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An Efficient Synthesis of 2,6-Disubstituted Benzobisoxazoles: New Building Blocks for Organic Semiconductors

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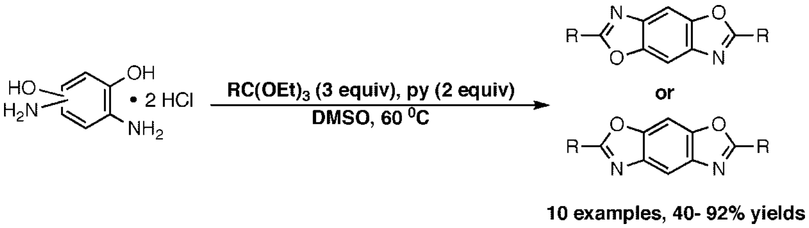
ABSTRACT



2,6-Disubstituted benzobisoxazoles have been synthesized by a highly efficient reaction of diaminobenzene diols with various orthoesters. The scope of this new reaction for the synthesis of substituted benzobisoxazoles has been investigated using four different orthoesters. The utility of these compounds as building blocks for the synthesis of conjugated polymers is demonstrated.

Conjugated polymers and oligomers are of interest for use as organic semiconductors in applications such as thin-film transistors (TFTs),[1] light-emitting diodes (OLEDs),[2] and photovoltaic cells (PVCs).[3] While there are a large number of π-conjugated small molecules, oligomers, and polymers which have been reported in the literature, the design and synthesis of new π-conjugated organic materials remains an important area of research. Of particular interest is the creation of materials with good electron transport properties (n-type), which are less abundant in the literature than those with hole transport (p-type) properties.[4] n-type materials with efficient electron transport are essential for improving the performance of TFTs, OLEDs, and PVCs and to enable other cost-effective applications such as complementary circuits.[5]

We are interested in developing benzobisoxazoles for their use as building blocks for novel organic semiconductors because conjugated small molecules and polymers based on benzobisoxazoles are well suited for use in organic semiconducting applications. These materials combine efficient electron transport, photoluminescence, and third-order nonlinear optical properties[6] with excellent mechanical strength and thermal stability.[7] Unfortunately, the fused benzobisoxazole ring system, the rodlike conformation of the resulting

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(1) (a) Mas-Torrent, M.; Rovira, C. *Chem. Soc. Rev.* **2008**, *37*, 827. (b) Usta, H.; Lu, G.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 9034. (c) Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J.; Frechet, J. M. J.; Toney, M. F. *Macromolecules* **2005**, *38*, 3312. (d) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99.

(2) (a) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913. (b) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121.

(3) (a) Thompson, B. C.; Frechet, J. M. J. *Angew, Chem., Int. Ed.* **2008**, *47*, 58. (b) Coakley, K. M.; McGehee, M. D. *Chem. Mater.* **2004**, *16*, 4533. (c) Scharber, M. C.; Muehlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. *Adv. Mater.* **2006**, *18*, 789.

(4) (a) Cornil, J.; Bredas, J.-L.; Zaumseil, J.; Sirringhaus, H. *Adv. Mater.* **2007**, *19*, 1791. (b) Cravino, A. *Polym. Int.* **2007**, *56*, 943. (c) McNeill, C. R.; Abrusci, A.; Zaumseil, J.; Wilson, R.; McKiernan, M. J.; Burroughes, J. H.; Halls, J. J. M.; Greenham, N. C.; Friend, R. H. *Appl. Phys. Lett.* **2007**, *90*, 193506/1. (d) Zhu, Y.; Alam, M. M.; Jenekhe, S. A. *Macromolecules* **2003**, *36*, 8958. (e) Babel, A.; Jenekhe, S. A *J. Phys. Chem. B* **2002**, *106*, 6129.

(5) (a) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4556. (b) Kietzke, T.; Egbe, D. A. M.; Horhold, H.- H.; Neher, D. *Macromolecules* **2006**, *39*, 4018. (c) Alam, M. M.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4647.

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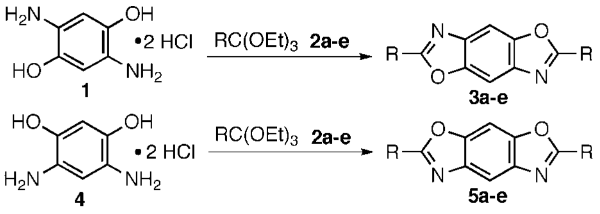
polymers, and efficient π-stacking between chains render fully conjugated poly(benzobisoxazoles) (PBOs) insoluble in aprotic solvents. As a result, PBOs are typically processed from acidic solvents, such as Lewis acid/nitromethane, methanesulfonic acid, trifluoromethanesulfonic acid, and sulfuric acid,[8] which are impractical for use in device manufacturing.

Generally, the solubility of π-conjugated materials can be improved through structural modifcation. In the case of small molecules and polymers containing the benzobisoxazole moiety, the synthesis is achieved by the high-temperature condensation of bis-*o*-aminophenols and aromatic diacids in the melt, in polyphosphoric acid (PPA), in phosphorus pentoxide/methanesulfonic acid, or in trimethylsilyl polyphosphate (PPSE)/*o*-dichlorobenzene.[9] These conditions are rather harsh, thereby limiting the types of substituents that can be incorporated into the benzobisoxazole moiety.

In this contribution, we report the synthesis of optoelectronic building blocks based on benzo[1,2-*d*;4,5-*d*′] bisoxazole (*trans*-BBO) (**3a**−**e**) and benzo[1,2-*d*;5,4-*d*′] bisoxazole (*cis*-BBO) (**5a**−**e**) by the reaction of various orthoesters (**2a**−**e**) with 2,5-diaminohydroquinone (DAHQ) (**1**) and 4,6-diaminoresorcinol (DAR) (**4**), respectively (Scheme 1). In all cases, the target compounds have been obtained cleanly and in high yield. Using our strategy, we have synthesized several building blocks suitable for the synthesis of benzobisoxazole monomers.

Scheme 1. Synthesis of 2,6-Disubstituted Benzobisoxazoles

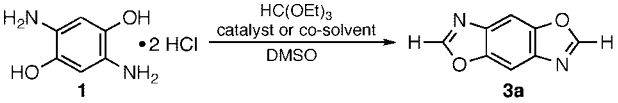


a: R = H, **b**: R = CH_3, **c**: R = CH_2Br, **d**: R = C≡C−TMS, **e**: R = CH_2Cl

We rationalized that orthoesters could be used for the synthesis of benzobisoxazoles since they have been used for the synthesis of benzimidazoles, benzoxazoles, and benzothiazoles.[10] The standard reaction conditions use 10 equiv of orthoester, which serves as both a reagent and the solvent, a catalytic amount of acid, and temperatures of 130 °C. Using the reaction of triethyl orthoformate and DAHQ as our model system, we first explored catalyst-free conditions, relying on the acid coordinated with the diamino diol to catalyze the reaction (entry 1). This yielded *trans*-BBO **3a** in 61% yield. When the reaction was performed under traditional conditions, using catalytic amounts of H_2SO_4, the target compound **3a** was obtained in 65% yield (entry 3). While the yields were moderate in both cases, the product was contaminated with a significant amount of dark red oxidation products, complicating purification.

Due to the tendency of DAHQ **1** and DAR **4** to decompose at higher temperatures, we needed to reduce the reaction temperature. Furthermore, the use of such a large excess of orthoester is undesirable since the substituted orthoesters are costly. To reduce the need for excess orthoester, we used DMSO as a cosolvent since it can dissolve both DAHQ and DAR. We then explored the use of rare earth metal triflates as catalysts since they have been demonstrated to reduce reaction times and increase yields when used instead of traditional Lewis acid catalysts.[11] In the case of our model reaction, we found several effective catalysts as shown in Table 1. Interestingly, the Lewis acid cataysts do not work in the absence of the DMSO solvent. With the exception of $Bi(OTf)_3$ and $Hf(OTf)_3$, all of the metal triflates gave improved yields when compared to the traditional acid catalysts. The low reactivity of Bi(III) and Hf(III) may be attributed to their larger ionic radii.[11]

Table 1. Investigation of the Effect of Catalyst on the Reaction of DAHQ (**1**) with Triethyl Orthoformate **2a**[a]



entry	solvent	catalyst/ cosolvent	temp (°C)	time (h)	yield[b] (%)
1	none	none	130	5	61
2	DMSO	none	60	2.5	64
3	none	H_2SO_4	130	2.5	65
4	DMSO	H_2SO_4	130	1	64
5	DMSO	PTSA	110	4	71
6	DMSO	$Bi(OTf)_3$	60	4	0
7	DMSO	$Hf(OTf)_3$	60	4	36
8	DMSO	$Eu(OTf)_3$	60	4	82
9	DMSO	$Sc(OTf)_3$	60	4	82
10	DMSO	$Y(OTf)_3$	60	4	81
11	none	$Yb(OTf)_3$	60	4	0
12	DMSO	$Yb(OTf)_3$	60	4	75
13	DMSO	$Y(OTf)_3$/Py	60	1	92[c]
14	DMSO	pyridine	45	1	78[c]

[a] Standard reaction conditions: substrate 1 M in DMSO, 10 equiv of orthoester, 5 mol % of catalyst, or py 2 equiv. [b] Isolated yields. [c] 3 equiv of orthoester.

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(6) (a) Osaheni, J. A.; Jenekhe, S. A. *Macromolecules* **1994**, *27*, 739. (b) Osaheni, J. A.; Jenekhe, S. A. *Chem. Mater.* **1995**, *7*, 672. (c) Jenekhe, S. A.; Osaheni, J. A.; Meth, J. S.; Vanherzeele, H. *Chem. Mater.* **1992**, *4*, 683. (d) Reinhardt, B. A.; Unroe, M. R.; Evers, R. C. *Chem. Mater.* **1991**, *3*, 451.

(7) (a) Wolfe, J. F. *Encyclopedia of Polymer Science and Engineering*; John Wiley and Sons: New York, NY, 1988; *Vol. 11*, p 601. (b) Wolfe, J. F.; Loo, B. H.; Arnold, F. E. *Macromolecules* **1981**, *14*, 909.

(8) (a) Roberts, M. F.; Jenekhe, S. A. *Chem. Mater.* **1993**, *5*, 1744. (b) So, Y. H.; Heeschen, J. P. *J. Org. Chem.* **1997**, *62*, 3552.

(9) (a) Osman, A. M.; Mohamed, S. A *Indian J. Chem.* **1973**, *11*, 868. (b) Osman, A. M.; Mohamed, S. A. *U.A.R.J. Chem.* **1971**, *14*, 475. (c) Imai, Y.; Itoya, K.; Kakimoto, M.-A. *Macromol. Chem. Phys.* **2000**, *201*, 2251. (d) Imai, Y.; Taoka, I.; Uno, K.; Iwakura, Y. *Makromol. Chem.* **1965**, *83*, 167. (e) So, Y. H.; Zaleski, J.; Murlick, C.; Ellaboudy, A. *Macromolecules* **1996**, *29*, 5229. (f) Kricheldorf, H. R.; Domschke, A. *Polymer* **1994**, *35*, 198.

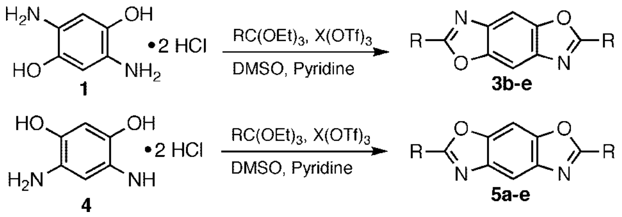
(10) (a) Jenkins, G. L.; Knevel, A. M.; Davis, C. S. *J. Org. Chem.* **1961**, *26*, 274. (b) Jois, Y. H. R.; Gibson, H. W. *J. Heterocycl. Chem.* **1992**, *29*, 1365.

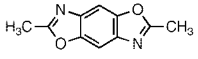
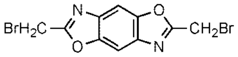
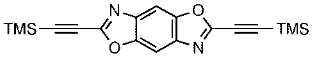
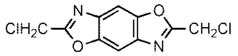
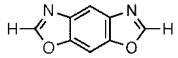
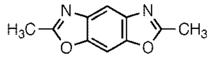
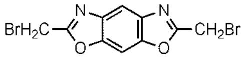
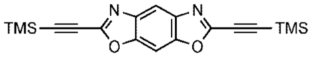
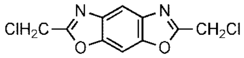
Unfortunately, we found that even with the addition of the DMSO the reaction yields significantly decreased when less than 10 equiv of orthoester was used. Moreover, we found that when the optimium reaction conditions, which were established for our model reactions, were used with ethyl orthobromoacetate[12a] (**2c**) and trimethylsilyl ethyl orthopropiolate[12b] (**2d**), the yields of the target BBOs decreased. We rationalized that the substituted orthoesters were unstable to the current reaction conditions and set out to further improve our reaction conditions. We explored the use of pyridine as a cosolvent with DMSO since it has been reported that it improved the yields of orthoester reactions.[13]

This modification was fortuitious, and we were able to reduce the reaction temperatures and times while increasing the reaction yields. While it was previously reported that the addition of pyridine stabilizes the DMSO, we believe that this improvement is a result of the removal of the acid coordinated with the DAHQ and DAR, increasing their reactivity and preventing protic acid catalyzed decomposition of the orthoesters. Using yttrium triflate, the pure product **3a** was obtained in 91% yield after the addition of water to the reaction mixture and simple filtration (entry 13). In the absence of the catalyst, the product was obtained in 78% yield (entry 14). The advantages of this method are the fact that the reaction occurred at a lower temperature, preventing the formation of side products, and the desired product can be precipitated out from the reaction mixture, allowing for easy purification.

On the basis of the model reactions, we have determined the optimum reaction conditions to be: substrate 1 M in DMSO, 2 equiv of pyridine, 3 equiv of orthoester, and 5% $Y(OTf)_3$ for DAHQ or $La(OTf)_3$ for DAR. Using these conditions, we set out to investigate the scope of the reaction with respect to the orthoester (Table 2). We found that triethyl orthoacetate (**2b**) and trimethylsilyl ethyl orthopropiolate[12b] (**2d**) could be employed to yield the corresponding BBOs in good yield. However, the reaction of triethyl orthobromoacetate (**2c**) only worked under traditional conditions, in the case of the trans-derivative, and failed to yield product in the case of the *cis*-derivative. The inability to synthesize benzobisoxazole **3c** using **2c** and our modified reaction conditions is most likely due to the competing side reaction of the alkyl bromide of the orthoester with DMSO.[14] Thus, we explored the use of triethyl orthochloroacetate (**2e**),[12c] which is less prone to side reactions and gives good results using our reaction conditions. In all cases, the products can be purified by simple recrystallization, and this method can easily be scaled up to multigram quantities. Thus, by utilizing the corresponding orthoesters, we can incorporate methyl, bromomethyl, chloromethyl, and alkynyl groups into the BBO's. Compounds containing the latter three groups cannot be prepared using traditional approaches. Moreover, direct bromination of **3b** or **5b** also fails to yield **3c** and **5c**.

Table 2. Reaction of **1** and **4** with Various Orthoesters **2b−e**

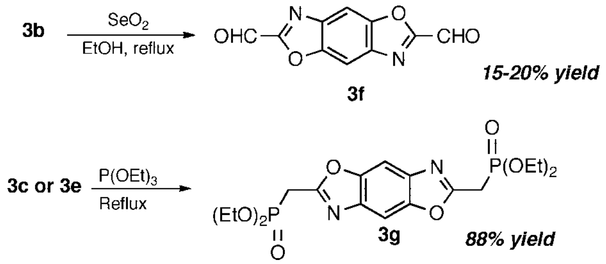


diamino diol	ortho ester	benzobisoxazole	% yield[a]
1	2b	 **3b**	86
1	2c	 **3c**	48[b]
1	2d	 **3d**	67
1	2e	 **3e**	40
4	2a	 **5a**	91
4	2b	 **5b**	83
4	2c	 **5c**	0
4	2d	 **5d**	40
4	2e	 **5e**	73

[a] Isolated yields. [b] Synthesized using standard conditions.

To demonstrate the utility of the new BBOs as building blocks for the synthesis of conjugated polymers, we first attempted the synthesis of monomer **3f**, by the oxidation of compound **3b** (Scheme 2). The reaction yields were very

Scheme 2. Synthesis of Benzobisoxazole Monomers



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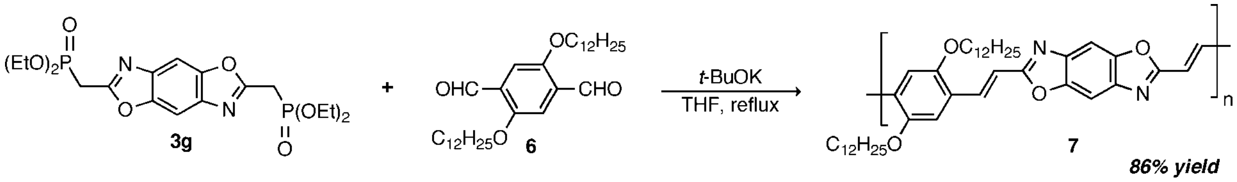
(11) (a) Wang, L.; Sheng, J.; Tian, H.; Qian, C. *Synth. Commun.* **2004**, *34*, 4265. (b) Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W. W. L. *Chem. Rev.* **2002**, *102*, 2227.

(12) (a) Beyerstedt, F.; McElvain, S. M. *J. Am. Chem. Soc.* **1937**, *59*, 1273. (b) Yamamoto, K.; Abrecht, S.; Scheffold, R. *Chimia* **1991**, *45*, 86. (c) Mylari, B. L.; Scott, P. J.; Zembrowski, W. J. *Synth. Commun.* **1989**, *19*, 2921.

(13) Dudgeon, C. D.; Vogl, O. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 1831.

Scheme 3. Synthesis of Benzobisoxazole Polymer **7**



low (15−20%). Thus, we explored the synthesis of diphosphonate ester **3g**. Monomer **3g** can be synthesized by the Arbuzov reaction of **3c** or **3e** and triethylphosphite. The polymerization of monomer **3g** with 2,5-didodecyloxybenzaldehyde **6**[15] by a Horner−Wadsworth−Emmons (HWE) olefination reaction produced a red polymer in 86% yield (Scheme 3). The resultant polymer was soluble in THF and chloroform, and the structure of the polymer was verified by ^{1}H NMR spectroscopy. Gel permeation chromatography (GPC) of the polymer showed monomodal distributions with number average molecular weight (Mn) of 5672, PDI = 1.77, which corresponds to a number averaged degree of polymerization of approximately 8. We measured the emission and absorption spectra of the polymer in solution and found that the absorption maximum is 476 nm. The polymer exibits green fluorescence with an emission maximum at 515 nm, which is blue-shifted from the photoluminescence of MEH-PPV (ca. 600 nm).[16] This represents the first synthesis of a PBO derivative which is soluble in aprotic organic solvents. We are currently working to optimize the reaction conditions to obtain a higher molecular weight polymer.

In summary, the reaction of orthoesters and DAHQ or DAR affords new 2,6-disubstituted benzobisoxazoles in good yields. Subsequent reactions can transform these compounds into monomers for the synthesis of novel polymers containing the electron-deficient benzobisoxazole moiety. Future efforts will focus on the synthesis of other monomers based on these materials, as well as device construction and evaluation of the electronic and optical properties of oligomers and polymers containing the benzobisoxazole moiety.

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Supporting Information Available: Experimental procedures and ^{1}H and ^{13}C NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) (a) Nace, H.; Monagle, J. *J. Org. Chem.* **1959**, *24*, 1792. (b) Kornblum, N.; Jones, W. J.; Anderson, G. J. *J. Am. Chem. Soc.* **1959**, *81*, 4113.

(15) Liao, J.; Wang, Q. *Macromolecules* **2004**, *37*, 7061.

(16) Chen, S. H.; Su, A. C.; Chou, H. L.; Peng, K. Y.; Chen, S. A. *Macromolecules* **2004**, *37*, 167.