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Borylation on Benzo[1,2-*b*:4,5-*b*′]- and Naphtho[1,2-*b*:5,6-*b*′]dichalcogenophenes: Different Chalcogene Atom Effects on Borylation Reaction Depending on Fused Ring Structure

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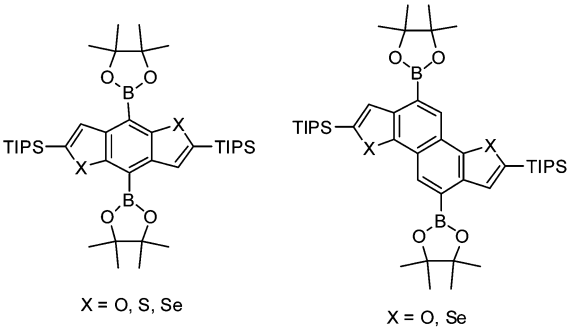
ABSTRACT



The direct borylation reactions of two types of α-silyl-protected acenedichalcogenophenes, i.e., benzo[1,2-*b*:4,5-*b*′]- and naphtho[1,2-*b*:5,6-*b*′]dichalcogenophenes, were examined, and it was observed that the reaction efficiency largely depends on the fused ring structure and chalcogenophene ring.

Direct borylation of aromatic compounds catalyzed by Ir complexes in the presence of bis(pinacolato)diboron, first reported by Ishiyama and co-workers,[1] is a useful reaction for the synthesis of arylboronic acid pinacol esters,[1] vital reagents for the Suzuki–Miyaura cross-coupling reaction.[2] Acenes such as naphthalene,[3] anthracene,[4] and tetracene[5] can be directly borylated by the reaction to give a regioisomeric mixture of *syn*- (2,7-isomer for naphthalene and anthracene, 2,9-isomer for tetracene) and *anti*-diborylated acenes (2,6-isomer for naphthalene and anthracene, 2,8-isomer for tetracene). These borylated acenes, after separation into each isomer, are useful intermediates for the synthesis of π-extended macrocycles[4] and organic semiconductors applicable to organic field-effect transistors (OFETs).[5]

We have recently found that the direct borylation can take place selectively at the naphthalene core part on

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α-protected naphtho[1,2-*b*:5,6-*b*′]dithiophene (NDT3)[6−8] and demonstrated that the resulting core-borylated NDT3 (**1**) is a versatile intermediate (Figure 1), which allows us to synthesize new NDT3-based building blocks with various substituents, including 5,10-dibromo, dichloro, dicyano, dialkyl, dihydroxy, dialkoxy, and diester derivatives as well as isomeric NDT3-based polymers with different main chain structures.[9] In addition, we have also found that the same methodology consisting of the α-protection and the core borylation reactions is applicable to other isomeric naphthodithiophenes (NDTs),[9] but the efficiency of the borylation reaction fairly depends on the fused ring structure of NDTs. Although angular-shaped NDT4 readily afforded the corresponding borylated compound in an excellent yield, linear-shaped NDT1 required a long reaction time and excess reagent and catalyst to effect the borylation reaction. Even under such intensified reaction conditions, desired 5,10-diborylated NDT1 was isolated in 42% yield with a monoborylated one (57% isolated yield).

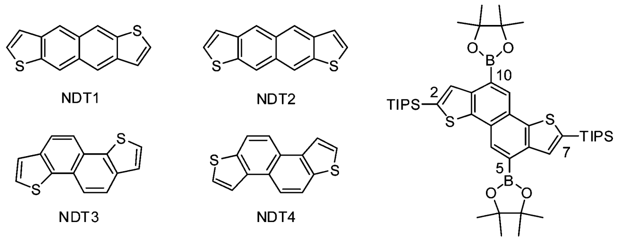


Figure 1. Molecular structures of four isomeric naphthodithiophenes[7] and orthogonally functionalized NDT3 (**1**).

With these results on the borylation chemistry on the isomeric NDTs, we were interested in similar borylation reactions on other acenedichalcogenophenes[10] for the following reasons. First, as demonstrated by the usefulness of **1**, analogous orthogonally functionalized acenedichalcogenophenes should be useful and can contribute to the development of new opto/electronic materials.[10] Second, chalcogenophenes such as furan and selenophene can give different structural perturbation on the borylation reaction from that of thiophene, which will give the scope of direct borylation on acenedichalcogenophenes. We here report on the borylation chemistry of two acenedichalcogenophene series, i.e., naphtho[1,2-*b*:5,6-*b*′]dichalcogenophenes[6a,11] and benzo[1,2-*b*:4,5-*b*′]dichalcogenophenes (Figure 2).[12,13]

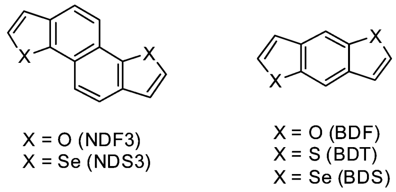
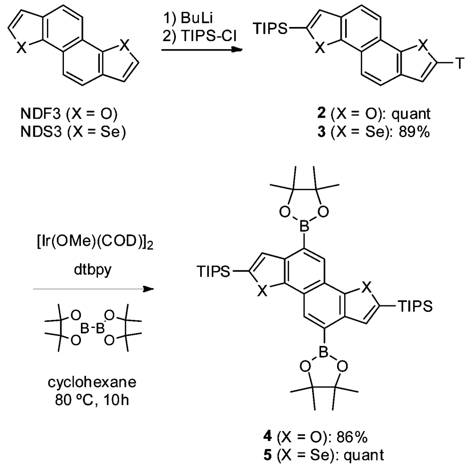


Figure 2. Molecular structures of acenedichalcogenophenes.

Scheme 1 shows the synthesis of 5,10-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,7-bis(triisopropylsilyl)naphtho[1,2-*b*;5,6-*b*′]difuran (**4**) and -diselenophene (**5**). As in the case of NDT3 with basically the same molecular geometry, both the initial introduction of TIPS groups and the following direct borylation under typical reaction conductions,[1] (substrate: 1 mmol, bis(pinacolato)diboron: 2 mmol, $[\mathrm{Ir(OMe)(COD)}]_2$: 5 μmol, dtbpy: 10 μmol, 80 °C for 10 h in dry cyclohexane) were straightforward in giving the corresponding α-TIPS-protected and core borylated naphthodichalcogenophenes in good yields.

Scheme 1. Synthesis of Borylated NDF3 (**4**) and NDS3 (**5**)



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(7) The present numbering of NDT isomers, i.e., NDT1 for naphtho[2,3-*b*:6,7-*b*′]dithiophene, NDT2 for naphtho[2,3-*b*:7,6-*b*′]dithiophene, NDT3 for naphtho[1,2-*b*:5,6-*b*′]dithiophene, and NDT4 for naphtho[2,1-*b*:6,5-*b*′]dithiophene, is just for convenience without any scientific significance, which follows our recent publications (ref 6b, 6c). The same numbering for naphthodifuran (NDF) and naphthodiselenophene (NDS) isomers are used in this communication, although not all the isomers are discussed.

(8) Recently effective synthesis of NDT1 and NDT3 derivatives and their application to the synthesis of oligomers and polymers were reported. See: (a) Loser, S.; Bruns, C. J.; Miyauchi, H.; Ortiz, R. P.; Facchetti, A.; Stupp, S. I.; Marks, T. J. *J. Am. Chem. Soc.* **2011**, *133*, 8142–8145. (b) Loser, S.; Miyauchi, H.; Hennek, J. W.; Smith, J.; Huang, C.; Facchetti, A.; Marks, T. J. *Chem. Commun.* **2012**, *48*, 8511–8513. (c) Sanjaykumar, S. R.; Badgujar, S.; Song, C. E.; Shin, W. S.; Moon, S.-J.; Kang, I.-N.; Lee, J.; Cho, S.; Lee, S. K.; Lee, J.-C. *Macromolecules* **2012**, *45*, 6938–6945.

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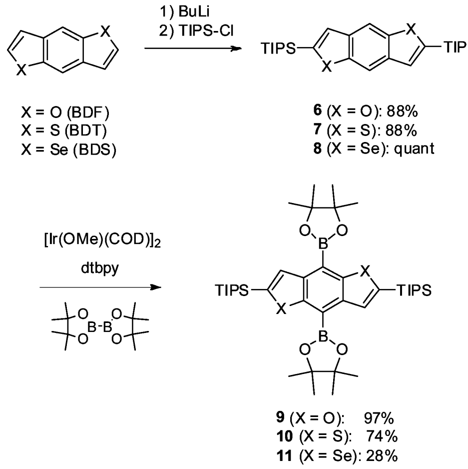
We then examined direct borylation on the benzene core of the benzo[1,2-*b*:4,5-*b*′]dichalcogenophenes (BDF, BDT, and BDS). Note that the direct borylation on anthracene, an isoelectronic hydrocarbon of the present benzodichalcogenophenes, selectively occurs at the 2-, 6-/7-positions and completely no borylation takes place at the peri-positions.[12] Depicted in Scheme 2 is the synthesis of 4,8-diborylated derivatives of benzodichalcogenophenes. Different from the former angular-shaped naphthodithiophene cases, the borylation was not only just less effective than the former cases, requiring a long reaction time ($\sim$2 days) to obtain the diborylated compound, but also largely affected by the chalcogen atoms, though the initial introduction of TIPS groups, regardless of the chalcogen atoms in the molecular framework, can be done easily.

Scheme 2. Synthesis of Borylated BDF (**9**), BDT (**10**), and BDS (**11**)



These results suggest that steric effects caused by the adjacent chalcogenophene ring in the linear-shaped benzodichalcogenophenes change the reactivity of borylation. In fact, single crystal X-ray analyses of **9**, **10**, and **11** indicate that the borylated sites, 4- and 8-positions, are fairly crowded, though at a glance they seem to have room enough to accommodate the pinacolatoboryl groups (Figure 3); nonbonded intramolecular distances between the boron atom and the adjacent oxygen (for **9**, 2.99 Å), sulfur (for **10**, 3.30 Å), or selenium (for **11**, 3.36 Å) in the benzodichalcogenophene cores are shorter than the sum of van der Waals radii (for B–O, 3.07 Å, B–S: 3.45 Å, for B–Se: 3.55 Å).[13] Among these reaction sites, the ones on the BDS core are most sterically hindered, being consistent with the poor reactivity in the borylation reaction (Figure S1). Although the large selenophene rings in BDS tend to reduce the reactivity, it should be emphasized that the present results are distinct from the case of anthracene, in which the borylation does not take place at the peri-positions. Again, this difference can be explained by steric effects; the steric relaxation caused by the chalcogenophene rings without a hydrogen atom on one side should play a critical role in allowing the borylation reaction on the central benzene ring in benzodichalcogenophenes.

Although all these orthogonally functionalized acenedichalcogenophenes (**4**, **5**, **9**–**11**) have not been exploited fully yet,[9] the boryl functionality should be a useful handle for the synthesis of interesting molecules, via not only the Suzuki Miyaura coupling[2] but also the corresponding dibromo derivatives, which are readily converted from the diboryl compounds. As an example for such conversions, the synthesis of 4,8-dibromo-BDF (**12**), -BDT (**13**), and -BDS (**14**) were demonstrated (Scheme 3).[9,15,16] Recent fruitful results on the BDT building blocks functionalized with alkyl, alkyloxy, or aromatic substituents at 4,8-positions in the application to semiconducting polymer for OPVs[17] make **9**–**14** potential intermediates for further material development. In fact, not just the BDT-based polymers, the related BDF-[18] or BDS-based polymers[19] have been recently examined as donor materials for OPV devices. Compared to the BDT building blocks, such BDF and BDS building blocks functionalized at the 4,8-positions are less accessible by using the conventional synthetic methods, and thus the present intermediates (**9**, **11**, **12**, and **14**) would accelerate the development of furan- and selenophene-based materials.

In summary, we have studied the direct borylation reaction of two series of acenedichalcogenophenes and found that the reaction is fairly affected not only by the molecular shape of the ring system but also by the chalcogene atoms in the case of the linear-shaped benzodichalcogenophenes. The reactivity elucidated here can be

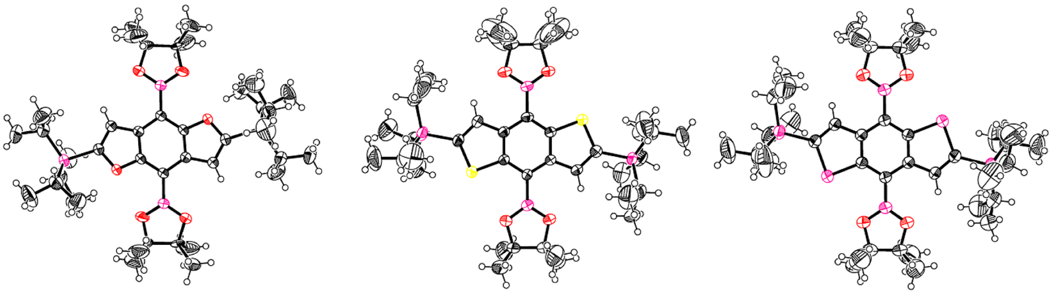
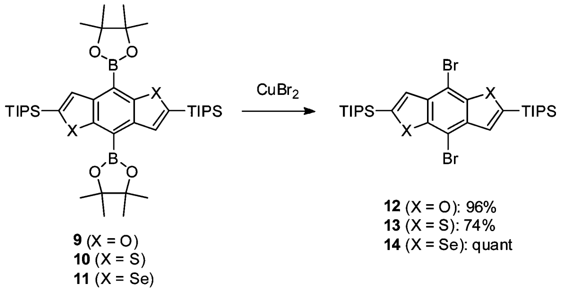


Figure 3. Molecular structures of **9**, **10**, and **11** elucidated by single crystal X-ray analysis.

Scheme 3. Conversion of **9**−**11** to Corresponding Bromide (**12**−**14**)



generally understood by the steric bulk around the borylation sites. We also demonstrated that these orthogonally functionalized compounds are readily converted into the corresponding dibromo compounds, which can also be a useful intermediate for further elaborated materials applicable to organic semiconductors. We thus hope that further material developments based on acenedichalcogenophenes will be accelerated in the near future by using these intermediates.[20]

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Supporting Information Available. Experimental details, spectroscopic data, and crystallographic information files (CIF) for **9**−**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.