Conjugated Polymers Containing 2,3-Dialkoxybenzene and Iptycene Building Blocks
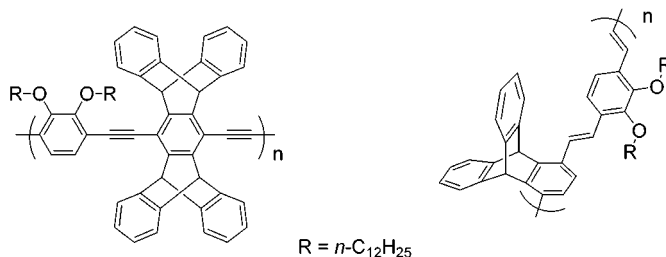
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ABSTRACT

R = *n*-C₁₂H₂₅

New poly(phenylene ethynylene)s (PPEs) and poly(phenylene vinylene)s (PPVs) that are highly emissive in solution and thin films were prepared utilizing palladium-catalyzed cross-coupling between new 1,4-diiodo-2,3-dialkoxybenzene- and iptycene-containing monomers. The absorption and emission spectra of the resulting polymers consistently showed a significant blue shift relative to the corresponding polymer analogues containing 2,5-dialkoxyphenylenes.

Pendant groups such as alkoxy,[1] alkyl,[2] alkylsilyl,[3] and phenyl[4] substituents are frequently employed to adjust a conjugated polymer's redox potential, absorption, emission, solubility, and solid-state structure. As a result of the ease of synthesis, alkoxy groups are by far the most frequently used substituents, particularly to increase the solubility of conjugated polymers. Recent reports have also shown that substitution patterns can significantly alter the electronic properties of conjugated polymers. Holmes et al. reported the synthesis of a poly(*p*-phenylene vinylene) (PPV) with alkoxy substitution at the 2,3-positions of phenylenes.[5] This polymer emits at higher frequency and possesses higher

photoluminescence (PL) and electroluminescence (EL) quantum efficiencies than the corresponding 2,5-dialkoxy substituted PPVs, such as poly(2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene), MEH-PPV. This change of absorption and emission was attributed to an increased steric interaction between the two *ortho*-dialkoxy groups with the adjacent vinyl moieties. The synthetic route in these previous studies was limited to the formation of a PPV homopolymer and random copolymers. Monomers that are amendable to palladium-catalyzed cross-coupling reactions may be used in a modular fashion to form a range of electroactive and luminescent homopolymers, copolymers (random and alternating). To investigate the effect of the change of the alkoxy substitution pattern on other types of conjugated polymers, we synthesized 1,4-diiodo-2,3-dialkoxybenzene, which can

(1) (a) Askari, S. H.; Rughooputh, S. D.; Wudl, F. *Synth. Met.* **1989**, *29*, E129.

(2) Son, S.; Dodabalapur, A.; Lovinger, A. J.; Galvin, M. E. *Science* **1995**, *269*, 376.

(3) (a) Hoger, S.; McNamara, J. J.; Schricker, S.; Wudl, F. *Chem. Mater.* **1994**, *6*, 171. (b) Hwang, D.-H.; Kim, S. T.; Shim, H.-K.; Holmes, A. B.; Moratti, S. C.; Friend, R. H. *Chem. Commun.* **1996**, 2241.

(4) Hsieh, B. R.; Yu, Y.; Forsythe, E. W.; Schaaf, G. M.; Feld, W. A. *J. Am. Chem. Soc.* **1998**, *120*, 231. (b) Hsieh, B. R.; Wan, W. C.; Yu, Y.; Gao, Y.; Gonzalez, S. A.; Feld, W. A. *Macromolecules* **1998**, *31*, 631.

(5) (a) Cacialli, F.; Chuah, B. S.; Kim, J. S.; Dos Santos, D. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B.; Bredas, J. L. *Synth. Met.* **1999**, *102*, 924. (b) Martin, R. E.; Geneste, F.; Chuah, B. S.; Holmes, A. B.; Riehn, R.; Cacialli, F.; Friend, R. H. *Chem. Commun.* **2000**, 291. (c) Chuah, B. S.; Cacialli, F.; Dos Santos, D. A.; Feeder, N.; Davies, J. E.; Moratti, S. C.; Holmes, A. B.; Friend, R. H.; Bredas, J. L. *Synth. Met.* **1999**, *102*, 935.

be readily incorporated into various conjugated polymers through cross-coupling reactions. We have further integrated triptycene and pentiptycene functionalities that enhance solubility and fluorescence quantum yields by eliminating the tendency of these materials to aggregate. Herein we report the first triptycene-containing PPVs, and the properties of PPEs and PPVs containing *ortho*-dialkoxy substituents are compared to the analogous polymers containing *para*-dialkoxy substitution.

Direct iodination of 1,2-dialkoxybenzenes produces 4,5-diiodobenzenes.[6] A reported synthesis of 1,4-diiodo-2,3-dimethoxybenzene involved the double lithiation of 1,2-dimethoxybenzene (veratrole) followed by treatment with iodine.[7] However, this reaction required a large amount of butyllithium and was low yielding. To synthesize 1,4-diiodo-2,3-dialkoxybenzene more efficiently, veratrole was transformed to 1,4-bis(trimethylsilyl)-2,3-dimethoxybenzene through a two-step, subsequent monolithiation and treatment with trimethysilyl chloride (Scheme 1) following a modified

Scheme 1
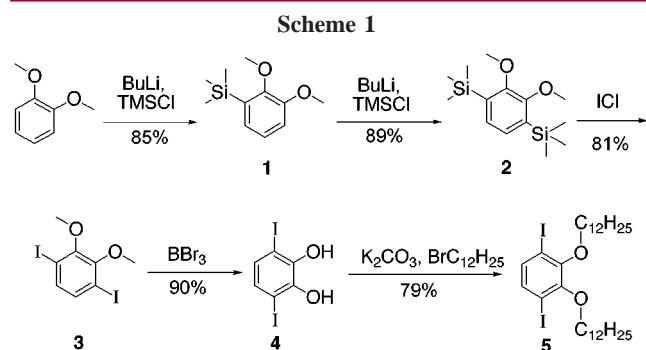
literature procedure.[8] Thus, veratrole was treated with 1.1 equiv of *n*-butyllithium followed by trimethysilyl chloride to give the 1-trimethysilyl-2,3-dimethoxybenzene (**1**). The monosilane was again treated with 1.2 equiv of *n*-butyllithium followed by trimethysilyl chloride to give the bis-(trimethylsilane) **2**. The best results were obtained when the reactions were carried out in the presence of TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) with hexane as a solvent. This procedure can be carried out in large scale (>50 g), and the products can be purified easily by either chromatography or fractional distillation. Treatment of **2** with iodine monochloride afforded the diiodide **3** in good yield. Demethylation with BBr₃ afforded the 1,4-diiodo-2,3-dihydroxybenzene **4**, and subsequent realkylation with 1-bromo-dodecane afforded the corresponding 1,4-diiodo-2,3-di-(dodecyloxy)benzene **5**.

Previous work from our research group has shown that the incorporation of iptycenes in poly(phenylene ethynylene)s (PPEs) can effectively minimize interchain interactions so

as to maintain high fluorescence efficiencies in thin films.[9] Thus, diiodide **5** was polymerized with pentiptycene diacetylene **6** under modified Sonogashira conditions[9,10] to afford polymer **7** as a high-molecular-weight material ($M_n = 72$ kDa, Scheme 2). Likewise, polymer **9** with dialkoxy sub-

Scheme 2
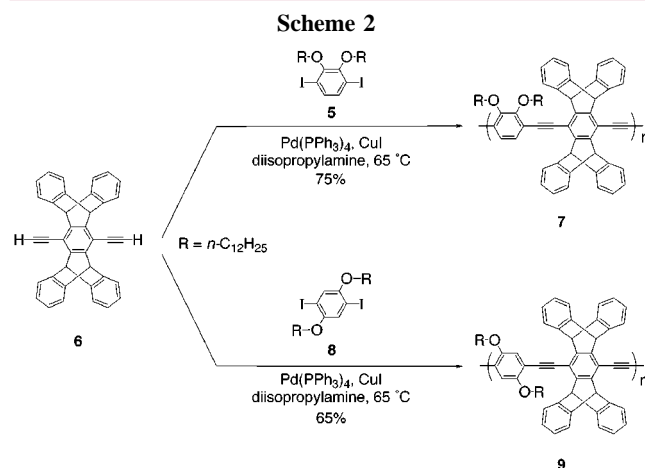
stituents on the *para* positions of phenylenes was prepared through the coupling of **6** and 1,4-di(dodecyloxy)-2,5-diiodobenzene **8**. The absorption and fluorescence spectra of polymers **7** and **9** were recorded in dichloromethane (Figure 1, A). It was observed that both the absorption ($\lambda_{max} = 391$ nm) and emission ($\lambda_{max} = 423$ nm) of **7** are shifted to the shorter wavelength side of the corresponding absorption ($\lambda_{max} = 438$ nm) and emission spectra ($\lambda_{max} = 455$ nm) of **9**. This is an interesting finding, because as mentioned previously the blue shift in PPVs was suggested to be steric in origin. However, in the case of PPEs the cylindrical symmetry of the acetylene group precludes a direct steric disruption of conjugation. As a result we believe that the blue shift is electronic rather than steric in origin.

Triptycene-containing PPVs were synthesized through a Suzuki-type coupling of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxoborolan-2-yl-ethenyl)-9,10-dihydro-9,10-[1′,2′]benzenoanthracene (**10**) with the diiodides **5** and **8** (Scheme 3). The coupling of boronates and aryl halide is frequently used in biaryl syntheses.[11] Similar reactions involving the coupling of vinylboronates and aryl halides were reported to afford monomeric[12] and oligomeric[13] phenylene vinylenes. Although there were no previous reports of the synthesis of PPVs through this reaction, we expected these reactions to meet

(6) Zhou, Q.; Carroll, P. J.; Swager, T. M. *J. Org. Chem.* **1994**, *59*, 1294.

(7) Pring, B. G. *Acta Chem. Scand.* **1973**, *27*, 3873.

(8) Crowther, G. P.; Sundberg, R. J.; Sarpeshkar, A. M. *J. Org. Chem.* **1984**, *49*, 4657.
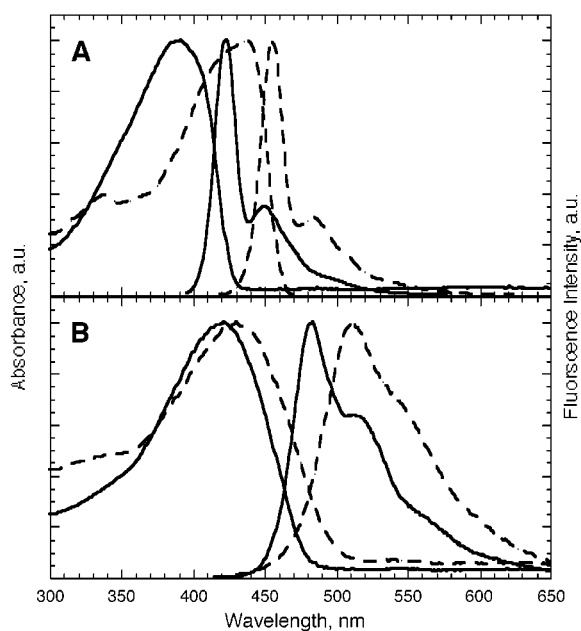
(9) (a) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864. (b) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 5321. (c) Williams, V. E.; Swager, T. M. *Macromolecules* **2000**, *33*, 4069.

(10) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467.

(11) (a) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Comun.* **1981**, *11*, 513. (b) Wright, S. W.; Hageman, D. L.; McClure, L. D. *J. Org. Chem.* **1994**, *59*, 6095.

(12) (a) Burk, M. J.; Lee, J. R.; Martinez, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 10847. (b) Murata, M.; Watanabe, S.; Masuda, Y. *Tetrahedron Lett.* **1999**, *40*, 2585.

(13) Prinz, P.; Lansky, A.; Haumann, T.; Boese, R.; Noltemeyer, M.; Knieriem, B.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1289.

Figure 1. Absorption and fluorescence spectra of the conjugated polymers in dichloromethane: (A) PPEs; solid line, **7**; dashed line, **9**. (B) PPVs; solid line, **11**; dashed line, **12**. The excitation wavelength of the fluorescence spectra was 380 and 400 nm for PPEs and PPVs, respectively. All spectra were normalized for comparison.

high yield requirements of a step-growth polymerization. Because of the general requirement of highly pure difunctional monomers in these types of polymerizations, pinacol ester derivatives of the bis(vinyl borate)s were chosen as PPV monomers. These organo-boronates are stable to column chromatography and therefore can be readily purified.

The synthesis of triptycene bis(vinyl-dioxoborolane) **10** is shown in Scheme 4. The starting material 9,10-dihydro-9,10[1′,2′]-benzenoanthracene-1,4-diol (**13**) was prepared from commercially available anthracene and 1,4-benzoquinone following a literature procedure.[14] Aryl nonafluo-

Scheme 3

robutanesulfonates (nonaflates) have been reported to react readily with organozinc reagents in the presence of palladium catalysts and have a higher reactivity compared to the corresponding aryl triflates.[15] To activate the hydroxy groups in **13** for cross-coupling, the hydroquinone derivative was treated with commercially available $CF_3(CF_2)_3SO_2F$ in the presence of triethylamine at room temperature to afford the bisnonaflate **14**.[16] The conversion was complete within 12 h, and the product was obtained in high yield (98%). The palladium-catalyzed cross-coupling reaction of bisnonaflate **14** with trimethylsilylethyne under modified Sonogashira conditions furnished the bis(trimethylsilylethynyl) triptycene (**15**) in 86% yield. Treatment of **15** with a solution of KOH in methanol in THF afforded the diethynyltriptycene (**16**) in 90% yield. Heating **16** with 4,4,5,5-tetramethyl-1,3,2-dioxoborolane in dry toluene afforded the bisborolane **10**, which was purified by chromatography.

Scheme 4
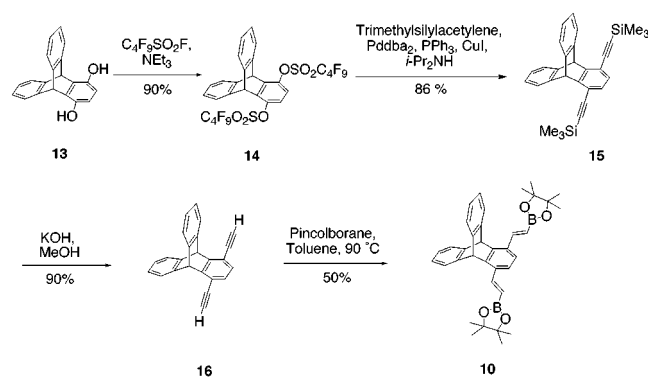
Both polymers **11** and **12** were obtained by heating bis-(vinyldioxaborolane) **10** with suitable dialkoxy diiodides in dioxane in the presence of a base (i.e., cesium carbonate) or cesium fluoride and palladium catalyst. Under these conditions, we obtained polymers with molecular weights around 12 kDa (as determined by GPC, corresponding to ca. 15−20 repeating units).

Figure 1B shows the absorption and emission spectra of polymer **11** ($\lambda^{ab}_{max} = 422$, $\lambda^{fl}_{max} = 484$ nm) and **12** ($\lambda^{ab}_{max} = 439$, $\lambda^{fl}_{max} = 512$ nm). It is clear that like polymer **7**, polymer **11** with *ortho*-dialkoxy substitutions has a shorter absorption and emission wavelength than polymer **12**, which has dialkoxy substitutions at the *para* positions of phenylenes.

Thin films of the conjugated polymers were prepared by spin-casting solutions of the polymers onto the surfaces of glass substrates. These films are highly fluorescent and have similar absorption and emission features as in solutions, indicating the minimized interchain interactions in the solid
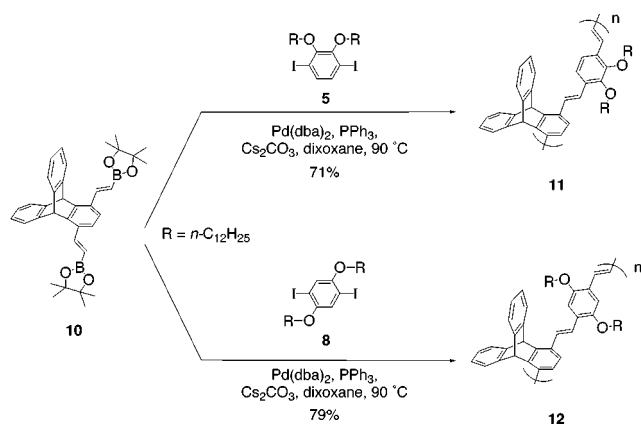
(14) Bartlett, P. D.; Ryan, M. J.; Cohen, S. G. *J. Am. Chem. Soc*. **1942**, *64*, 2649.
(15) Rottlaender, M.; Knochel, P. *J. Org. Chem.* **1998**, *63*, 203.
(16) (a) Subramanian, L. R.; Bentz, H.; Hanack, M. *Synthesis* **1973**, 293. (b) Niederpruem, H.; Voss, P.; Beyl, V. *Liebigs. Ann. Chem.* **1973**, 20.

state. The emission from thin films of **11** ($\lambda^{fl}_{max} = 516$ nm) and **12** ($\lambda^{fl}_{max} = 524$ nm) shift slightly to the longer wavelength of those displayed in solution. For polymers containing monomer **6** the thin film emission spectra ($\lambda^{fl}_{max} = 424$ nm for **7** and $\lambda^{fl}_{max} = 460$ nm for **9**) are almost identical to those in solution, thereby confirming the higher efficiency of pentiptycenes in preventing interchain aggregation than triptycenes.

Our observation that conjugated polymers (both PPEs and PPVs) with dialkoxy substitution on the *ortho* positions of phenylenes absorb and emit at higher frequencies than the corresponding *para*-substituted polymers is consistent with the previous reports on PPVs with alkoxy substitutions. The efficient preparation of 1,4-diiodo-2,3-alkoxybenzene allows the synthesis of a variety of conjugated polymers through cross-coupling so that the electronic properties of the polymers can be tuned by the control of alkoxy substitution patterns. We have conducted preliminary calculations on small model chromophores that reveal significant differences in the frontier molecular orbital characteristics between molecules having the *ortho*- versus *para*-dialkoxy substitution patterns. This supports our assertion that the origin of the different spectroscopic characteristics is mainly electronic rather than a pure steric effect as previously suggested.[5]

In conclusion, we have established an efficient synthesis of 1,4-diiodo-2,3-dimethoxybenzene through a sequential activation of the two positions *ortho* to the two methoxy groups of veratrole by the formation of arylsilanes. Subsequent iodination and demethylation provided diiodocatechol **4**, which proved to be a versatile precursor for diiodo-dialkoxybenzenes such as **5**. We also demonstrated that both PPEs and PPVs from such monomers can be synthesized by cross-coupling-based step-growth polymerizations. The incorporation of 2,3-dialkoxyphenylenes into both PPEs and PPVs results in a blue shift in absorption and emission of the polymers relative to corresponding polymers containing 2,5-dialkoxyphenylenes. The incorporation of iptycene units in the polymer backbone was further found to enhance the solubility and fluorescence quantum yields in thin films.

Supporting Information Available: Experimental procedures and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0164886