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# Synthesis of penta- and hexa(3,4-thienylene): size-dependent structural properties of cyclic oligothiophenes†

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Penta- and hexa(3,4-thienylene)s were synthesized as a potential precursor for thiophene-containing polyarenes, and the structures were determined via X-ray crystallography. The interconversion of thiophene rings is fast in penta(3,4-thienylene), and slow in hexa(3,4-thienylene) reflecting the activation energy for enantio-merization. Size-dependent bathochromic shifts were observed in UV-vis absorption spectra.

Cyclic oligoarylenes have long received considerable attention due to their structural, electronic, and optical properties.<sup>1</sup> The most representative arylenes are phenylenes, in which the phenyl groups can be connected to each other in three ways, *i.e.*, at the *o*-, *m*-, or *p*-positions. Of these, cyclo-*o*-phenylenes are of little interest and are not very well explored. Even so, biphenylene, triphenylene, tetraphenylene, hexaphenylene, and octaphenylene derivatives have already been synthesized (Fig. 1a), and their reactivity, structural properties, and applications have been investigated.<sup>2</sup> Replacing the benzene rings with thiophene rings allows modifying the electronic and structural properties to induce, for example, weaker aromaticity, lower steric hindrance, and intermolecular S...S interactions in the solid state.<sup>3</sup> Structurally, cyclo-*o*-phenylenes correspond approximately to cyclic oligo(3,4-thienylene)s in as much that the thiophene rings are linked at the  $\beta,\beta'$ -positions (Fig. 1b). To date, cyclic oligo(3,4-thienylene)s with two to four thiophene rings<sup>4</sup> have been explored. Given that all their  $\alpha$ -positions are reactive sites, tri- and tetra(3,4-thienylene)s can be transformed into a variety of electron-rich  $\pi$ -conjugated molecules, such as heterosumanenes<sup>5</sup> and hetero[8]circulenes,<sup>6</sup> as well as tetra(3,4-thienylene)s can be employed as *e.g.*, 3D building blocks<sup>7</sup> or solvent-responsive molecular assemblies.<sup>8</sup>

In addition, tri(3,4-thienylene)s have been studied as charge-transfer complexes<sup>9</sup> or planar [6]radialenes.<sup>10</sup> However, cyclic oligo(3,4-thienylene)s with five or more thiophene rings have not yet been synthesized.<sup>11</sup> To create larger  $\beta,\beta'$ -linked cyclic oligo(3,4-thienylene)s, building blocks that contain functional groups at the  $\beta$ -positions are a prerequisite. In 2017, a practical synthetic method for a  $\beta$ -substituted unit, *i.e.*, a 3,4-diborylated thiophene derivative, was developed by Osuka, Tanaka, and co-workers, which widened the range of synthetic approaches for cyclic compounds that contain 3,4-thienylenes and other heteroarenes.<sup>12</sup>

Herein, we report the synthesis of penta- and hexa(3,4-thienylene)s (**5T** and **6T**) via Pd-catalyzed cross-coupling and Ni-mediated homocoupling reactions using 3,4-diborylthiophene **1** or the newly synthesized 4,4'-diboryl-3,3'-bithiophene **2** (Fig. 1c and 2a). The structures and electronic properties of **5T** and **6T** were determined using NMR and X-ray crystallography as well as UV-vis absorption spectroscopy. The structural characteristics and optoelectronic properties of **5T** and **6T** were compared to



**Fig. 1** Representative cyclic oligoarylenes. (a) Cyclo-*o*-phenylenes. (b) Cyclic oligo(3,4-thienylene)s. (c) Penta- and hexa(3,4-thienylene)s (**5T** and **6T**).

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**Fig. 2** (a) Synthesis of **5T** and **6T**; (i) Pd<sub>2</sub>(dba)<sub>3</sub>, XPhos, K<sub>3</sub>PO<sub>4</sub>, THF/H<sub>2</sub>O, 40 °C, 22–23 h; (ii) Ni(cod)<sub>2</sub>, 2,2′-bipyridine, THF, reflux, 2.5 h; (iii) HBpin, Zn powder, Et<sub>3</sub>N, NiCl<sub>2</sub>(dppp), DPPF, toluene, reflux, 60 h. (b) <sup>1</sup>H NMR spectra of **4T**–**6T** in CD<sub>2</sub>Cl<sub>2</sub>. The signals of **6T** are indicated by colored marks. Abbreviations: dba = dibenzylideneacetone; XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl; cod = 1,5-cyclooctadiene; Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl; dppp = 1,3-bis(diphenylphosphino)propane; DPPF = 1,1′-bis(diphenylphosphino)ferrocene.

those of **4T**, and examined using density functional theory (DFT) calculations.

Penta- and hexa(3,4-thienylene)s (**5T** and **6T**) were synthesized *via* sequential Suzuki–Miyaura cross-coupling and Ni(0)-mediated intramolecular homocoupling reactions (Fig. 2a). For that purpose, diborylthiophene **1** and 4,4′-dibromo-3,3′-bithiophene (**3**) were prepared initially according to reported methods.<sup>12,13</sup> The Suzuki–Miyaura cross-coupling reaction of **1** with an excess of **3** (8.0 equiv.) was carried out using Pd<sub>2</sub>(dba)<sub>3</sub> (2.5 mol%), XPhos (10 mol%), and K<sub>3</sub>PO<sub>4</sub> (4.0 equiv.) to produce dibromoquinquethiophene **4** in 73% yield. Dibromobithiophene **3** was used in excess in order to suppress the generation of polymers. The resulting **4** was treated with Ni(cod)<sub>2</sub> (2.2 equiv.) and 2,2′-bipyridine (2.2 equiv.) for 3 h in refluxing tetrahydrofuran (THF) (2 mM), which allowed isolating the desired cyclic oligothiophene **5T** in 36% yield. Increasing the substrate concentration provided **5T** in low yield in this reaction step. Next, a cyclic oligothiophene containing an additional thiophene ring, **6T**, was synthesized by applying analogous reaction conditions. A borylation reaction similar to that used to synthesize **1**<sup>12,14</sup> was performed to obtain **2** in 48% yield. The reaction of **2** with an excess of **3** under Pd catalysis furnished dibromosexithiophene **5** in 52% yield. The obtained **5** was subsequently treated with Ni(cod)<sub>2</sub> (3.3 equiv.) and 2,2′-bipyridine (3.3 equiv.) in THF. In contrast to **5T**, **6T** was obtained in low yield (1.5%), presumably due to the formation of polymeric compounds. Both **5T** and **6T** were slightly soluble in common organic solvents (see Table S1 in ESI† for details).

To identify the thus-obtained compounds **5T** and **6T**, and to investigate their size-dependent structural characteristics, NMR spectra were recorded (Fig. 2b). In the room-temperature <sup>1</sup>H NMR spectrum of **5T** in dichloromethane-*d*<sub>2</sub>, the α-protons of the thiophene rings appear as a singlet at 7.01 ppm. Even at –95 °C, the singlet remains almost unchanged. In the <sup>13</sup>C NMR spectrum in chloroform-*d*<sub>1</sub>, two signals were observed at 124.6 and 137.6 ppm. These results indicate that the dynamic inter-conversion of the thiophene rings is fast on the NMR timescale. Unlike that of **5T**, the <sup>1</sup>H NMR spectrum of **6T** in dichloromethane-*d*<sub>2</sub> at room temperature displays three signals, *i.e.*, doublets at 6.5 and 6.9 ppm as well as a singlet at 7.3 ppm. Only very slight broadening of the signals was observed even at 140 °C in tetrachloroethane-*d*<sub>2</sub>, indicating that **6T** has three diastereotopic protons and those are not exchanged in the NMR timescale. The <sup>1</sup>H NMR spectra of **4T**–**6T** presented in Fig. 2b clearly demonstrate the size dependence of the symmetry in solution. The NMR assignments were supported by chemical shift calculations using the GIAO method (see Fig. S2 in ESI† for details).

The solid-state structures of **5T** and **6T** were determined *via* X-ray diffraction analysis of single crystals obtained from a hexane/chloroform and a pentane/THF solution, respectively (Fig. 3a and b). Compound **5T** adopts a C<sub>2</sub>-symmetric structure in which five thiophene rings are fused at the 3,4-positions to form a 10-membered ring. Compound **6T** adopts a screw (or helical) structure with D<sub>2</sub> symmetry, similar to hexaphenylene<sup>2b,e-h</sup> and hexa(2,3-thienylene)s.<sup>11b,f</sup> The distance between the centroids of the central thiophene rings (av. 3.4 Å) is typical for intramolecular π–π interactions. In both crystals, the enantiomers are aligned alternately reflecting the centric space group (*I*2/*a*). The average dihedral angles (θ) of the α–β–β–α and β–β–β–β positions of the 3,3′-bithiophene moieties are shown in Fig. 3a and b. The dihedral angles in **5T** and **6T** are 46.0° (θ<sub>a</sub>), 90.8° (θ<sub>b</sub>), and 87.8° (θ<sub>c</sub>), and 41.8° (θ<sub>d</sub>), 46.0° (θ<sub>e</sub>), and 124.5° (θ<sub>f</sub>), respectively (see Fig. S3 in ESI† for details). Considering the dihedral angle in **4T** (54.3°), determined using X-ray crystallography,<sup>4c</sup> the smallest dihedral angle in **4T**, **5T**, and **6T** decreases with increasing number of thiophene rings.

In order to gain insight into the size-dependent structural characteristics, DFT calculations were conducted. The structures of **5T** and **6T**, optimized at the B3LYP-D3/6-31G(d) level nicely reproduced the structures observed by X-ray



**Fig. 3** (a) and (b) Molecular structures of **5T** (a) and **6T** (b) with thermal ellipsoids at 50% probability; gray = carbon; yellow = sulfur; white = hydrogen. The C<sub>2</sub> axis of **5T** and one of the C<sub>2</sub> axes of **6T** are noted with dashed lines. The hydrogen atoms indicated by the colored marks correspond to the <sup>1</sup>H NMR signals shown in Fig. 2b.





homocoupling reaction that involved the synthesis of a new  $\beta,\beta'$ -substituted moiety **2**. Using an excess of **3** effectively suppressed the formation of polymers. While only a single singlet was observed in the NMR spectra of **4T** and **5T**, three different signals were observed for **6T**. The solid-state structures of **5T** and **6T** were determined using X-ray crystallography; a corresponding analysis of the metric parameters revealed that the smallest dihedral angle of the 3,3'-bithiophene moiety decreases with increasing number of thiophene rings. The size-dependence observed in the NMR spectra can be rationally interpreted in terms of the activation energies for the inter-conversion of the thiophene rings. The size-dependence manifests in the optoelectronic measurements, in which the longest-wavelength absorption maxima are by 13 nm bathochromically shifted with increasing size of the molecules. The results of our DFT calculations suggest that gradually increasing the number of thiophene rings gradually increases the HOMO energy and decreases the LUMO energy. With synthetic routes to **5T** and **6T** established, it will now be possible to explore the synthetic chemistry of a variety of unprecedented thiophene-containing arenes.

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## Conflicts of interest

There are no conflicts to declare.

## Notes and references

‡ Crown conformer is observed in hexaphenylene<sup>2b,c,g</sup> and hexa(2,3-thienylene)s.<sup>4a,11a</sup>

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