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## Molecular conductance

Valkenier-van Dijk, Elisabeth Hendrica

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# Chapter 6

## Methano[10]annulene in Molecular Wires and Polymers

*We have synthesized 2,7-dibromo-9,10-methano[10]annulene and incorporated this building block in a molecular wire to study the influence of this ten  $\pi$ -electron aromatic building block on the conductance of the wire. We found that the HOMO-LUMO gap of this wire is smaller than that of its naphthalene analogue.*

*We have incorporated methano[10]annulene in a copolymer with didecylbithiophene and compared this to similar copolymers with either naphthalene or benzothiadiazole incorporated. The optical band gap of the methano[10]annulene-based copolymer was found in between those of the other two polymers, though all band gaps were larger than expected, which we attribute to a torsion angle in the backbone of the polymers.*

## 6.1 Introduction

In Chapters 4 and 5 we have investigated the influence of the incorporation of various building blocks in molecular wires: acenes of increasing size (i.e., benzene, naphthalene, and anthracene) and different conjugation patterns. The ultimate aim of this Chapter was to investigate the influence of aromaticity on the conductance of  $\pi$ -conjugated molecular wires. We compare two linear conjugated building blocks: 2,7-disubstituted 1,6-methano[10]annulene and 1,5-disubstituted naphthalene (Figure 6.1). Both have 10  $\pi$ -electrons, either in one or two rings of  $sp^2$  hybridized carbon atoms, which gives rise to a difference in aromaticity.



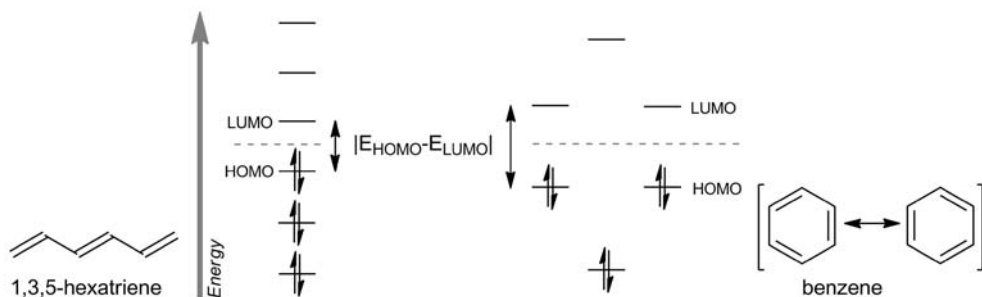
**Figure 6.1** a. 2,7-disubstituted 1,6-methano[10]annulene, b. 1,5-disubstituted naphthalene.

Furthermore, having synthesized the methano[10]annulene building block, we expand the scope of this thesis on molecular wires and their conductance, by incorporating this building block in  $\pi$ -conjugated polymers to study their conductivity in films, in line with other ongoing research in our group.

### 6.1.1 Aromaticity

In Chapter 1.2 we have explained the concept of  $\pi$ -conjugation, in which the  $p_z$ -orbitals of  $sp^2$  hybridized carbon atoms combine into molecular orbitals. This was illustrated with 1,3,5-hexatriene in Figure 1.2, for which six molecular orbitals were obtained with an increasing number of nodal planes (from zero to five) and a corresponding increase in energy (Figure 6.2). However, for an annulene molecule, of which the  $sp^2$  hybridized carbon atoms form a cycle, nodal planes can be drawn in different ways, resulting in degenerate molecular orbitals. The most famous example is benzene, which has two degenerate HOMOs (with one nodal plane each) and two degenerate LUMOs (with two nodal planes each), besides a bonding orbital in which all  $p_z$  orbitals have an identical symmetry (this orbital is the lowest in energy) and an anti-bonding orbital which has three nodal planes that cross each

other in the center of the molecule (this orbital is the highest in energy). Thus, as shown in Figure 6.2, the six molecular  $\pi$ -orbitals of benzene correspond to only four different energy levels, where the six orbitals of hexatriene correspond to six energy levels. This results in a larger energy difference between the HOMO and the LUMO of benzene compared to hexatriene. Furthermore, the overall energy of benzene is lower than of hexatriene, which is called "aromatic stabilization". From a valence-bond theory perspective, this can be understood by the presence of the resonance structures that are equal in energy (see Figure 6.2).



**Figure 6.2** Energy levels of the  $\pi$ -orbitals of 1,3,5-hexatriene (left) and benzene (right).

A molecule is considered to be aromatic when it has  $4n+2$   $\pi$ -electrons in one (nearly) planar ring of all  $sp^2$  hybridized atoms, according to Hückel's rule.<sup>1</sup> The origin of this  $4n+2$  rule can be found in the energy diagram of benzene in Figure 6.2: if we would add two more electrons ( $4n$ ), these have to be placed in each of the two empty degenerate orbitals according to Hund's rule, resulting in an open shell compound with two unpaired electrons. Addition of another two electrons results in a closed-shell compound with 10  $\pi$ -electrons.

### 6.1.2 Methano[10]annulene

After benzene with 6  $\pi$ -electrons ( $C_6H_6$ ), the first neutral aromatic compound would be [10]annulene, a ring structure with the molecular formula  $C_{10}H_{10}$ . However, this structure is not planar and has not sufficient overlap between the  $p_z$ -orbitals to satisfy Hückel's rule; [10]annulene is therefore not aromatic.<sup>2</sup> In 1964 Vogel and Roth reported the synthesis of 1,6-methano[10]annulene, in which a  $CH_2$ -bridge was used to force the [10]annulene structure into a nearly planar geometry (Figure 6.1).<sup>3</sup> Vogel and Roth reported a  $^1H$  NMR spectrum with resonances from eight protons between 7.5-6.8 ppm and two at -0.5 ppm. This

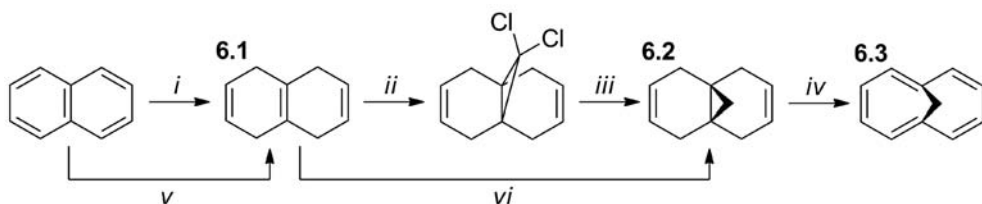
indicates the presence of a ring current, resulting in shielding of the protons at the methano group and deshielding of the protons outside the ring. The presence of such a ring current in a magnetic field is a strong indication for aromaticity. Another indication for the aromaticity of methano[10]annulene is obtained from crystallographic data, which show a symmetric structure in which the lengths of opposite carbon-carbon bonds in the ten-membered ring differ less than 1%.<sup>4</sup> Besides classical aromaticity, also homoaromaticity<sup>5</sup> has been found for methano[10]annulene: through space interactions between orbitals on both sides of the methano bridge give rise to a small additional stabilization.<sup>6,7</sup>

Recently, methano[10]annulene has been incorporated in conjugated structures for OLED applications,<sup>8</sup> in molecular wires with and without donor-acceptor groups,<sup>9</sup> in quinoidal structures,<sup>10</sup> and in electrochemically synthesized copolymers with thiophene<sup>11,12</sup> or furan.<sup>13</sup> Peart and Tovar performed spectroelectrochemical experiments on these polymer films and concluded that the effective conjugation is significantly larger in the polymers with 2,7-disubstituted methano[10]annulene incorporated than in those with 1,5-disubstituted naphthalene. They attribute this to the olefinic character of methano[10]annulene that is present in addition to its aromatic character<sup>12</sup> (which is less pronounced compared to naphthalene<sup>7</sup>). The smaller HOMO-LUMO gap found for methano[10]annulene compared to naphthalene is also attributed to its partial olefinic character. Thus, methano[10]annulene is found to have some degree of aromatic stabilization and other aromatic properties (compare to right part of Figure 6.2), combined with olefinic properties, as found in hexatriene (Figure 6.2 left) and in polyacetylene. The conductivity of polyacetylene can be tuned over a very wide range by doping,<sup>14</sup> however, the problematic stability of the polymer limits its applications. Its olefinic nature, combined with aromatic stabilization, makes methano[10]annulene an interesting building block to study in our dithiolated molecular wires for conductance measurements (Section 6.3) and in soluble thiophene-based copolymers (Section 6.4).

## 6.2 Synthesis of 2,7-Dibromo-1,6-methano[10]annulene

As mentioned above, the synthesis of 1,6-methano[10]annulene **6.3** was first

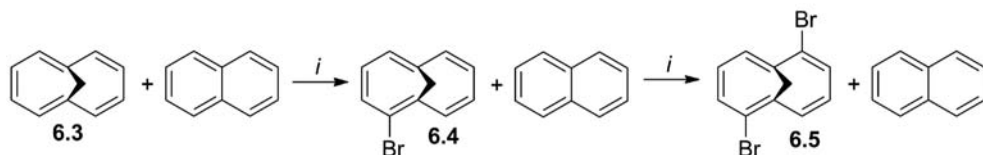
reported by Vogel and Roth in 1964.<sup>3</sup> The strategy for the synthesis of **6.3**, which has been reported in detail in *Organic Synthesis*,<sup>15</sup> is outlined in Scheme 6.1. Naphthalene was reduced to isotetralin **6.1** in a Birch reduction in 75-80% yield. Dichlorocarbene was generated from chloroform and potassium *tert*-butoxide and added to the central double bond of **6.1** in 40-45%. Subsequently, the chlorine atoms were removed in another Birch reduction, resulting in compound **6.2** in 85-90%. Compound **6.2** was in the original report from Vogel and Roth<sup>3</sup> converted into the aromatic target compound **6.3** by a bromination, followed by a dehydrobromination. Instead, 2,3-dichloro-5,6-dicyano-1,6-benzoquinone (DDQ) can be used to convert **6.2** into **6.3** in 85-90%, as reported by Nelson and Untch in 1969<sup>16</sup> and included in the *Organic Synthesis* procedure.<sup>15</sup>



**Scheme 6.1** Synthesis of methano[10]annulene: (i) Na, NH<sub>3</sub>, EtOH, Et<sub>2</sub>O, -78°C; (ii) CHCl<sub>3</sub>, KO<sup>t</sup>Bu, -30-0°C; (iii) Na, NH<sub>3</sub>, MeOH, Et<sub>2</sub>O, -78°C; (iv) DDQ, AcOH, dioxane, reflux; (v) Li, (CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>, n-PrNH<sub>2</sub>, *t*BuOH, 0°C; (vi) Zn, CuCl, MeI<sub>2</sub>, Et<sub>2</sub>O, reflux.

Although this *Organic Synthesis* procedure is widely used for the synthesis of 1,6-methano[10]annulene,<sup>11,12</sup> the handling of large volumes of liquid ammonia for the Birch reductions and the purification of the dichlorocarbene adduct were highly time consuming.<sup>17</sup> For that reason, we used an alternative method. We reduced naphthalene into isotetralin **6.1** using lithium in ethylenediamine and *n*-propyl amine cooled with an ice-salt bath according to the recently reported procedure of Garst *et al.*<sup>18</sup> and obtained **6.1** in 56% (Garst *et al.* reported 74% yield). Then we did an addition of methylene (:CH<sub>2</sub>) onto **6.1** in a modified Simmons-Smith reaction,<sup>16,19</sup> which yielded a mixture of products, consisting of **6.2** (30-50%), its isomer with the carbene added on one of the other double bonds (1-30%), the bis-adduct (10-50%), and traces of tetralin and  $\Delta^2$ -decalin. Instead of isolating **6.2** from this mixture (which is very difficult), we treated the mixture of compounds with DDQ in the next step, which yielded, after purification by column chromatography, a mixture of methano[10]annulene **6.3** and naphthalene.<sup>20</sup> This mixture is not easily separated, due to similar boiling points and co-crystallization

of the two compounds. We should note that solutions containing **6.3** and its precursors are better not concentrated by rotary evaporation, since their high vapor pressures cause the compounds to evaporate together with the solvent to be removed.



**Scheme 6.2** Bromination of methano[10]annulene: (i) NBS,  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ -reflux.

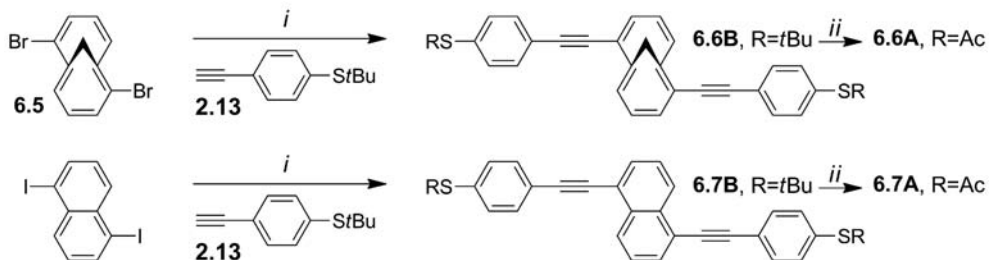
Treatment of the mixture of methano[10]annulene **6.3** and naphthalene with N-bromosuccinimide (NBS) resulted in selective bromination of **6.3** into 2-bromo-1,6-methano[10]annulene **6.4**, which was in a second treatment with NBS converted into 2,7-dibromo-1,6-methano[10]annulene **6.5**.<sup>21,22</sup> Apart from the desired 2,7-dibromo compound **6.5**, its isomer 2,5-dibromo-1,6-methano[10]annulene can be formed, especially when **6.3** is directly treated with two equivalents of NBS. The boiling point of **6.4** and **6.5** is significantly increased compared to that of naphthalene and **6.3**, thus naphthalene can be easily removed by distillation. After recrystallization, we obtained pure **6.5** (in 3.5% overall yield from isotetralin), which was incorporated into molecular wires and conjugated polymers.

## 6.3 Methano[10]annulene-Based Molecular Wire

### 6.3.1 Synthesis of the Molecular Wires

We have synthesized methano[10]annulene-based molecular wire **6.6A** (Scheme 6.3), which consists of a 2,7-disubstituted-1,6-methano[10]annulene core unit, phenylene ethynylene spacers and thioacetate end groups, to anchor the molecule to gold electrodes (see Chapter 1.5). To compare the special aromatic methano[10]annulene unit with the more common naphthalene unit, we synthesized molecular wire **6.7A** as a reference compound. Wires **6.6A** and **6.7A** are similar to reported wires, apart from the acetyl-protected thiol anchoring

groups.<sup>23,9,11</sup> Wire **6.7B** was synthesized in two steps by a Sonogashira cross-coupling of 1,5-diiodonaphthalene<sup>24</sup> and 1-tert-butylthio-4-ethynylbenzene **2.13** (see Chapter 2.2) in 77% and subsequently converted with into **6.7A** in 85%, using boron tribromide and acetyl chloride.<sup>25</sup>



**Scheme 6.3** Syntheses of molecular wires **6.5** and **6.6**: (i) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, iPr<sub>2</sub>NH, THF, reflux; (ii) BBr<sub>3</sub>, AcCl, CHCl<sub>3</sub>, toluene.

Methano[10]annulene wire **6.6A** was synthesized according to the same strategy. The synthesized 2,7-dibromo-1,6-methano[10]annulene **6.5** was cross-coupled with acetylene **2.13** to give **6.6B** in 47% yield. The reaction of **6.6B** with boron tribromide (20 equivalents) and acetyl chloride according to the standard procedure<sup>25</sup> gave a mixture of products, similar to our results for the conversion of anthracene wire **4.5B** into **4.5A** (see Chapter 4.2). We therefore adopted the procedure that was used to convert **4.5B** into **4.5A**, by adding only two equivalents of boron tribromide to a solution of **6.6B** at 0°C.<sup>26</sup> However, besides the desired **6.6A**, a side product was formed, which showed an additional signal at 2.32 ppm in the <sup>1</sup>H NMR spectrum and the signal from the methylene group was split into a doublet, indicating that an asymmetric compound was formed. Furthermore, many small signals in the aromatic region were found. We attribute these additional signals in the <sup>1</sup>H NMR spectrum to a molecule similar to **6.6A**, with an additional acetyl group at the methano[10]annulene core, which can be formed by a Friedel-Crafts acylation.<sup>27</sup> We have not succeeded in the separation of this compound (35-38%) from target wire **6.6A**.

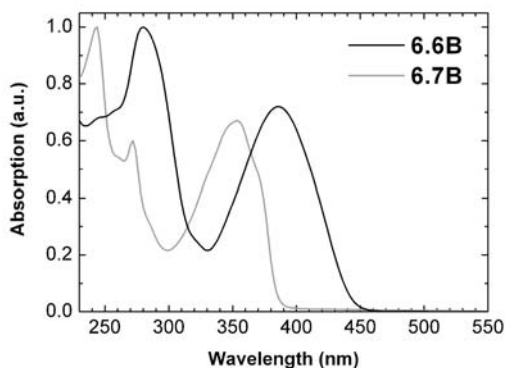
As for wire **4.5A**, the synthetic difficulties in obtaining **6.6A** pure are attributed to the relatively low HOMO-LUMO gap of the compound (see Section 6.3.2), which increases its reactivity. An alternative approach to the synthesis of **6.6A** could be by a Sonogashira cross-coupling of **6.5** and 4-ethynyl-1-thioacetylbenzene **2.10**, although coupling of this acetylene with 9,10-dibromoanthracene in an attempt to



synthesize 4.5A gave only 5% yield.<sup>26</sup> The yield of this coupling might be increased by the use of a more active diiodo-compound instead of a dibromo-compound. 2,7-Diiodo-9,10-methano[10]annulene has not been reported yet. Alternatively, the use of other thiol protecting groups or alternative anchoring groups can be explored.

### 6.3.2 UV-Vis Absorption Spectra

We have measured the UV-Vis absorption spectra of compounds **6.6B** and **6.7B** (Figure 6.3). In good agreement with the absorptions that were measured for the compounds without the *tert*-butyl thioethers,<sup>11</sup> the absorption of the methano[10]annulene-containing wire **6.6B** is redshifted by 33 nm compared to the absorption of naphthalene wire **6.7B**. The optical HOMO-LUMO gaps as determined from the onset of the absorptions are 2.81 eV for **6.6B** and 3.23 eV for **6.7B**. This is in good agreement with the relatively low aromatic stabilization of methano[10]annulene, when compared to naphthalene (as described in Section 6.1.2). Based on the trends that we observed in Chapter 4, we expect a higher conductance for methano[10]annulene wire **6.6** than for naphthalene-wire **6.7**.<sup>28</sup>

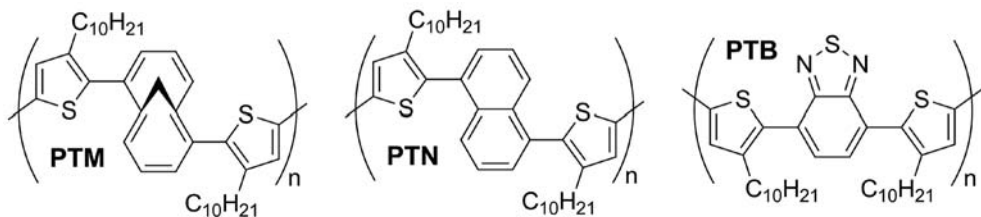


**Figure 6.3** Normalized UV-Vis absorption spectra of molecular wires **6.6B** (black) and **6.7B** (gray) as  $10^{-5}$ M solutions in  $\text{CH}_2\text{Cl}_2$ .

## 6.4 Copolymer of Methano[10]annulene and Bithiophene

In the aforementioned work of Peart and Tovar, 2,7-dibromo-1,6-methano[10]annulene **6.5** was cross-coupled with bithiophene units and the resulting monomer was polymerized electrochemically.<sup>11</sup> Electrochemical doping (oxidation) of this polymer resulted in a decrease of its optical absorption at 480 nm and the appearance of an absorption around 875 nm, whereas the naphthalene-analogue of this polymer showed a decreasing absorption at 430 nm and an increasing absorption at 650 nm upon oxidation. The 200 nm difference between the new absorptions was attributed to the improved delocalization of the generated carbocation in the methano[10]annulene-quarterthiophene copolymer. These experiments showed the potential for copolymers of thiophene and methano[10]annulene as conductive polymers for organic electronics. However, for organic electronic purposes soluble polymers are preferred.

In our group, Frank Brouwer has established a method to improve the quality of soluble conjugated copolymers which consist of a bithiophene and another conjugated unit by the use of bis(pinacolato)diboron (BiPi) in a Suzuki-type polymerization.<sup>29,30,31</sup> For that reason, we have incorporated methano[10]annulene in this conjugated copolymers as shown in Figure 6.4. The quality of the copolymers synthesized by this "BiPi-method" is higher compared to other polymerization methods, because the polymerization itself is a homopolymerization. The conjugated building blocks are functionalized with two decylthiophene units, subsequently brominated, and polymerized upon *in situ* formation of the boronic esters (Scheme 6.4).<sup>29</sup> A more common approach is to copolymerize a dibromo-functionalized monomer with a bis(trimethylstannyl)- or bis(boronic ester)-functionalized monomer.<sup>32</sup> However, this leads to a great diversity in end-groups of the polymers<sup>33</sup> and non-balanced amounts of both



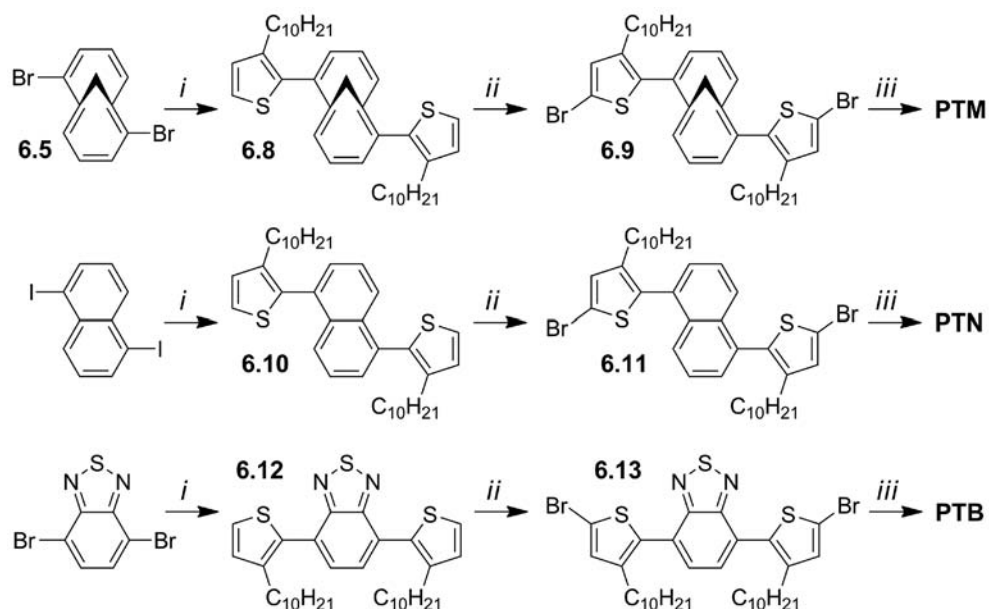
**Figure 6.4** The copolymers of methano[10]annulene (**PTM**), naphthalene (**PTN**), and benzothiadiazole (**PTB**) with didecyl-bithiophene, which are described in this Chapter.

monomers can result in lower molecular weights.

We have synthesized poly(2,7-bis(3-decylthiophen-2-yl)-1,6-methano[10]annulene) (**PTM**) and its naphthalene-analogue poly(1,5-bis(3-decylthiophen-2-yl)naphthalene) (**PTN**). Furthermore, we have synthesized poly(4,7-bis(3-decylthiophen-2-yl)-2,1,3-benzothiadiazole) (**PTB**), since benzothiadiazole is a well known building block for small band gap polymers.<sup>34,35</sup>

### 6.4.1 Synthesis of the Monomers

Monomers **6.8**, **6.10**, and **6.12** were synthesized by a Kumada coupling: the Grignard reagent of 2-bromo-3-decylthiophene was formed in a separate flask and transferred into a solution of nickel catalyst and 2,7-dibromo-9,10-methano[10]annulene, 1,5-diiodonaphthalene,<sup>24</sup> or 4,7-dibromo-2,1,3-benzothiadiazole.<sup>36</sup> These Kumada couplings afforded methano[10]annulene monomer **6.8** in 62% yield and naphthalene monomer **6.10** in 47% yield. The Kumada coupling with 4,7-dibromo-2,1,3-benzothiadiazole to form monomer **6.12** was less successful and gave only 9% yield after two subsequent coupling steps (see Experimental Section 6.6.3). Though a yield of 55% has been reported for the Kumada coupling of 2-bromo-3-decylthiophene and 4,7-dibromo-2,1,3-

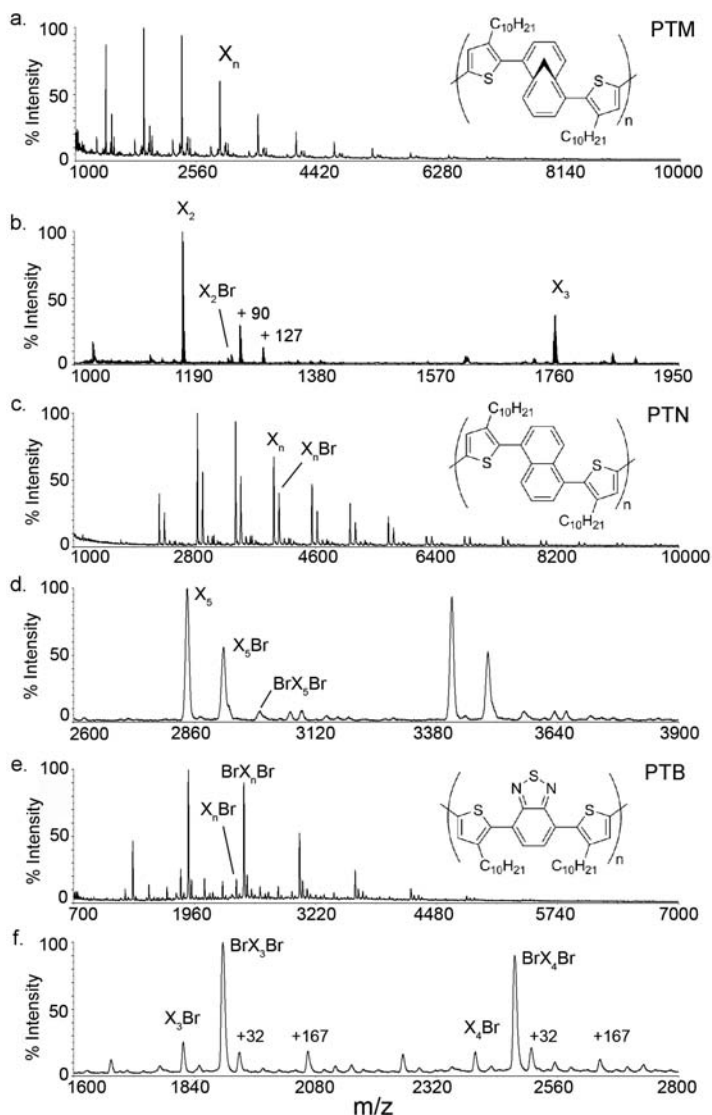


**Scheme 6.4** Syntheses of polymers **PTM**, **PTN**, and **PTB** via the BiPi-method: (i) 3-decyl-2-thienylmagnesium bromide, Ni(dppp)Cl<sub>2</sub>, THF, toluene, reflux; (ii) NBS, THF, 0-20°C; (iii) bis(pinacolato)diboron, Pd(dppf)Cl<sub>2</sub>, K<sub>3</sub>PO<sub>4</sub>, DMF, toluene, 110-120°C.

benzothiadiazole,<sup>37</sup> the Suzuki coupling is more widely applied in the synthesis of hexyl-analogues of **6.12**.<sup>36,38</sup> The brominations of monomers **6.8**, **6.10**, and **6.12** with NBS to obtain **6.9**, **6.11**, and **6.13** respectively were performed successfully.

## 6.4.2 BiPi-Polymerizations

The three brominated monomers **6.9**, **6.11**, and **6.13** were polymerized according to the BiPi-method, using bis(pinacolato)diboron, palladium-catalyst and the base



**Figure 6.5** MALDI-TOF mass spectra of polymers **PMT** (a, b), **PNT** (c, d), and **PBT** (e, f).

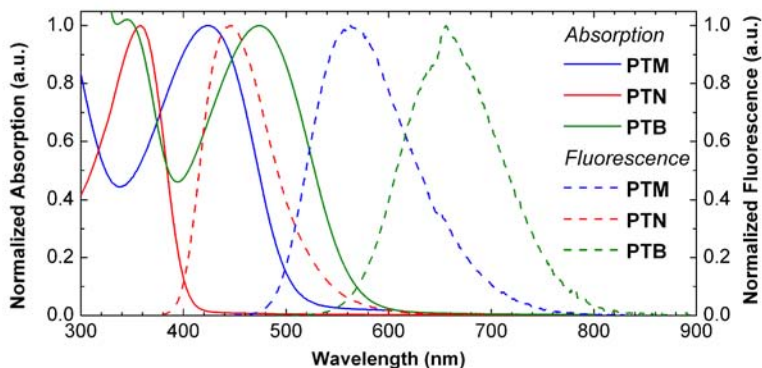
$K_3PO_4$ .<sup>29</sup> We determined the molecular weights by gel permeation chromatography (GPC) -though this is known to overestimate the weights of conjugated polymers- and found similar values for **PTM** ( $M_n = 6.2$  kg/mol,  $M_w = 23$  kg/mol) and **PTN** ( $M_n = 11$  kg/mol,  $M_w = 33$  kg/mol), though significantly lower values for **PTB** ( $M_n = 2.9$  kg/mol,  $M_w = 4.7$  kg/mol), which was furthermore obtained in low yield (44% versus ~90% for **PTM** and **PTN**). Additional information was obtained from the MALDI-TOF mass spectra of these polymers, which show the end-group distributions of the polymers (Figure 6.5). For polymer **PTM** we did not observe any brominated chains, whereas polymer **PTN** consisted of proton-terminated chains (H- $X_n$ -H) and a significant amount of bromine-terminated (Br- $X_n$ -H) chains. Assuming that direct debromination does not take place, bromine atoms are first replaced by boronic esters and proton-terminated chains are formed upon deboration. In the DMF/toluene solvent mixture that we used, deboration was also found for poly(3,3'-didecyl-quarterthiophene).<sup>29</sup> We attribute the small signal with an additional mass of 127 (in the spectrum of **PTM** in Figure 6.5b) to one boronic ester group (indicating incomplete deboration) and the additional mass of 90 could originate from the addition of a toluene radical to the polymer. Significant amounts of Br- $X_n$ -H being found for **PTN** could be due to the fast reaction of the monoboronated monomer in the Suzuki coupling (see ref. 29 for details).

In the MALDI-TOF mass spectrum of **PTB** we found mainly polymer chains with two bromine end groups (Br- $X_n$ -Br), besides Br- $X_n$ -H, chains that had reacted with the terthiophene matrix (+167), and oxidized chains (+32). The combination of the low yield, low molecular weight and high percentage of Br- $X_n$ -Br indicates that the replacement of bromine groups by boronic esters is seriously suppressed, due to the electron-poor nature of the benzothiadiazole unit.

### 6.4.3 UV-Vis Absorption and Fluorescence Spectra

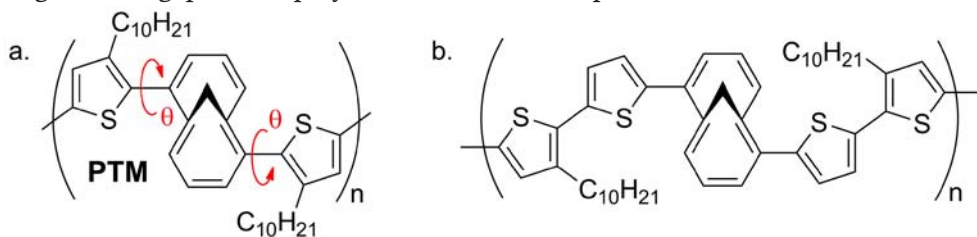
We have measured the UV-Vis absorption and the fluorescence spectra of the polymers **PTM**, **PTN**, and **PTB**. The naphthalene-based copolymer **PTN** was isolated as a light gray powder, in agreement with an absorption maximum at only 358 nm and optical band gap of 3.10 eV. The methano[10]annulene-based copolymer **PTB** shows an absorption maximum at 423 nm and an optical band gap of 2.47 eV. This band gap is lower than that of **PTN**, as predicted, but not as low as that of the benzothiadiazole-based copolymer **PTB**, which has a maximum at 474

nm and an optical band gap of only 2.20 eV. The fluorescence spectra show the same trend, with emission maxima at 446 nm, 563 nm, and 656 nm for **PTN**, **PTM**, and **PTB** respectively.



**Figure 6.6** Normalized UV-Vis absorption spectra of polymers **PMT**, **PNT**, and **PBT** (solid lines) and normalized fluorescence spectra of these polymers (dashed lines) as solutions in  $\text{CHCl}_3$ .

The optical band gaps of the soluble polymers **PTM** and **PTN** are significantly larger than those of the methano[10]annulene- and naphthalene-containing electrochemically polymerized films of Peart and Tovar ( $\sim 2.0$  and  $2.4$  eV respectively).<sup>11</sup> This difference is not caused by the difference in the number of thiophene units between the methano[10]annulene or naphthalene units, as can be concluded from a comparison of the electrochemically formed polymers with either two or four repeating thiophene units, for which the band gaps differ only marginally.<sup>12</sup> Most likely, the difference between our polymers and the electrochemically polymerized films is caused by the solubilizing decyl chains, which cause the thiophene units to bend out of the plane of the naphthalene or methano[10]annulene  $\pi$ -system, introducing a torsion angle ( $\theta$ ) in the polymer backbone (Figure 6.7a). This torsion angle decreases the  $\pi$ -overlap and results in larger band gaps. The polymer backbone is expected to be less twisted when



**Figure 6.7** **a.** The solubilizing decyl chains on the thiophenes introduce a torsion angle ( $\theta$ ) in the backbone of the polymer, increasing its band gap. **b.** In this second generation methano[10]annulene polymer, which contains additional thiophene units, this torsion angle is expected to be smaller.

additional thiophene rings are introduced between the decyl-functionalized thiophene units and the naphthalene or methano[10]annulene units (Figure 6.7b).<sup>39</sup>

## 6.5 Conclusions

We have developed a convenient, though not high yielding, synthetic protocol for 2,7-dibromo-9,10-methano[10]annulene and incorporated this building block in a molecular wire, which we compared with an analogous naphthalene-based wire. In the UV-Vis absorption spectra, we found a redshift of the methano[10]annulene-based wire compared to the naphthalene-based wire, which is a clear indication that methano[10]annulene, though being a ten  $\pi$ -electron aromatic system, has less aromatic stabilization compared to naphthalene. We expect therefore a higher conductance for the methano[10]annulene-wire than for the naphthalene-wire. However, its relatively small HOMO-LUMO gap increased the reactivity of the methano[10]annulene-wire, which resulted in the formation of a side-product in the final step of the synthesis. We have not been able to isolate the pure methano[10]annulene-wire with thioacetate end groups and suggest to follow an alternative synthetic approach towards methano[10]annulene-based wires.

We have incorporated the methano[10]annulene moiety successfully into soluble conjugated copolymers with didecyl-bithiophene, according to the strategy that was recently developed in our group. We compared the methano[10]annulene-based copolymer with naphthalene- and benzothiazole-based copolymers and found its band gap to be in between. We attribute the larger than expected band gap to a torsion angle in the backbone, caused by the solubilizing decyl chains. We suggest to incorporate additional non-substituted thiophene units to prevent the backbone of the polymer from twisting. Preliminary mobility measurements that compared methano[10]annulene-based copolymer **PTM** with naphthalene-based copolymer **PTN** in Field Effect Transistors gave a mobility of  $8 \cdot 10^{-6} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  (saturated regime), with a threshold voltage of -27 V and an on/off ratio of  $10^3$  for **PTM**, whereas no transistor behavior was found for **PTN**.<sup>40</sup> Better mobilities are expected for the next generation methano[10]annulene-based copolymers. We should note that the methano group of methano[10]annulene hinders the crystallization of the monomers and polymers. A methano[10]annulene-based polymer will therefore not adopt a crystalline structure in the film, which probably limits the mobility of charge carriers in the polymer.

## 6.6 Experimental Section

### General

All reactions were performed under a nitrogen atmosphere, using oven-dried glassware (150°C) and dry solvents. NBS was recrystallized from water and all brominations were performed in the dark. Diisopropylamine was distilled over NaOH. Copper iodide was heated and dried under vacuum. The catalysts used are: bis(triphenylphosphine)palladium(II) chloride ( $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ , CAS: 13965-03-2), 1,1'-bis(diphenylphosphino)ferrocene-palladium(II)dichloride dichloro-methane complex ( $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$ , CAS: 72287-26-4), [1,3-Bis(diphenylphosphino)propane] nickel(II) chloride ( $\text{Ni}(\text{dppp})\text{Cl}_2$ , CAS: 15629-92-2).

1,5-Diiodonaphthalene and 4,7-dibromo-2,1,3-benzothiadiazole were synthesized according to the literature procedures.<sup>24,36</sup> See Chapter 2 for the synthesis of 1-*tert*-butylthio-4-ethynylbenzene (2.13) and details on the analyses of organic compounds.

GPC measurements were performed on a Spectra Physics AS 1000 series machine equipped with a Viskotek H-502 viscometer and a Shodex RI-71 refractive index detector. The columns (PLGel 5 $\mu$  mixed-C, Polymer Laboratories) were calibrated using narrow disperse polystyrene standards (Polymer Laboratories). Samples were made in  $\text{CHCl}_3$  at a concentration of 1 mg/mL. MALDI-TOF measurements were performed on a Biosystems Voyager apparatus. Samples were prepared by mixing the matrix (terthiophene, 20 mg/mL in  $\text{CHCl}_3$ ) and the sample (1 mg/5 mL in  $\text{CHCl}_3$ ) in a 1:1 ratio. All the samples were measured in negative ion mode.

### 6.6.1 Synthesis of 2,7-dibromo-9,10-methano[10]annulene

#### Isotetralin (6.1)



This compound was made by a modification of the literature procedure.<sup>18</sup> Naphthalene (75.2 g, 0.59 mol), ethylenediamine (270 g, 4.5 mol), and *tert*-butanol (272 g, 3.6 mol) were placed in a 3 L three-necked flask under nitrogen. The setup was cooled to -3°C with an ice-salt bath and *n*-propylamine (600 mL) was added. Pieces of lithium wire (25.3 g, 3.65 gram-atoms) were added to the solution over 3 hours, while the temperature was kept below 20°C. The reaction mixture was stirred overnight, after which 1 L ice water was added. The mixture was filtered to remove the white precipitate, layers were separated, and the aqueous layer was extracted with ether (2 x 600 mL). The combined organic layers were washed with water (2 x 600 mL) and brine (600 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered, and the solvent was removed under reduced pressure. The crude product was recrystallized from methanol, yielding 42 grams (0.32 mol, 56%) of 6.1 as white crystals.

<sup>1</sup>H-NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.73 (s, 4H), 2.54 (s, 8H). <sup>13</sup>C-NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  124.4, 123.3, 30.8.

#### 1,6-Methano[10]annulene (6.3)



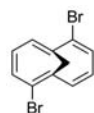
This compound was made by a modification of the literature procedure.<sup>16</sup> Zinc (93 g,



1.41 mol) and copper chloride (44 g, 0.44 mol) were placed in an oven-dried 3 L three-necked flask and dry ether was added (750 mL). The suspension was refluxed for 40 minutes and methylene iodide (329 g, 1.23 mol) was added dropwise in 2 hours, upon which the mixture foamed heavily and turned dark red. Ether was added (500 mL) to compensate the volume that was lost and the mixture was refluxed for another 2 hours. Then a solution of **6.1** (30 g, 0.23 mol) in ether (250 mL) was added dropwise in 15 minutes and the reaction mixture was refluxed for 16 hours. An aqueous solution of  $\text{NH}_4\text{Cl}$  (100 mL) was added, followed by 2 M HCl (100 mL). The reaction mixture was filtered through cotton wool and pentane (300 mL) was used to rinse the flask. The resulting organic layer was washed with water (2 x 500 mL) and brine (350 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to a volume of 200 mL. This yellow solution was run through a plug of silica gel, eluted with pentane. Around 80% of the solvent was removed by rotary evaporation and the remaining solvent was distilled through a vigreux column at ambient pressure, to leave 36.3 g of a colorless liquid, which contained ~50% **6.2**, as determined by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  5.52 (s, 4H), 2.31 (d,  $J = 15$ , 4H), 2.15 (d,  $J = 15$ , 4H), 0.58 (s, 2H).

Dioxane (900 mL) was distilled from KOH (45 g) into a 1 L three-necked flask. DDQ (110 g, 0.485 mol) was dissolved in the dioxane upon heating, to give a dark red solution. Crude **6.2** (36.2 g) was added to this solution and the reaction mixture was refluxed for 63 hours, after which 600 mL of the dioxane was removed by distillation through a vigreux column. The remaining slurry was filtered through a glass filter and washed with warm pentane (500 mL), which resulted in the formation of a black precipitate in the filtrate. The filtrate was filtered through cotton wool and all solvents were removed by distillation over a vigreux column. The resulting black liquid was purified by column chromatography (silica gel, pentane), yielding 11.2 g of a yellow liquid, which contained 5 g (35 mmol, 15% yield) **6.3**, besides naphthalene and solvent, as determined by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.45 (dd,  $J = 6.3$ , 2.2, 4H), 7.10 (dd,  $J = 6.2$ , 2.2, 4H), -0.44 (s, 2H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 50 MHz):  $\delta$  129.1, 126.5, 115.3, 35.3.

### 2,7-Dibromo-1,6-methano[10]annulene (**6.5**)



This compound was made by a modification of the literature procedure.<sup>22</sup> A 3:1 mixture of methano[10]annulene and naphthalene (6.12 g, 34.0 mmol **6.3**) was placed in an oven-dried 500 mL three-necked flask.  $\text{CH}_2\text{Cl}_2$  (200 mL) was added and the solution was cooled in an ice-salt bath. NBS (6.67 g, 37.5 mmol) was added and the reaction was stirred overnight at room temperature and refluxed for 5 hours. After cooling, the reaction mixture was filtered through a plug of silica gel, eluted with  $\text{CH}_2\text{Cl}_2$  and the solvent was removed by distillation through a vigreux column. The crude product was further purified by column chromatography (silica gel, pentane) and removal of the pentane by distillation through a vigreux column yielded 6.04 g of yellow liquid, which contained 3.9 g (17.7 mmol) **6.4**.

$^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400MHz):  $\delta$  7.76-7.72 (m, 1H), 7.43 (d,  $J = 8.8$ , 2H), 7.29 (d,  $J = 10$ , 1H), 7.23 (dd,  $J = 2.9$ , 6.2, 2H), 7.01 (t,  $J = 9.5$ , 1H), -0.29 (d,  $J = 10$ , 1H), -0.43 (d,  $J = 10$ , 1H).

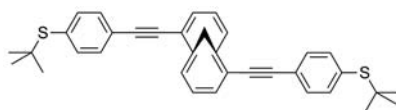
The yellow liquid (6.03 g, 17.7 mmol **6.4**) was placed in a 100 mL two-necked flask and  $\text{CH}_2\text{Cl}_2$  (70 mL) and NBS (3.18 g, 17.9 mmol) were added, in the dark. The reaction mixture was refluxed for 4 hours and stirred overnight at room temperature, after which it was filtered through a plug of silica gel, eluted with  $\text{CH}_2\text{Cl}_2$ . The solvent was removed by distillation through a vigreux column and the naphthalene was removed by distillation in microdistillation setup at

70 mTorr. The residual dark brown oil was a mixture of **6.4** and **6.5**, which was run over a column of silica gel, eluted with pentane, after which the solvent was removed by distillation through a vigreux column. To the resulting 4.61 g yellow oil were added CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and NBS (1.80 g, 10.1 mmol) and the mixture was refluxed for 15 hours in the dark. After cooling, the reaction mixture was filtered through a plug of silica gel, eluted with CH<sub>2</sub>Cl<sub>2</sub> and the solvent was removed by distillation through a vigreux column. The crude product was further purified by column chromatography (silica gel, pentane) and removal of the pentane by distillation through a vigreux column yielded a yellow oil. This was recrystallized from ethanol (25 mL), yielding 2.31 g (7.70 mmol, 23% over two steps) of the title compound as yellow crystals.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.71 (d, *J* = 9.0, 2H), 7.41 (d, *J* = 9.8, 2H), 7.13 (t, *J* = 9.4, 2H), -0.26 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 130.77, 130.49, 129.28, 117.87, 114.45, 33.88. IR (cm<sup>-1</sup>): 3039, 1900, 1715, 1519, 1446, 1383, 1219, 1153, 1010, 964, 951, 741, 917, 749, 702, 649.

## 6.6.2 Synthesis of Molecular Wires 6.6 and 6.7

### 2,7-Bis[(4-*tert*-butylthiophenyl)ethynyl]-1,6-methano[10]annulene (**6.6B**)

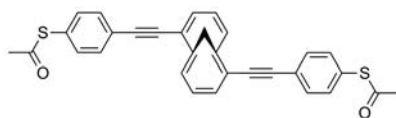


To a suspension of **6.5** (480 mg, 1.60 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (125 mg, 0.178 mmol), and copper iodide (41.1 mg, 0.216 mmol) in THF (80 mL) were added diisopropylamine (16 mL) and **2.13** (764 mg, 4.01 mmol). The reaction mixture was refluxed for 15 hours,

concentrated, and run over a plug of silica gel, eluted with CH<sub>2</sub>Cl<sub>2</sub>. The crude material was preadsorbed onto silica gel and purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/heptane 1:3), yielding 389 mg (0.750 mmol, 47%) of the title compound as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.83 (d, *J* = 8.6, 2H), 7.55 – 7.48 (m, 8H), 7.48 (d, *J* = 9.7, 2H), 7.21 (t, *J* = 9.1, 2H), 1.31 (s, 18H), -0.13 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 137.27, 133.28, 132.09, 131.40, 130.04, 127.52, 123.67, 121.93, 118.00, 92.59, 88.70, 46.54, 35.00, 30.99. IR (cm<sup>-1</sup>): 2972, 2956, 2935, 2915, 2890, 2856, 2201, 1919, 1588, 1526, 1481, 1468, 1453, 1393, 1363, 1164, 1147, 1015, 830, 762. HRMS (APCI) calculated for [M+H]<sup>+</sup> 519.2175, found 519.2161.

### 2,7-Bis[(4-acetylthiophenyl)ethynyl]-1,6-methano[10]annulene (**6.6A**)

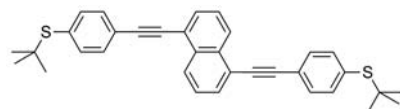


**6.6B** (100 mg, 0.19 mmol) was dissolved in chloroform/toluene (1:1, 15 mL) and acetyl chloride (0.55 mL) was added. The solution was cooled with an ice-salt bath and BBr<sub>3</sub> (1 M in CH<sub>2</sub>Cl<sub>2</sub>, 0.50 mL, 0.50 mmol) was added slowly. The reaction mixture was stirred for 1 hour while cooled and for another 18 hours at room temperature, after which it was poured into ice water (200 mL). This mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 x 50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and all volatiles were removed by rotary evaporation. The crude material was preadsorbed onto silica gel and purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/heptane 2:1) yielding 56 mg (0.114 mmol, 60%) of the impure title compound as a red oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.83 (d, *J* = 8.7, 2H), 7.58 (d, *J* = 8.0, 4H), 7.49 (d, *J* = 9.6, 2H),

7.41 (d,  $J = 8.0$ , 4H), 7.22 (t,  $J = 9.2$ , 2H), 2.44 (s, 6H), -0.13 (s, 2H); 2.32 (d,  $J = 2.6$ ), -0.25 (d,  $J = 8.7$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  193.47, 134.25, 132.17, 132.07, 130.13, 128.03, 127.56, 124.55, 121.76, 117.98, 92.35, 88.88, 34.98, 30.29, 29.69. IR ( $\text{cm}^{-1}$ ): 3032, 2920, 2851, 2200, 1907, 1702, 1590, 1484, 1396, 1350, 1113, 1087, 1014, 946, 824, 763, 606. HRMS (APCI) calculated for  $[\text{M}+\text{H}]^+$  491.1134, found 491.1123.

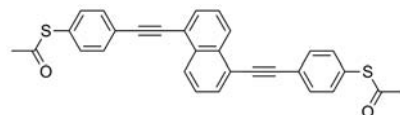
### 1,5-Bis[(4-*tert*-butylthiophenyl)ethynyl]naphthalene (6.7B)



To a suspension of 1,5-diidodonaphthalene (339 mg, 0.891 mmol),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (62.5 mg, 0.089 mmol), and copper iodide (34.8 mg, 0.18 mmol) in THF (50 mL) were added diisopropylamine (10 mL) and **2.13** (567 mg, 2.28 mmol). The reaction mixture was refluxed for 20 hours, concentrated, and run over a plug of silica gel, which was eluted with  $\text{CH}_2\text{Cl}_2$ . The crude material was preadsorbed onto silica gel, purified by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ /heptane 1:3), and recrystallized from heptane, yielding 342 mg (0.685 mmol, 77%) of the title compound as light yellow crystals.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.45 (d,  $J = 8.5$ , 2H), 7.82 (d,  $J = 7.0$ , 2H), 7.64 – 7.54 (m, 10H), 1.33 (s, 18H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  137.32, 133.55, 133.07, 131.53, 131.06, 127.14, 126.21, 123.55, 121.20, 94.18, 88.76, 46.57, 31.00. IR ( $\text{cm}^{-1}$ ): 2973, 2953, 2935, 2917, 2892, 2857, 2163, 1943, 1588, 1481, 1364, 1165, 1147, 1097, 1016, 833, 788, 609. HRMS (APCI) calculated for  $[\text{M}+\text{H}]^+$  505.2018, found 505.2005.

### 1,5-Bis[(4-acetylthiophenyl)ethynyl]naphthalene (6.7A)



**6.7B** (203 mg, 0.402 mmol) was dissolved in chloroform/toluene (1:1, 40 mL) and acetyl chloride (4 mL) was added. While stirring,  $\text{BBr}_3$  (1 M in  $\text{CH}_2\text{Cl}_2$ , 8 mL, 8 mmol) was added slowly. The reaction mixture was stirred for 4 hours and poured into ice water (400 mL). This was extracted with  $\text{CH}_2\text{Cl}_2$  (4 x 200 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered, and all volatiles were removed by rotary evaporation. The crude material was preadsorbed onto silica gel and purified by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ /heptane 2:1), yielding 164 mg (0.343 mmol, 85%) of the title compound as a light yellow solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.44 (d,  $J = 8.6$ , 2H), 7.82 (d,  $J = 7.1$ , 2H), 7.71 – 7.65 (m, 4H), 7.59 (t,  $J = 7.7$ , 2H), 7.48 – 7.43 (m, 4H), 2.46 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  193.42, 134.33, 133.07, 132.22, 131.19, 128.33, 127.23, 126.26, 124.45, 121.07, 93.94, 88.94, 30.32. IR ( $\text{cm}^{-1}$ ): 3044, 2923, 2192, 1924, 1683, 1590, 1483, 1396, 1360, 1135, 1113, 1091, 1014, 958, 822, 782, 627, 606. HRMS (APCI) calculated for  $[\text{M}+\text{H}]^+$  477.0978, found 477.0963.

## 6.6.3 Synthesis of Monomers and Polymers PTM, PTN and PTB

### 3-Decylthiophene



This compound was synthesized according to a literature procedure.<sup>41</sup> Magnesium (4.79 g, 197 mmol) was activated by stirring with glass shatters. 1-Bromodecane (43.17 mL, 195 mmol) in dry ether (125 mL) was added dropwise to the magnesium in dry

ether (60 mL) and the mixture was refluxed for 1 hour. Ni(dppp)Cl<sub>2</sub> (125 mg, 0.24 mmol) and 3-bromothiophene (21.3 g, 131 mmol) were suspended in dry ether (200 mL) and cooled with an ice-salt bath. The Grignard reagent was added via a cannula and the mixture was stirred for 3 days at room temperature. The reaction was quenched with water (125 mL), which caused the formation of solids and severe effervescence to occur. The mixture was extracted with pentane (3 x 150 mL) and the combined organic layers were washed with water (300 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. Distillation under reduced pressure (3.60 mTorr; 125°C) yielded 26.14 g of pure 3-decylthiophene (89% yield) as a colorless liquid.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.24 (dd, *J* = 2.4, *J* = 3.0, 1H); 6.93 (t, *J* = 4.3 2H); 2.63 (t, *J* = 7.2 Hz, 2H); 1.66-1.57 (m, 2 H); 1.36-1.24 (m, 14H); 0.89 (t, *J* = 6.7 Hz, 3H). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>): δ 143.50, 128.52, 125.24, 119.96, 32.14, 30.80, 30.52, 29.86, 29.85, 29.71, 29.58, 29.57, 22.53, 14.36.

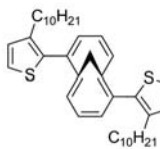
### 2-Bromo-3-decylthiophene



This compound was synthesized according to a literature procedure.<sup>42</sup> NBS (9.20 g, 51.3 mmol) was dissolved in DMF (40 mL) added dropwise to a solution of 3-decylthiophene (11.78 g, 52.5 mmol) in DMF (60 mL), cooled with an ice-salt bath. The mixture was stirred overnight at room temperature, quenched with 2M HCl solution (200 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 150 mL). The organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent was removed. The crude product was distilled under reduced pressure (19 mTorr, 110 °C), which yielded 11.25 g (37.1 mmol, 72%) of pure 2-bromo-3-decylthiophene as a colorless liquid.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.18 (d, *J* = 5.6, 1H) 6.79 (d, *J* = 5.6, 1H) 2.56 (t, *J* = 7.6, 2 H) 1.62-1.51 (m, 2H) 1.31-1.20 (m, 14H) 0.88 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz): δ 141.66, 127.97, 124.81, 108.80, 32.00, 29.80, 29.72, 29.69, 29.53, 29.45, 29.39, 29.30, 22.78, 14.17.

### 2,7-Bis(3-decylthiophen-2-yl)-1,6-methano[10]annulene (6.8)

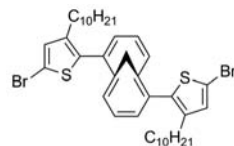


Magnesium (224 mg, 9.22 mmol) was activated by stirring with glass shatters for 1 hour and 5 mL THF was added. 2-Bromo-3-decylthiophene (2.501 g, 8.25 mmol) in 10 mL THF was added dropwise, the reaction was initiated by addition of a crystal of iodine, and the mixture was refluxed for three hours. After cooling to room temperature, the Grignard reagent was added dropwise (via a Teflon cannula) to a mixture of **6.5** (848 mg, 2.83 mmol) and Ni(dppp)Cl<sub>2</sub> (12.2 mg, 0.023 mmol) in 20 mL THF/toluene (1:2) and refluxed for 15 hours. The reaction was quenched with 50 mL NH<sub>4</sub>Cl and 50 mL water and extracted with DCM (3 x 100 mL). The organic layers were washed with water (75 mL) and brine (75 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. The solvent was removed and the obtained oil was purified by column chromatography (silica gel, pet. ether 40-60) to give 1.03 g (1.76 mmol, 62%) of the title compound as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.35 (d, *J* = 8.7, 2H), 7.29 (d, *J* = 5.2, 2H), 7.21 (d, *J* = 9.4, 2H), 7.10 – 7.02 (m, 4H), 2.98 – 2.86 (m, 2H), 2.81 – 2.69 (m, 2H), 1.67 – 1.51 (m, 4H), 1.36 – 1.05 (m, 28H), 0.84 (t, *J* = 6.9, 6H), -0.09 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 140.89, 136.50, 134.04, 129.68, 129.18, 129.09, 126.75, 124.99, 117.23, 35.17, 31.88, 30.55, 29.56, 29.51, 29.33, 29.30 (multiple signals), 22.67, 14.12. IR (cm<sup>-1</sup>): 3034, 2922, 2852, 1540, 1464, 1399, 1377, 1290,

1020, 836, 765, 720, 657. HRMS (APCI) calculated for  $[M+H]^+$  587.3740, found 587.3746. Calcd for  $C_{39}H_{54}S_2$ : C, 79.80; H, 9.27; S, 10.93. Found: C, 79.86; H, 9.12; S, 10.81.

### 2,7-Bis(5-bromo-3-decylthiophen-2-yl)-1,6-methano[10]annulene (6.9)

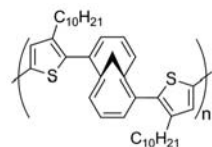


**6.8** (0.840 g, 1.43 mmol) was dissolved in 40 mL THF and cooled with an ice-salt bath. NBS (0.535 g, 3.95 mmol) in 15 mL THF was added dropwise over 20 minutes. The yellow mixture was stirred for 18 hours while warming to room temperature and then quenched with 200 mL 2M HCl and extracted with DCM (3 x 200 mL). The organic layers were

washed with water (200 mL) and brine (200 mL), dried over  $Na_2SO_4$ , and filtered. The solvent was removed under reduced pressure and the product was purified by column chromatography (silica gel, heptane), yielding 0.831 g (1.12 mmol, 78%) of the title compound as a brown oil.

$^1H$  NMR (400 MHz,  $CD_2Cl_2$ ):  $\delta$  7.39 (d,  $J = 8.7$ , 2H), 7.17 (d,  $J = 9.5$ , 2H), 7.07 (t,  $J = 9.1$ , 2H), 7.02 (s, 2H), 2.89 – 2.77 (m, 2H), 2.72 – 2.59 (m, 2H), 1.61 – 1.41 (m, 4H), 1.33 – 1.05 (m, 28H), 0.85 (t,  $J = 6.9$ , 6H), -0.14 (s, 2H).  $^{13}C$  NMR (50 MHz,  $CDCl_3$ ):  $\delta$  141.65, 138.00, 132.85, 131.90, 129.95, 129.20, 127.00, 117.24, 111.66, 34.98, 31.88, 30.35, 29.54, 29.46, 29.29, 29.22, 29.18, 22.67, 14.11. IR ( $cm^{-1}$ ): 3034, 2920, 2851, 1540, 1524, 1455, 1432, 1376, 1187, 984, 829, 764, 720. HRMS (APCI) calculated for  $[M+H]^+$  745.1930, found 745.1931. Calcd for  $C_{39}H_{52}Br_2S_2$ : C, 62.89; H, 7.04; Br, 21.46; S, 8.61. Found: C, 62.37; H, 6.97; S, 8.51.

### Poly(2,7-bis(3-decylthiophen-2-yl)-1,6-methano[10]annulene) (PTM)

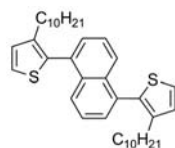


**6.9** (0.505 g, 0.678 mmol) and bis(pinacolato)diboron (173 mg, 0.680 mmol) were mixed with 23 mL DMF/toluene (1:3) and degassed.  $K_3PO_4$  (0.730 g, 3.44 mmol) and  $Pd(dppf)Cl_2 \cdot CH_2Cl_2$  (14.6 mg, 0.018 mmol) were added and the mixture was heated for 18 hours at 110 °C. The solvent was removed and the resulting solid was dissolved in 30 mL chloroform,

precipitated in 400 mL cold methanol, and 5 mL conc. HCl was added. The polymer was collected by centrifugation and purified by soxhlet extraction using methanol (450 mL, 23 hours), acetone (2 x 450 mL, 23 hours), and chloroform (450 mL, 23 hours). The chloroform was partially evaporated and the product was precipitated in a vortex of cold methanol and collected by centrifugation. The resulting dark yellow polymer was dried in vacuum, yielding 0.361 g (91%) **PTM**.

$^1H$  NMR (400 MHz,  $CD_2Cl_2$ )  $\delta$  7.47 (bd,  $J = 8.1$ , 2H), 7.26 (bt,  $J = 9.0$ , 2H), 7.17 (bs, 2H), 7.15 – 7.04 (m, 2H), 2.92 (bs, 2H), 2.75 (bs, 2H), 1.62 (bs, 4H), 1.34 – 0.93 (m, 28H), 0.83 (bt,  $J = 6.0$ , 6H), -0.05 (d,  $J = 9.3$ , 2H). IR ( $cm^{-1}$ ): 3034, 2920, 2850, 1523, 1455, 1437, 1376, 1253, 1196, 1020, 956, 827, 764, 720. GPC (chloroform):  $M_n = 6174$  g/mol,  $M_w = 22869$  g/mol, PDI = 3.69.

### 1,5-Bis(3-decylthiophen-2-yl)naphthalene (6.10)

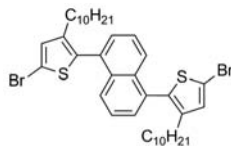


Magnesium (193 mg, 7.98 mmol) was activated by stirring with glass shatters. 2-Bromo-3-decylthiophene (2.251 g, 7.33 mmol) in 5.5 mL ether was added dropwise and the mixture was refluxed several hours. The Grignard reagent was then added dropwise to a mixture of 1,5-diiodonaphthalene (1.359 g, 3.58 mmol) and  $Ni(dppp)Cl_2$  (21 mg, 0.039 mmol) in 26 mL ether/toluene (1:2) and

refluxed overnight. The reaction was quenched with 80 mL  $\text{NH}_4\text{Cl}$  and extracted with DCM (3 x 100 mL). The organic layers were washed with aq. sat.  $\text{Na}_2\text{CO}_3$  (150 mL), brine (150 mL), and water (100 + 200 mL), dried over  $\text{Na}_2\text{SO}_4$ , and filtered. The solvent was removed and the obtained oil was purified by column chromatography (silica gel, pet. ether) and recrystallized from isopropanol/methanol (3:1), which yielded 0.957 g (1.67 mmol, 47%) of the title compound as white powder.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.78 (d,  $J$  = 8.7, 2H), 7.48 – 7.43 (m, 4H), 7.37 (d,  $J$  = 5.2, 2H), 7.07 (d,  $J$  = 5.2, 2H), 2.38 (t, 4H), 1.52 – 1.43 (m, 4H), 1.27 – 1.12 (m, 28H), 0.86 (t,  $J$  = 7.1, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.92, 135.20, 133.22, 132.21, 129.26, 128.38, 126.71, 125.26, 124.37, 31.87, 30.52, 29.53, 29.48, 29.30 (2 signals), 29.19, 28.72, 22.66, 14.11. IR ( $\text{cm}^{-1}$ ): 3061, 2953, 2922, 2852, 1713, 1590, 1500, 1465, 1393, 1377, 1310, 1227, 1208, 1092, 1069, 1016, 946, 901, 876, 835, 792, 720, 687, 655. HRMS (APCI) calculated for  $[\text{M}+\text{H}]^+$  573.3583, found 573.3583. Calcd for  $\text{C}_{38}\text{H}_{52}\text{S}_2$ : C, 79.66; H, 9.15; S, 11.19. Found: C, 79.34; H, 9.04; S, 11.11.

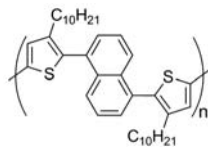
### 1,5-Bis(5-bromo-3-decylthiophen-2-yl)naphthalene (6.11)



**6.11** (0.841 g, 1.47 mmol) was dissolved in 50 mL THF and NBS (0.708 g, 3.95 mmol) in 15 mL THF was added dropwise over 40 minutes. The yellow mixture was stirred overnight and then quenched with 200 mL 2M HCl and extracted with DCM (3 x 200 mL). The organic layers were washed with brine (200 mL), dried over  $\text{Na}_2\text{SO}_4$ , and filtered. The solvent was removed under reduced pressure and the product was recrystallized from isopropanol/methanol (3:1), yielding 0.868 g (1.19 mmol, 81%) of **6.11** as a white powder.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.90 – 7.76 (m, 2H), 7.51 – 7.40 (m, 4H), 7.03 (s, 2H), 2.31 (bs, 4H), 1.50 – 1.40 (m, 4H), 1.32 – 1.01 (m, 28H), 0.87 (t,  $J$  = 7.0, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.70, 136.62, 133.03, 131.17, 131.05, 129.55, 126.90, 125.52, 110.97, 31.87, 30.31, 29.52, 29.43, 29.29, 29.23, 29.05, 28.69, 22.66, 14.10. IR ( $\text{cm}^{-1}$ ): 2945, 2921, 2849, 1591, 1504, 1467, 1448, 1393, 1373, 1261, 1209, 1183, 1102, 1069, 1018, 984, 968, 953, 913, 888, 875, 856, 827, 811, 794, 742, 732, 722, 664, 640, 593, 571. HRMS (APCI) calculated for  $[\text{M}+\text{H}]^+$  731.1773, found 731.1772. Calcd for  $\text{C}_{38}\text{H}_{50}\text{Br}_2\text{S}_2$ : C, 62.46; H, 6.90; S, 8.78. Found: C, 62.44; H, 6.85; S, 8.76.

### Poly(1,5-bis(3-decylthiophen-2-yl)naphthalene) (PTN)

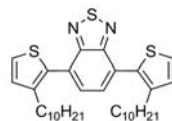


**6.11** (0.497 g, 0.68 mmol) and bis(pinacolato)diboron (174 mg, 0.68 mmol) were mixed with 22 mL DMF/ toluene (1:3) and degassed.  $\text{K}_3\text{PO}_4$  (0.750 g, 3.54 mmol) and  $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$  (13 mg, 0.016 mmol) were added and the mixture was heated to 110 °C and stirred overnight at this temperature.

Most of the solvent had evaporated and the resulting solid was dissolved in chloroform and precipitated in 400 mL cold methanol. The polymer was collected by centrifugation and purified by soxhlet extraction using methanol (400 mL, 23 hours), acetone (400 mL, 23 hours), and chloroform (400 mL, 23 hours). The chloroform was partially evaporated and the product was precipitated in a vortex of cold methanol and collected by centrifugation. The resulting light gray polymer was dried in vacuum, yielding 0.342 g (88%) of PTN.

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95 (bd,  $J=7.6$  Hz, 2H) 7.61-7.46 (b, 4H) 7.20 (b, 2H) 2.39 (b, 4H) 1.61-1.42 (b, 4H) 1.32-1.00 (b, 28H) 0.86 (bt,  $J= 6.8$  Hz, 6H). IR ( $\text{cm}^{-1}$ ): 2920, 2850, 1589, 1503, 1455, 1395, 1376, 1207, 1180, 1076, 903, 824, 791, 720, 575, 546. GPC (chloroform):  $M_n = 10993$  g/mol,  $M_w = 32919$  g/mol, PDI = 2.98.

#### 4,7-Bis(3-decylthiophen-2-yl)-2,1,3-benzothiadiazole (6.12)



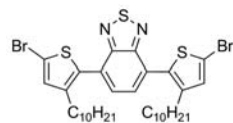
Magnesium (413 mg, 17.01 mmol) was activated by stirring with glass shatters. 2-Bromo-3-decylthiophene (4.295 g, 14.17 mmol) in 11 mL THF was added dropwise and the mixture was refluxed for 3 hours. After cooling to room temperature the Grignard reagent was added dropwise to a mixture 4,7-dibromo-2,1,3-benzothiadiazole (1.705 g, 5.80 mmol) and  $\text{Ni(dppp)Cl}_2$  (48 mg, 0.089 mmol) in 49 mL THF/toluene (4:3) and refluxed overnight. The reaction was quenched with 200 mL  $\text{NH}_4\text{Cl}$  and extracted with DCM (3 x 200 mL). The organic layers were washed with aq. sat.  $\text{Na}_2\text{CO}_3$  (250 mL), brine (200 mL), and water (2 x 200 mL), dried over  $\text{Na}_2\text{SO}_4$ , and filtered. The solvent was removed and obtained oil was purified by column chromatography (silica gel, pet. ether) to give a mixture of mono- and bis-coupled products. This mixture was treated with more Grignard reagent.

Magnesium (162 mg, 6.68 mmol) was activated by stirring with glass shatters. 2-Bromo-3-decylthiophene (1.68 g, 5.55 mmol) in 4 mL THF was added dropwise and the mixture was refluxed for 3 hours. After cooling to room temperature the Grignard reagent was added dropwise to  $\text{Ni(dppp)Cl}_2$  (28 mg, 0.052 mmol) and the mixture of mono- and bis-coupled products in 29 mL THF/toluene (4:3) and the resulting reaction mixture was refluxed overnight. The reaction was quenched with 100 mL  $\text{NH}_4\text{Cl}$  and extracted with DCM (3 x 90 mL). The organic layers were washed with aq. sat.  $\text{Na}_2\text{CO}_3$  (120 mL), brine (120 mL), and water (2 x 120 mL), dried over  $\text{Na}_2\text{SO}_4$ , and filtered. Solvent were removed and the resulting brown oil was purified by column chromatography (silica gel, pet. ether/DCM 2:1) and recrystallized from acetonitrile at  $-35^\circ\text{C}$ , which yielded 0.316 g (0.54 mmol, 9%) of **6.12** as a dark yellow oil at room temperature.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.64 (s, 2H), 7.44 (d,  $J = 5.2$ , 2H), 7.10 (d,  $J = 5.2$ , 2H), 2.66 (t,  $J = 7.7$ , 4H), 1.68 – 1.57 (m, 4H), 1.33 – 1.00 (m, 28H), 0.86 (t,  $J = 7.0$ , 6H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  154.25, 141.68, 132.14, 129.87, 129.19, 127.43, 125.83, 31.86, 30.71, 29.55, 29.52, 29.44, 29.37, 29.34, 29.30, 22.66, 14.10.

IR ( $\text{cm}^{-1}$ ): 2953, 2922, 2852, 1577, 1537, 1524, 1465, 1436, 1377, 1336, 1269, 1230, 1094, 876, 847, 832, 720, 692, 663. HRMS (APCI) calculated for  $[\text{M}+\text{H}]^+$  581.3052, found 581.3052.

#### 4,7-Bis(5-bromo-3-decylthiophen-2-yl)-2,1,3-benzothiadiazole (6.13)

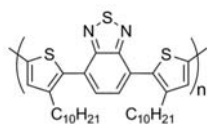


**6.12** (0.523 g, 0.90 mmol) was dissolved in 25 ml THF and NBS (0.343 g, 1.93 mmol) in 8 mL THF was added dropwise over 40 minutes. The yellow mixture was stirred overnight and then quenched with 100 mL 2M HCl and extracted with DCM (3 x 125 mL). The combined organic layers were washed with brine (150 mL) and dried on  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure to give an orange oil, which contained mono- and bis-brominated products (1:1 ratio) and a trace of starting material. Attempts to purify by column chromatography or recrystallization were not successful. Therefore, the mixture was dissolved in 25 mL THF and

cooled with an ice-salt bath. NBS (0.175 g, 0.98 mmol) in 10 mL THF was added dropwise over 15 minutes and the reaction mixture was stirred for 2 hours and quenched with 120 mL 2M HCl. The mixture was extracted with DCM (3 x 100 mL), washed with brine (150 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. The solvent was removed under reduced pressure and the product was purified by column chromatography (silica gel, heptane/DCM 1:1), yielding 0.715 g (0.97 mmol, 108%) of **6.13** as a red oil (that contained traces of solvent).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.60 (s, 2H), 7.06 (s, 2H), 2.60 (t, *J* = 7.5, 4H), 1.65 – 1.56 (m, 4H), 1.35 – 1.08 (m, 28H), 0.87 (t, *J* = 7.0, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 153.89, 142.42, 133.51, 131.96, 129.67, 126.59, 113.18, 31.87, 30.52, 29.55, 29.49, 29.39, 29.34, 29.32, 29.30, 22.66, 14.10. IR (cm<sup>-1</sup>): 2951, 2920, 2850, 1726, 1576, 1525, 1485, 1465, 1431, 1376, 1261, 1185, 1070, 1018, 983, 924, 873, 828, 795, 721, 678. HRMS (APCI) calculated for [M+H]<sup>+</sup> 739.1242, found 739.1240. Calcd for C<sub>34</sub>H<sub>46</sub>Br<sub>2</sub>N<sub>2</sub>S<sub>3</sub>: C, 55.28; H, 6.28; N, 3.79; S, 13.02. Found: C, 55.91; H, 6.44; N, 3.74; S, 12.98.

### Poly(4,7-bis(3-decylthiophen-2-yl)-2,1,3-benzothiadiazole) (PTB)



**6.13** (0.666 g, 0.90 mmol) and bis(pinacolato)diboron (158 mg, 0.62 mmol) were mixed with 25 mL DMF/ toluene (1:3) and degassed. K<sub>3</sub>PO<sub>4</sub> (0.804 g, 3.8 mmol) and Pd(dppf)Cl<sub>2</sub>.CH<sub>2</sub>Cl<sub>2</sub> (11 mg, 0.013 mmol) were added and the mixture was heated to 120 °C and stirred overnight at this temperature.

The solvent was removed and the resulting solid was dissolved in chloroform, precipitated in 400 mL cold methanol, and a few drops of conc. HCl were added. The polymer was collected by centrifugation and purified by soxhlet extraction using methanol (400 mL, 23 hours), acetone (2 x 400 mL, 23 hours each), and chloroform (400 mL, 23 hours). The chloroform was partially evaporated and the product was precipitated in a vortex of cold methanol and collected by centrifugation. The resulting dark red polymer was dried in vacuum, yielding 0.233 g (44%) of **PTB**.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.74-7.61 (m, 2H), 7.07 (s, 2H), 2.76-2.54 (m, 4H), 1.73-1.62 (b, 4H), 1.35-0.92 (b, 28H), 0.85 (bt, *J* = 6.1 Hz, 6H). IR (cm<sup>-1</sup>): 2952, 2918, 2849, 1569, 1533, 1483, 1465, 1433, 1376, 1338, 1262, 1184, 1026, 874, 844, 822, 720, 700, 684. GPC (chloroform): M<sub>n</sub> = 2941 g/mol, M<sub>w</sub> = 4679g/mol, PDI = 1.58.



## 6.7 References and Notes

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