



Derivation of saddle shaped cyclooctatetrathiophene: increasing conjugation and fabricating pentamer



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ABSTRACT

With cyclooctatetrathiophene (**COTh**) as building block, two $\alpha,\alpha,\alpha,\alpha$ -tetraaryl **COThs**, **COThP** and **COThTh** have been efficiently synthesized. Phenyl and thienyl were employed as end-capping groups to introduce to **COTh** and increase its conjugation. For enlarging the special 'saddle' shaped structure, a pentamer of **COTh** was synthesized via Negishi reaction and CuCl_2 -promoted oxidative coupling reaction. The pentamer (**COThF**) is a new type of dendrimer with **COTh** as dendron, which presents an artistic configuration possessing a large saddle shape. All compounds were fully characterized by ^1H NMR, ^{13}C NMR, HRMS and IR. The crystal structures of **COThP** and **COThTh** were confirmed by X-ray analysis. The molecular configuration of **COThF** was optimized by theoretical calculations. Their UV–vis properties, electrochemical behaviours and thermo-gravimetric analysis of **COThP**, **COThTh** and **COThF** were also described.

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1. Introduction

Thiophene derivatives have attracted more attentions due to their potential applications in organic optoelectronics.¹ Usually, these derivatives are possessing linear/planar structures with extended π system.² In fact, thiophene derivatives not only possess linear/planar structure but also can present 3D conformation with large flexible π -conjugated skeleton.³ These large flexible π -conjugated skeleton structures may be potentially applied in electro-mechanical actuators,³ molecular tweezers,⁴ and self-assembly building blocks.⁵ Cyclooctatetrathiophene (tetra[2,3-thienylene], **COTh**) composed of four thiophene rings, is one of the special flexible π -conjugated skeletons with an 8π annulene as centre. The single crystal of $[\text{TMS}]_4\text{-COTh}$ ⁶ indicates that the four thiophene rings present 'saddle' form, which can be transformed into 'planar' form for aromaticity of the reduced 10π dianion or the oxidized 6π dication.³ Furthermore, **COTh** may be also developed in the field of organic electronics because of the rich thiophene units, which can be modified with various functional groups. However, the low yield

in the process of synthesizing **COTh** and its derivatives limits its advanced development.

COTh was firstly synthesized with yield of 18% and 23% by Kauffmann et al.⁷ in 1978 via CuCl_2 promoting oxidative homocoupling of 3,3'-dilithio[2,2']bithiophene and 2,2'-dilithio[3,3']bithiophene, respectively. Until twenty years later, Marsella et al.^{3,8} reported a series work about the synthesis of dimer and oligomer of **COTh** and their application in organic electronics. In our previous work, we reported an improvement of the efficient synthesis of **COTh** with yield up to 40%⁶ and a dithieno[2,3-*b*:3',2'-*d*]thiophene fused **COTh** forming double helicene,⁹ in which the sophisticated structure not only possesses the general **COTh** character, but also shows a double helical configuration. Although **COTh** has been reported for about 40 years, however, only a few papers about **COTh** derivatives were achieved.^{3a,6–11} It is still a huge challenge to efficiently synthesize its derivatives with various architectures.

Herein, we demonstrate an efficient approach to build up **COTh** derivatives with aryl groups, $\alpha,\alpha,\alpha,\alpha$ -tetraphenyl-cyclooctatetrathiophene (**COThP**) and $\alpha,\alpha,\alpha,\alpha$ -tetra(3-thienyl)-cyclooctatetrathiophene (**COThTh**) via Suzuki reaction with high yields of 83% and 71%, respectively. Their crystal structures indicate that the end-capping groups of phenyl and thienyl are approximately coplanar with the thiophene rings of **COTh**. Furthermore, a novel pentamer, **COThF**, has also been prepared via Negishi reaction and

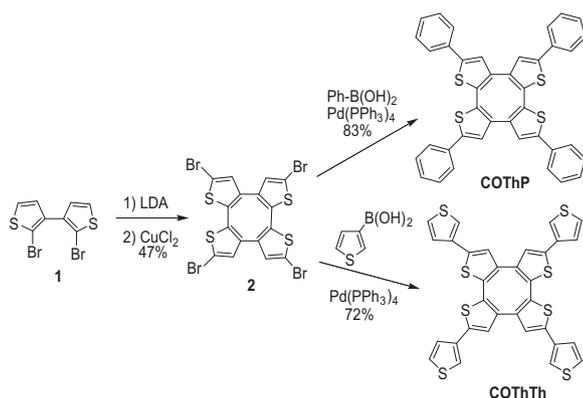
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CuCl₂-promoted oxidative coupling reaction. More interestingly, the molecular configuration of **COThF** optimized by theoretical calculation, presents an artistic configuration possessing a large saddle shape, which is composed of five independent saddle shaped **COTh** units. This architecture of **COThF** is different from the thiophene-based dendrimers with terthiophene¹² or tetrakis(-thiophene-2-yl)ethene¹³ as dendrons as reported. In addition, the UV–vis properties, electrochemical behaviours and thermogravimetric analysis of **COThP**, **COThTh** and **COThF** were also described.

2. Results and discussion

2.1. Synthesis of **COThP** and **COThTh**

The synthetic route to **COThP** and **COThTh** are shown in Scheme 1. Tetrabromo-**COTh** (**2**)^{10a} is the key scaffold for the preparation of $\alpha,\alpha,\alpha,\alpha$ -tetraaryl **COTh**s. Normally, it is hard to be efficiently functionalized to each α -position available on the parent **COTh**. To avoid such problem, we directly made **COTh** bearing four functionalized groups, namely tetrabromo-**COTh** (**2**) through an efficient synthetic route (Scheme 1), which was developed by two steps: bromine dance (BD) reaction^{9,14} of 2,2'-dibromo-[3,3']bithiophene (**1**)⁶ and following CuCl₂-promoted oxidative coupling. The yield of **2** was efficiently obtained in one-pot. Thus, using **2** as a versatile building block, we first synthesized **COThP** in 83% via four-fold Suzuki couplings between **2** and phenylboronic acid. Furthermore, we successfully prepared **COThTh** in 72% yield with the same process by using **2** and thiophen-3-boronic acid (Scheme 1).

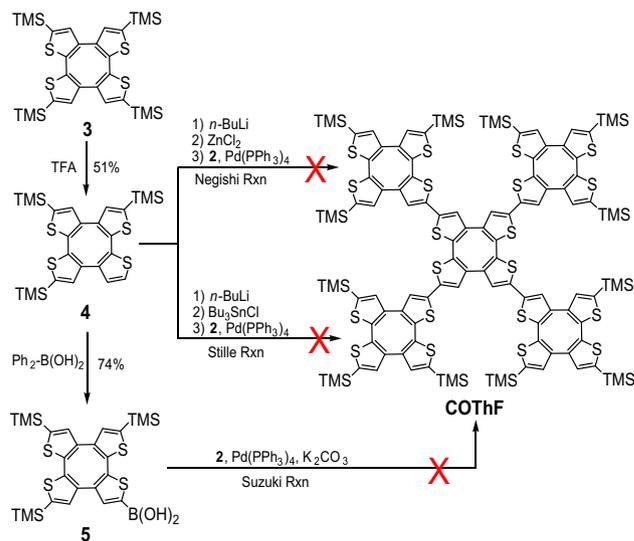


Scheme 1. Synthetic route to **COThP** and **COThTh**.

2.2. Synthesis of **COThF**

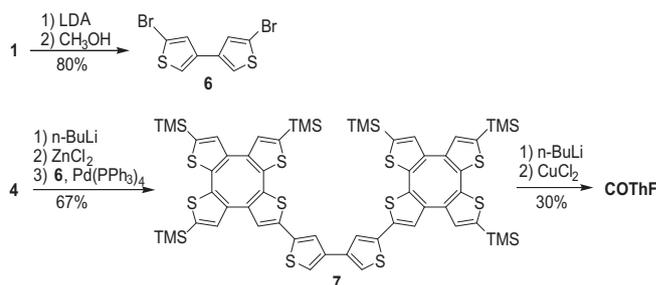
The same strategy was also applied for the synthesis of pentamer, **COThF**. The first synthetic route to **COThF** is shown in Scheme 2. The first step was to obtain tri(trimethylsilyl)-**COTh** (**4**) by directly treating tetra(trimethylsilyl)-**COTh** (**3**)⁶ with trifluoroacetic acid (TFA) in chloroform. At this step, one of the four TMS groups in **3** was removed selectively. It was found that the use of a high concentration of TFA led to complex products. Whereas a good yield of 51% could be achieved by using a low concentration of TFA (1.5%) in chloroform. At same time, 40% raw material could also be recovered. **COTh**-boronic acid pinacol ester (**5**) was efficiently prepared in 74% by using **4** and bis(pinacolato)diborane. Then, the preparation of **COThF** was tested by Pd(PPh₃)₄-catalyzed Suzuki coupling reaction between **2** and **5** in refluxing THF. Unfortunately, only complex mixtures were obtained and it is very difficult to be separated by column chromatography. More couplings including Stille coupling and Negishi coupling between **2**

and **4** were also tried for **COThF** (Scheme 2), and both were failed again. This failure may be due to the decreased activity and increased steric hindrance arising from the larger **COTh** substituents.



Scheme 2. The first synthetic route to **COThF**.

To overcome this problem, we tried another synthetic route as shown in Scheme 3 to respond to the challenge of making **COThF**. The synthesis of 5,5'-dibromo[3,3']bithiophene (**6**) was carried out using BD reaction of **1**, which was the key step in synthesis of **COThF**. Compound **1** was treated with LDA in THF at $-10\text{ }^{\circ}\text{C}$ and then quenched with methanol, **6** was efficiently obtained in a yield of 80%. The intermediate **7** was then prepared in 67% yield by two-fold Negishi couplings between **4** and **6**. Following the deprotonation on **7** with *n*-BuLi in ethyl ether, the resultant aryllithium species was oxidized with CuCl₂ to afford the target compound **COThF** in 30% isolated yield. The star-shaped **COThF** is a pentamer of **COTh**, in which four **4** units linked to the four peripheral α -positions available on the core **COTh**. The star-shaped **COThF** may also be taken as a new type of all-thiophene based dendrimer with **COTh** as new dendron. The ¹H NMR spectrum behaviour of **COThF** could be taken as a typical characteristic of dendrimers,^{12,15–17} which shows two broad peaks at both aromatic region of 7.03–7.10 ppm and alkyl region of 0.31–0.35 ppm in CDCl₃. We have also measured its ¹H NMR spectrum at 333 K (60 °C), however, its spectral behaviour did not show any obvious change. HRMS data of **COThF** clearly support its molecular structure (see Supplementary data).



Scheme 3. The second synthetic route to **COThF**.

2.3. Crystal structures of **COThP** and **COThTh**

The crystal structures of **COThP** and **COThTh** are confirmed by single-crystal X-ray analysis. Both of them belong to monoclinic,

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