ORGANIC LETTERS

2010
Vol. 12, No. 15
3340−3343

One-Pot Synthesis of 4,8-Dibromobenzo-[1,2-*c*;4,5-*c*′]bis[1,2,5]thiadiazole

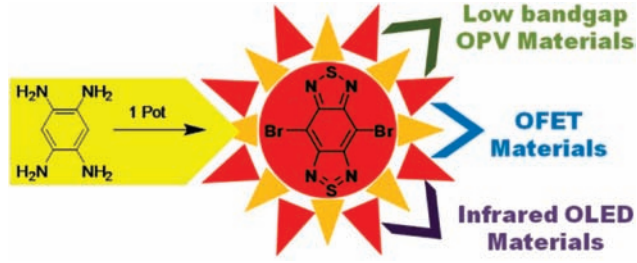
Teck Lip Tam, Hairong Li, Fengxia Wei, Ke Jie Tan, Christian Kloc, Yeng Ming Lam, Subodh G. Mhaisalkar, and Andrew C. Grimsdale*

School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

acgrimsdale@ntu.edu.sg

Received May 13, 2010

ABSTRACT



A one-step synthesis of 4,8-dibromobenzo[1,2-*c*;4,5-*c*′]bis[1,2,5]thiadiazole with use of 1,2,4,5-tetraaminobenzene tetrahydrobromide and thionyl bromide in good yield is reported. This unit can then be used in the synthesis of low bandgap materials via palladium-catalyzed coupling reactions. The approach offers a quick and easy way to prepare low bandgap materials as compared to the current literature methods.

The benzo[1,2-*c*;4,5-*c*′]bis[1,2,5]thiadiazole (BBT) unit (**1**) is a strong electron accepting unit that has been used to make low band gap donor−acceptor materials. This has potential applications in light-emitting devices (LED), ambipolar organic field-effect transistors (OFETs), and solar cells. As a sign of the effectiveness of BBT in promoting low bandgaps, even the small oligomers **2** and **3** are reported to possess bandgaps of only 1.5 eV (Figure 1).[1−3] Oligomer **3** has been used as emissive material in an LED displaying efficient emission in the near-infrared (NIR).[1] Polymeric films obtained by electropolymerization of **2** and **3** display bandgaps of about 0.5 eV.[2,3] The small bandgaps observed in these materials can be attributed to the high electron affinity and large quinoid contribution of the BBT unit.[2−9]

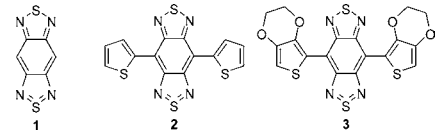


Figure 1. Structures of BBT (**1**) and some low bandgap 4,8-disubstituted BBT derivatives.

Oligomer **2** has also been used as the starting material for synthesis of soluble polymers **4** and **5** with bandgaps of 0.65−0.67 eV,[10] and of oligomer **6**, which has been used to make a NIR-emitting LED (Figure 2).[5] Another NIR-emitter

(1) Yang, Y.; Farley, R. T.; Steckler, T. T.; Eom, S.-H.; Reynolds, J. R.; Schanze, K. S.; Xue, J. *J. Appl. Phys.* **2009**, *106*, 044509.
(2) Steckler, T. T.; Abboud, K. A.; Craps, M.; Rinzler, A. G.; Reynolds, J. R. *Chem. Commun.* **2007**, *46*, 4904–4906.
(3) Karikomi, M.; Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Am. Chem. Soc.* **1995**, *117* (25), 6791–6792.
(4) Kitamura, C.; Tanaka, S.; Yamashita, Y. *Chem. Mater.* **1996**, *8* (2), 570–578.
(5) Qian, G.; Dai, B.; Luo, M.; Yu, D.; Zhan, J.; Zhang, Z.; Ma, D.; Wang, Z. Y. *Chem. Mater.* **2008**, *20* (19), 6208–6216.
(6) Li, X.; Liu, A.; Xun, S.; Qiao, W.; Wan, X.; Wang, Z. Y. *Org. Lett.* **2008**, *10* (17), 3785–3787.
(7) Wu, W. C.; Chen, W. C. *J. Polym. Res.* **2006**, *13* (6), 441–449.
(8) Pai, C. L.; Liu, C. L.; Chen, W. C.; Jenekhe, S. A. *Polymer* **2006**, *47* (2), 699–708.
(9) Ono, K.; Tanaka, S.; Yamashita, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33* (19), 1977–1979.

10.1021/ol100989v © 2010 American Chemical Society
Published on Web 07/08/2010

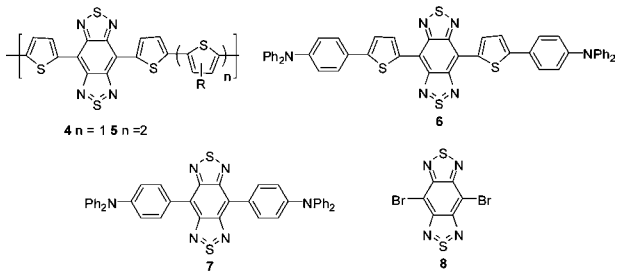
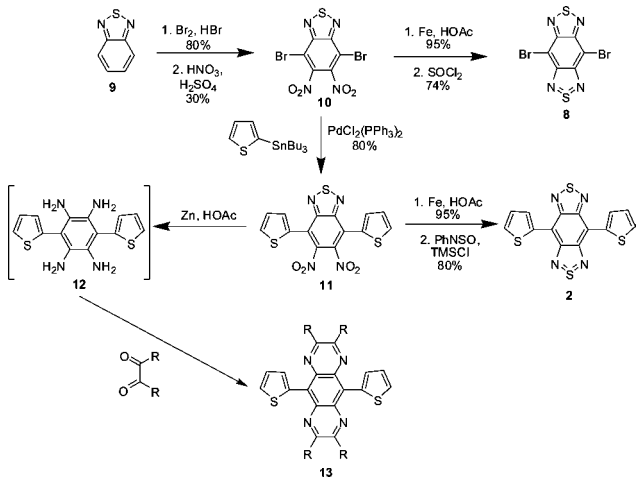


Figure 2. Structures of some BBT related low bandgap polymers and oligomers, and the synthetic precursor 4,8-dibromo-BBT (**8**).

7 was made from the 4,8-dibromo-BBT **8**.[5] As 4,8-dibromo-BBT **8** is an obvious synthetic precursor to **2**, it is thus an important intermediate for the synthesis of low bandgap oligomers and polymers.

There is, however, no short, efficient synthesis of compounds **2** or **8** available in the literature. The standard synthesis of these compounds starting from commercially available benzothiadiazole (BT, **9**) uses the 4,7-dibromo-5,6-dinitrobenzothiadiazole **10** as a common intermediate.[4] As the intermediate has to be made in two steps with harsh conditions from **9**, it can readily be seen that this is not a route suitable for commercially viable production of BBT-based materials (Scheme 1). Reduction of

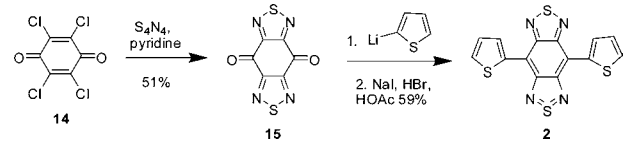
Scheme 1. Synthesis of **2**, **8**, and **13** According to the Literature



10 in acetic acid with zinc produces the tetraaminobenzene **12**, which on addition of 1,2-diketone yields 5,10-bis(2-thienyl)pyrazino[2,3-*g*]quinoxaline derivatives **13**, which have also been used to synthesize low band polymers.[4,11,12] Reduction of **2** should also generate the intermediate **12** and thus potentially provides a quick access to 5,10-disubstituted pyrazino[2,3-*g*]quinoxalines. Thus a convenient synthesis of **2** and **8** has great potential for assisting the preparation of a range of low bandgap materials.

A shorter approach to **2** has been demonstrated by using nucleophilic addition of 2-thienyllithium to the BBT-4,8-dione **15** followed by reduction (Scheme 2).[13] Even though

Scheme 2. Synthesis of **2** from *p*-Chloranil **12**



this approach cuts down the total number of steps to **3**, the overall yield is still only about 25%. Also, the reagent S_4N_4 used to make **15** directly from *p*-chloranil (**14**)[14] is a shock sensitive explosive, which prohibits the possibility of large-scale synthesis (there is a safer two-step alternative synthesis of **15** from **14** but this is less efficient[15]). As a result this approach has not been widely used.

We have now discovered a one-pot method for the efficient synthesis of **8**. In our first experiment we treated commercially available 1,2,4,5-tetraaminobenzene (TAB) tetrahydrochloride (**17**) with thionyl chloride, expecting to obtain **1**. To our surprise the product showed no signals in the ^{1}H NMR spectrum, and was identified by the presence of ions at *m*/*z* 261, 263, and 265 in the MALDI-TOF mass spectrum as the dichloride **16**, which was obtained in 50% yield. We were unable to obtain satisfactory microanalytical data for **16**, but were able to perform X-ray diffraction on a crystal of **16**. The crystallographic data obtained were very similar to those previously reported for the dibromide **8**.[9]

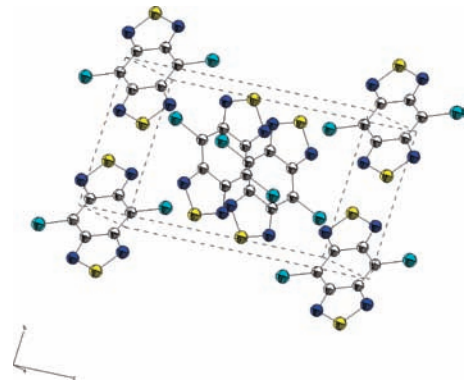


Figure 3. Crystal structure of **16**. Monoclinic, $P2_1/n$, $a = 3.8426$ Å, $b = 7.4348$ Å, $c = 15.2226$ Å, $\beta = 90.339°$, $V = 434.88(6)$ Å^3, $Z = 2$, $p_{calcd} = 2.01$ g/cm^3.

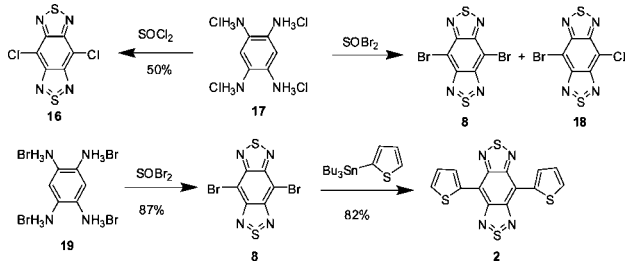
As shown in Figure 3, **16** forms a monoclinic crystal containing ribbon-like columns of molecules with an in-

(10) Bundgaard, E.; Krebs, F. C. *Macromolecules* **2006**, *39* (8), 2823–2831.
(11) Zoombelt, A. P.; Fonrodona, M.; Turbiez, M. G. R.; Wienk, M. M.; Janssen, R. A. J. *J. Mater. Chem.* **2009**, *19*, 5336–5342.
(12) Zhang, F.; Bijleveld, J.; Perzon, E.; Tvingstedt, K.; Barrau, S.; Inganas, O.; Andersson, M. R. *J. Mater. Chem.* **2008**, *18*, 5468–5474.

tramolecular spacing of 3.43 Å. This close packing indicates there are strong intermolecular interactions between the BBT units and helps explain the poor solubility of **16**, **8**, and **2** which precluded our obtaining ^{13}C NMR data for them.

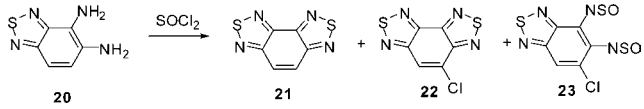
Treatment of TAB·4HCl with thionyl bromide gave impure dibromide **8**, which was found by MALDI-TOF analysis to be contaminated with the dichloride **16** and the mixed halide **18**. To obtain pure **8** it was found necessary to convert the tetrachloride salt to the tetrabromide salt **19**. Reaction of the resulting crude tetrabromide then gave the desired dibromide **8** in 56% yield. This was improved to 87% yield when **19** obtained from a commercial source (Hangzhou Trylead Chemical Technology Co., Ltd., 95% purity) was reacted with thionyl bromide. In view of the difficulty and expense of obtaining the bromide commercially, conversion of the cheaper and more readily available chloride is an attractive option, especially if further optimization of the halide exchange can improve the yield. Stille coupling of **8** with a thienyltin compound gave **2** in 82% yield (71% yield from **19** to **2**) (Scheme 3).

Scheme 3. Synthesis of 4,8-Disubstituted BBT via TAB



There has also been reported one example of a chlorination during synthesis of a benzothiadiazole from a diamine with thionyl chloride.[16] Treatment of the diamino-BT **20** with refluxing neat thionyl chloride gave a mixture, which by mass spectrometric analysis contained not only the desired benzobis(thiadiazole) **21** but also the monochloride **22** and the chlorinated bis-NSO compound **23** (Scheme 4). However,

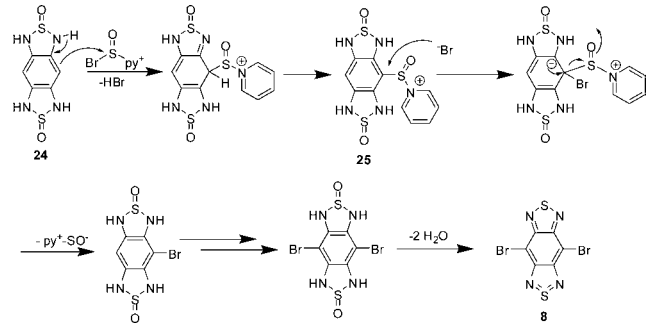
Scheme 4. Previously Reported Chlorination during a BT Synthesis



when thionyl chloride and pyridine was used only compound **21** was obtained. Chlorination of aromatic *N*-sulfinylamines by thionyl chloride via electrophilic attack of the chlorine has been reported elsewhere,[17] and it is likely that the chloro compound **22** arises from such an electrophilic attack to form **23** followed by dehydrogenation.

The importance of the anion on TAB in the current work, however, suggested that halogenation does not occur via electrophilic substitution but via a nucleophilic process. A direct nucleophilic attack on BBT **1**, while electronically favorable, we consider unlikely as the low solubility of BBT and its derivatives would most probably result in a mixture of mono- and dihalogenated products. Also this route would require the intermediate to be oxidized to form the product, and while thionyl chloride is known to oxidize hydroquinones to quinones,[14] we are not aware of any precedent for it being able to perform the oxidation that would be necessary here. We propose that, as shown in Scheme 5, there is an initial electrophilic attack of the

Scheme 5. Proposed Mechanism for the Formation of **8** via TAB



excessive thionyl bromide (which is complexed with pyridine) on the intermediate **24** generating the intermediate **25**, followed by nucleophilic displacement of the SOPy group by bromide. The four amine groups in TAB make it extremely electron rich, and even the less activated sulfinyl intermediate **24** should still be susceptible to electrophilic attack. Reaction of arenes with thionyl halides is used to prepare diaryl sulfoxides[18] with structures such as **25** being plausible intermediates in such processes in the presence of pyridine. (Similar sulfinyl-pyridine complexes have been accepted as intermediates in other processes involving thionyl halides and pyridine.[19,20]) The nucleophilic attack on intermediate **25** is proposed as it accounts for the dichloride **16** and the mixed halide **18** being formed upon treatment of the TAB hydrochloride with thionyl bromide. Such a nucleophilic aromatic substitution would be assisted by the strong electron withdrawing sulfinyl

(13) van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Mater. Sci. Eng., R* **2001**, *32*, 1.
(14) Shi, S.; Katz, T. J.; Yang, B. V.; Liu, L. *J. Org. Chem.* **1995**, *60* (5), 1285–1297.
(15) Anzenbacher, P., Jr.; Palacios, M. A.; Jursikova, K.; Marquez, M. *Org. Lett.* **2005**, *7* (22), 5027–5030.
(16) Komin, A. P.; Carmack, M. *J. Heterocycl. Chem.* **1975**, *12* (5), 829–833.
(17) Ottmann, G.; Hooks, H. *J. Org. Chem.* **1965**, *30* (3), 952–954.
(18) Smith, M. B.; March, J. In *March's Advanced Organic Chemistry*, 6th ed.; John Wiley and Sons: Hoboken, NJ , 2007; pp 697−698.
(19) Cram, D. J. *J. Am. Chem. Soc.* **1953**, *75*, 332–338.
(20) Smith, M. B.; March, J. In *March's Advanced Organic Chemistry*, 6th ed.; John Wiley and Sons: Hoboken, NJ, 2007; pp 468−469.

group on the aromatic ring. Repetition of this process, followed by dehydration during reflux, yields **8**. A similar mechanism is proposed for chlorination with thionyl chloride.

The main advantages of this new method are that the desired dibromide **8** can be obtained in a much higher yield, by a much shorter route and can be carried out on a larger synthetic scale than by existing procedures, thus greatly increasing the synthetic accessibility of oligomers and polymers containing the BBT unit, and potentially also other electron accepting units. We are currently investigating the reduction of **2** as a route to pyrazinoquinoxaline units, the results of which will be published separately. The main synthetic novelty of this new process is that by changing the counterion on the starting material we are able to selectively obtain either chlorinated or brominated BBT.

In conclusion, the one-step synthesis of dibromo BBT with TAB and thionyl bromide is an expeditious method to generate the important intermediates **2** and **8** for synthesis of low bandgap materials. Though the exact mechanism of this halogenation reaction is not yet elucidated, it is probable that halogenation proceeds via nucleophilic rather than electrophilic substitution.

Acknowledgment. This work was supported by Robert Bosch (SEA) Pte Ltd.

Supporting Information Available: Detailed descriptions of experimental procedures for compounds **2**, **8**, and **16**, plus mass spectra, NMR spectra, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

OL100989V