

Synthesis of Water-Soluble Poly(*p*-phenyleneethynylene) in Neat Water under Aerobic Conditions via Suzuki-Miyaura Polycondensation Using a Diborylethyne Synthone

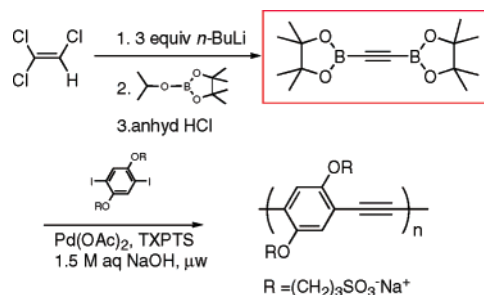
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ABSTRACT



We report the synthesis, structure, and characterization of a novel ethyne synthone, 1,2-bis(4',4',5',5'-tetramethyl[1',3',2']dioxaborolan-2'-yl)-ethyne (B2C2). We demonstrate the utility of B2C2 in the Suzuki-Miyaura polycondensation reaction, synthesizing a water-soluble poly(*p*-phenyleneethynylene) from [2,5-diiodo-1,4-bis(3-propoxy-sulfonic acid)benzene] sodium salt in neat water under an aerobic atmosphere.

Ethyne-bridged conjugated polymers impact a wide-range of technologies; the efficacy of these species derives not only from their established semiconducting and optical properties but also from the facts that these rigid, rod-like structures are readily processible and manifest high photo and thermal stabilities.^{1–7} Poly(*p*-phenyleneethynylene)s (PPEs) define the archetypal examples of ethyne-bridged conjugated polymers; these species have been utilized in organic light-emitting

diodes (OLEDs)^{8,9} field-effect transistors (FETs),¹⁰ molecular electronics,¹¹ nonlinear optical materials,¹² solar energy conversion devices,^{13–15} and in a variety of sensory applications.^{4,16} As such, considerable effort has been placed in the

- (1) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605–1644.
- (2) Bunz, U. H. F. *Adv. Polym. Sci.* **2005**, *177*, 1–52.
- (3) Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201–207.
- (4) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537–2574.
- (5) Yamamoto, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 621–638.
- (6) Tan, C. Y.; Pinto, M. R.; Schanze, K. S. *Chem. Commun.* **2002**, 446–447.
- (7) Nelson, J. C.; Saven, J. G.; Moore, J. S.; Wolynes, P. G. *Science* **1997**, *277*, 1793–1796.

- (8) Egbe, D. A. M.; Birckner, E.; Klemm, E. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2670–2679.
- (9) Breen, C. A.; Tischler, J. R.; Bulović, V.; Swager, T. M. *Adv. Mater.* **2005**, *17*, 1981–1988.
- (10) Xu, Y.; Berger, P. R.; Wilson, J. N.; Bunz, U. H. F. *Appl. Phys. Lett.* **2004**, *85*, 4219–4221.
- (11) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791–804.
- (12) Samori, P.; Francke, V.; Müllen, K.; Rabe, J. P. *Chem.–Eur. J.* **1999**, *5*, 2312–2317.
- (13) Hoppe, H.; Egbe, D. A. M.; Mühlbacher, D.; Sariciftci, N. S. *J. Mater. Chem.* **2004**, *14*, 3462–3467.
- (14) Egbe, D. A. M.; Kietzke, T.; Carbonnier, B.; Mühlbacher, D.; Hörhold, H. H.; Neher, D.; Pakula, T. *Macromolecules* **2004**, *37*, 8863–8873.
- (15) Mwaura, J. K.; Pinto, M. R.; Witker, D.; Ananthkrishnan, N.; Schanze, K. S.; Reynolds, J. R. *Langmuir* **2005**, *21*, 10119–10126.

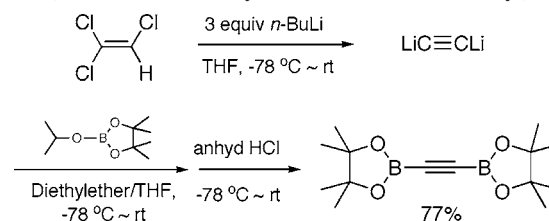
development of synthetic protocols for repeating arene-ethyne structural motifs.

The palladium-catalyzed Sonogashira reaction^{17,18} and acyclic diyne metathesis (ADIMET)^{19,20} represent widely used approaches to PPEs. Although the Sonogashira reaction is compatible with polar functional groups and water, it requires both dihaloarene and diethynylarene synthons; as such, this route is susceptible to the introduction of butadiyne defects in the PPE polymer, which are estimated to range from 1 to 10% even under the carefully controlled reaction conditions.² Although an ADIMET-based synthesis circumvents butadiyne defect sites, this method is generally incompatible with sensitive functional groups that include water-soluble side chains; furthermore, the syntheses of carbyne precursors for ADIMET protocols require inert reaction conditions and cannot be implemented in the presence of water.² Despite the fact that water-soluble PPEs have attracted increasing interest in biosensing²¹ and bio-conjugation applications,^{22,23} relatively few such materials have been reported.^{6,24–28} We report herein an environmentally benign synthetic approach²⁹ that exploits a new diborylethyne synthon that enables PPE synthesis, separation, and purification in neat water under an aerobic atmosphere.

The Suzuki-Miyaura coupling of alkynylboranes,³⁰ alkynylboronic acid or alkynylborate derivatives,^{31,32} and alkynyltrifluoroborates^{33,34} is well-precedented. Similar reactions involving reagents that possess boron functionality at the 1- and 2-carbon positions of ethyne have not yet been reported. This fact motivated the synthesis of [1,2-bis(4',4',5',5'-tetramethyl[1',3',2']dioxaborolan-2'-yl)ethyne (**B2C2**). The route to **B2C2** exploits a procedure developed by Brown and Srebnik,³⁵ in which dilithioacetylide is generated from trichloroethylene and 3 equiv of *n*BuLi in THF/diethylether.³⁶ Reaction of dilithioacetylide with 2-isopropoxy-4,4,5,5-

tetramethyl-1,3,2-dioxaborolane, followed by treatment with anhydrous HCl, cleanly affords **B2C2** in high yield (Scheme 1). **B2C2** can be recrystallized from hexanes, giving a robust

Scheme 1. Synthesis of 1,2-Bis(4',4',5',5'-tetramethyl[1',3',2']dioxaborolan-2'-yl)ethyne



crystalline solid (mp = 270 °C) that is stable under ambient atmosphere for at least 1 year. **B2C2** exhibits high solubility in basic water and virtually all organic solvents.

X-ray quality crystals of **B2C2** were obtained via evaporation of a benzene solution. During the process of structure determination, it became obvious that there were problems with the data: refinement of the structure was unstable and anisotropic refinement produced several nonpositive definite thermal parameters. A re-examination of the rotation images revealed many reflections that did not fit the derived cell. The crystal was found to be twinned with a total of four components (components 1 and 2 were related by a rotation of 180° around the normal to 110; components 1 and 3 were related by a rotation of 180° around the normal to 001; components 1 and 4 were related by a rotation of 180° around the normal to 110). Twin indexing and processing of twinned data were performed by the TwinSolve³⁷ module of CrystalClear.³⁸ ORTEP representations of the two **B2C2** forms (**B2C2-1** and **B2C2-2**) that define the asymmetric crystallographic unit are depicted in Figure 1; structural factors,

- (16) Kim, J.; Swager, T. M. *Nature* **2001**, *411*, 1030–1034.
 (17) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467–4470.
 (18) Giesa, R.; Schulz, R. C. *Macromol. Chem. Phys.* **1990**, *191*, 857–867.
 (19) Weiss, K.; Michel, A.; Auth, E. M.; Bunz, U. H. F.; Mangel, T.; Müllen, K. *Angew. Chem., Int. Ed.* **1997**, *36*, 506–509.
 (20) Brizius, G.; Pschirer, N. G.; Steffen, W.; Stitzer, K.; zur Loye, H. C.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2000**, *122*, 12435–12440.
 (21) Zheng, V.; Swager, T. M. *Adv. Polym. Sci.* **2005**, *177*, 151–179.
 (22) Wosnick, J. H.; Mello, C. M.; Swager, T. M. *J. Am. Chem. Soc.* **2005**, *127*, 3400–3405.
 (23) Lee, K.; Cho, J. C.; DeHeck, J.; Kim, J. *Chem. Commun.* **2006**, 1983–1985.
 (24) Häger, H.; Heitz, W. *Macromol. Chem. Phys.* **1998**, *199*, 1821–1826.
 (25) McQuade, D. T.; Hegedus, A. H.; Swager, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 12389–12390.
 (26) Pinto, M. R.; Kristal, B. M.; Schanze, K. S. *Langmuir* **2003**, *19*, 6523–6533.
 (27) Kuroda, K.; Swager, T. M. *Chem. Commun.* **2003**, 26–27.
 (28) Babudri, F.; Colangiuli, D.; Di Lorenzo, P. A.; Farinola, G. M.; Omar, O. H.; Naso, F. *Chem. Commun.* **2003**, 130–131.
 (29) Leadbeater, N. E. *Chem. Commun.* **2005**, 2881–2902.
 (30) Soderquist, J. A.; Matos, K.; Rane, A.; Ramos, J. *Tetrahedron Lett.* **1995**, *36*, 2401–2402.
 (31) Castanet, A. S.; Colobert, F.; Schlama, T. *Org. Lett.* **2000**, *2*, 3559–3561.
 (32) Oh, C. H.; Reddy, V. R. *Synlett* **2004**, 2091–2094.
 (33) Stefani, H. A.; Cella, R.; Dörr, F. A.; Pereira, C. M. P.; Zeni, G.; Gomes, M. *Tetrahedron Lett.* **2005**, *46*, 563–567.
 (34) Molander, G. A.; Katona, B. W.; Machrouhi, F. *J. Org. Chem.* **2002**, *67*, 8416–8423.

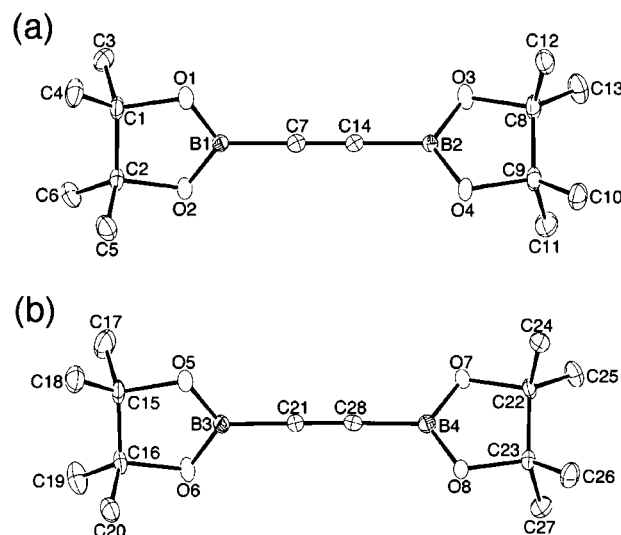
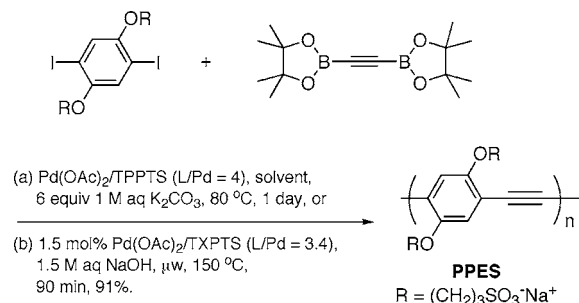


Figure 1. ORTEP views of: (a) **B2C2-1** and (b) **B2C2-2** with thermal ellipsoids at 30% probability.

bond distances, and bond angles are tabulated in the Supporting Information. Note that **B2C2** features a standard C–C triple bond distance of 1.20 Å.

Polymerization reactions of **B2C2** with [2,5-diiodo-1,4-bis(3-propoxy-sulfonic acid)benzene] sodium salt catalyzed by Pd(OAc)₂/tris(3-sulfonatophenyl)phosphine trisodium salt (TPPTS) were evaluated in DMF, EtOH, and H₂O at 80 °C (Scheme 2, protocol a). Only the reactions carried out in

Scheme 2. Synthesis of Water-Soluble PPES



DMF solvent gave appreciable conversion of polymer. This polymerization route to PPEs is unusual; in this regard, the synthesis of PPEs using a phenylene bisboronic acid and a bis(2-bromoethynyl)phenylene has been accomplished,³⁹ and poly(arylenevinylene)s have been fabricated from arylene bisboronate and bis(2-bromovinyl)arylene synthons⁴⁰ and through a cascade Suzuki-Heck coupling of dihaloarenes with potassium vinyltrifluoroboronate.⁴¹

Two recent advances in the palladium catalyzed Suzuki-Miyaura reaction have utilized microwave heating^{42–45} and employed tris(4,6-dimethyl-3-sulfonatophenyl)phosphine trisodium salt (TXPTS)^{46,47} as a water-soluble catalyst ligand. Utilizing the microwave heating reaction conditions outlined in Scheme 2 (protocol b), poly[*p*-{2,5-bis(3-propoxysulfonic acid sodium salt)}phenylene]ethynylene (**PPES**) can be produced in high conversion in aqueous solvent. Interestingly, this aqueous polymerization reaction can also be accomplished under an aerobic atmosphere; in this case, the conversion to polymer product (85%) was slightly lower than

that realized under inert conditions (91%; see Supporting Information for procedural details). GPC analysis of **PPES** showed that the number averaged molecular weight (M_n) ranges from 6.6 to 17.5 kD depending on the reaction conditions, which corresponds to degrees of polymerization (DP) of 18–47. Representative absorption and emission spectra of **PPES** (DP ≈ 30) in H₂O are shown in Figure 2.

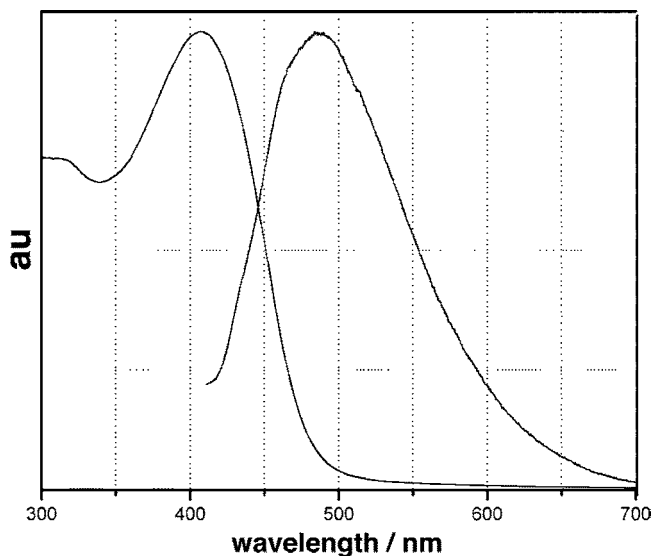


Figure 2. Absorption and emission spectra of **PPES** obtained via the synthetic procedure outlined in Scheme 2, protocol b. Experimental conditions: solvent = deionized H₂O, $T = 296$ K, $\lambda_{\text{ex}} = 390$ nm. Fluorescence quantum yield (Φ_f) = 0.064.

Note that not only the polymerization reaction, but **PPES** workup and purification steps can be carried out entirely in the aqueous phase as well.⁴⁸ In contrast to literature methods,⁶ **PPES** can be isolated simply via size exclusion chromatography (Supporting Information) using only unbuffered deionized water as an eluent. Given the nature of the small molecular weight impurities present in this synthesis of water-soluble **PPES**, the size exclusion stationary phase can be regenerated for subsequent **PPES** purifications simply by washing with water.

PPES ¹³C NMR spectra in D₂O/DMSO-*d*₆ cosolvent showed a broad ethynyl peak at 93 ppm (Supporting Information); notably, no resonances were evident between 75 and 85 ppm, where butadiynyl carbon peaks usually appear.⁴⁹ The absence of any detectable absorption signatures in this spectral region indicates that **PPES** polymer chain butadiyne defects are suppressed in this synthesis. PPEs prepared via Suzuki-Miyaura polycondensation of 1,4-benzenediboronic acid derivatives and 1,4-bis(2-bromoethynyl)benzene also show no evidence of butadiynyl signatures in ¹³C NMR;³⁹ these results and those presented herein underscore the utility

(35) Brown, H. C.; Bhat, N. G.; Srebnik, M. *Tetrahedron Lett.* **1988**, 29, 2631–2634.

(36) Ijdimaghsoodi, S.; Pang, Y.; Barton, T. J. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, 28, 955–965.

(37) *TwinSolve*; Christer Swensson; MaxLab: Lund, Sweden.

(38) *CrystalClear*; Rigaku Corporation, 1999.

(39) Koch, F.; Heitz, W. *Macromol. Chem. Phys.* **1997**, 198, 1531–1544.

(40) Lopez, L. C.; Strohrriegel, P.; Stübinger, T. *Macromol. Chem. Phys.* **2002**, 203, 1926–1930.

(41) Grisorio, R.; Mastrorilli, P.; Nobile, C. F.; Romanazzi, G.; Suranna, G. P. *Tetrahedron Lett.* **2005**, 46, 2555–2558.

(42) Caddick, S. *Tetrahedron* **1995**, 51, 10403–10432.

(43) Larhed, M.; Lindeberg, G.; Hallberg, A. *Tetrahedron Lett.* **1996**, 37, 8219–8222.

(44) Blettner, C. G.; König, W. A.; Stenzel, W.; Schotten, T. *J. Org. Chem.* **1999**, 64, 3885–3890.

(45) Leadbeater, N. E.; Marco, M. *Org. Lett.* **2002**, 4, 2973–2976.

(46) Western, E. C.; Daft, J. R.; Johnson, E. M.; Gannett, P. M.; Shaughnessy, K. H. *J. Org. Chem.* **2003**, 68, 6767–6774.

(47) Moore, L. R.; Shaughnessy, K. H. *Org. Lett.* **2004**, 6, 225–228.

(48) Li, C. J.; Slaven, W. T.; Chen, Y. P.; John, V. T.; Rachakonda, S. H. *Chem. Commun.* **1998**, 1351–1352.

(49) Egbe, D. A. M.; Tillmann, H.; Birckner, E.; Klemm, E. *Macromol. Chem. Phys.* **2001**, 202, 2712–2726.

of Suzuki-Miyaura polycondensation over Sonogashira polymerization conditions for the production of butadiyne defect free PPE.

In summary, we describe the synthesis and structure of a novel ethyne synthon, 1,2-bis(4',4',5',5'-tetramethyl[1',3',2'-dioxaborolan-2'-yl]ethyne (**B2C2**). We show the utility of **B2C2** in the Suzuki-Miyaura polycondensation reaction, synthesizing a water-soluble poly(*p*-phenyleneethynylene) (**PPES**) from [2,5-diiodo-1,4-bis(3-propoxy-sulfonicacid)-benzene] sodium salt in neat water under an aerobic atmosphere. This environmentally benign protocol for the preparation of ethyne-bridged conjugated polymers overcomes key drawbacks of commonly employed Sonogashira coupling and acyclic diyne metathesis methods, which include: the introduction of butadiyne defects along the polymer backbone, a requisite inert-atmosphere, and incompatibility of water-solubilizing functional groups with oli-

gomerization reaction conditions. Importantly, this conjugated rigid-rod polymer synthesis represents an example in which polymerization, purification, and isolation steps can be accomplished using only H₂O as a solvent.

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Supporting Information Available: Synthetic procedures, characterization, analytical, and X-ray crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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