4 Hz, 2H), 7.68 – 7.61 (m, 2H), 7.55 (s, 1H), 7.50 (s, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 4.35 – 4.26 (m, 6H), 4.05 (t, *J* = 6.7 Hz, 2H), 2.01 (m, 6H), 1.67 (m, 8H), 1.25 (m, 2H), 1.10 (m, 9H), 0.80 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 149.93, 149.64, 148.32, 148.16, 140.24, 135.78, 135.00, 134.54, 134.31, 132.51, 130.77, 129.02, 128.48, 127.86, 127.41, 126.28, 126.17, 125.83, 124.66, 124.45, 124.02, 122.91, 122.33, 121.62, 109.67, 106.78, 106.07, 105.47, 69.04, 68.93, 31.50, 31.28, 31.21, 19.41, 19.02, 14.06, 13.75. MS (Maldi-TOF, positive mode, DCTB in chloroform) Calcd for $C_{48}H_{50}O_4S_2$: 754.32, found: 754.92. Elemental Analysis: calcd for C, 76.36; H, 6.68. found C, 76.38; H, 6.66.

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Polycyclic Aromatics: The synthesis of sulphur-hybridized pyracylenes (SHPs) was reported. Quantitatively debromination vs phenyl ring-shift-mediated rearrangement induced by the substituents were observed. A retrosynthetic method was successfully adopted to confirm the unexpected reaction results in rearrangement of Scholl reaction.

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Synthesis of Sulfur-Hybridized Pyracylene and the Unexpected Phenyl Shift Mediated Rearrangement of Scholl Reaction