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Synthesis of α,α′-Linked Oligophospholes and Polyphospholes by Using Pd−CuI-Promoted Stille-Type Coupling

Arihiro Saito,[†] Yoshihiro Matano,[*,†] and Hiroshi Imahori[†,‡,§]

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan, Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan, and Fukui Institute for Fundamental Chemistry, Kyoto University, Sakyo-ku, Kyoto 606-8103, Japan

matano@scl.kyoto-u.ac.jp

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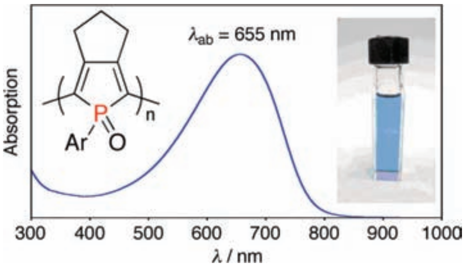
ABSTRACT



Palladium−copper-promoted Stille-type cross-coupling reactions between α-stannylphospholes and α-iodophospholes afforded α,α′-linked oligophospholes and polyphosphole efficiently. It has been revealed that the polyphosphole *P*-oxide possesses an extremely narrow band gap and a high electron-accepting ability as compared to polythiophene.

Polyheteroles (α,α′-linked polymers of heterocyclopentadiene) constitute an important group of conjugated polymers with applications in organic devices such as organic photovoltaic cells, organic field-effect transistors, and organic light-emitting diodes.[1] It is well-known that the inherent properties of polyheteroles depend heavily on the nature of each heterole monomer. Phosphole possesses a low-lying LUMO owing to the effective $\sigma^*-\pi^*$ orbital interaction and an active lone electron pair at phosphorus.[2] In this regard, polyphospholes are expected to show distinguished optical and electrochemical properties that cannot be attained by other classes of polyheteroles. Indeed, some theoretical studies predicted, for example, a considerably narrow band gap for polyphosphole compared with polypyrrole and polythiophene.[3] Experimentally, however, the chemistry of polyphospholes has been untouched due to the lack of promising synthetic methods as well as appropriate monomer precursors.[4] Although oligophospholes up to tetramer were synthesized by using oxidative coupling of α-lithiophosp-

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[†] Graduate School of Engineering.
[‡] Institute for Integrated Cell-Material Sciences.
[§] Fukui Institute for Fundamental Chemistry.

(1) For example, see: (a) Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324. (b) Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58. (c) Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. *Angew. Chem., Int. Ed.* **2008**, *47*, 4070. (d) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897. (e) Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. *Chem. Rev.* **2009**, *109*, 5868, and references cited therein.

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(3) (a) Salzner, U.; Lagowski, J. B.; Pickup, P. G.; Poirier, R. A. *Synth. Met.* **1998**, *96*, 177. (b) Ma, J.; Li, S.; Jiang, Y. *Macromolecules* **2002**, *35*, 1109. (c) Casanovas, J.; Alemán, C. *J. Phys. Chem. C* **2007**, *111*, 4823. (d) Zhang, G.; Ma, J.; Wen, J. *J. Phys. Chem. B* **2007**, *111*, 11670.

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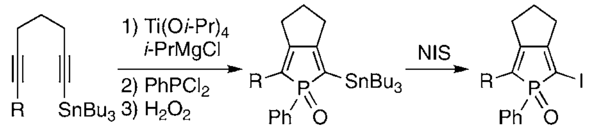
holes,[5] reductive dimerization of α-free phospholes,[6] [1,5] sigmatropic shift of 1,1′-biphosphole,[7] or hydrophosphination of 1,3-diyne[8] as key steps, these methods appeared to have difficulty in polymer synthesis in terms of availability of the precursors. Therefore, we decided to develop a new strategy that would allow a short-step synthesis of polyphospholes and focused on a cross-coupling methodology to link phosphole rings at their α and α′ positions.[9] Herein, we report the first synthesis of α,α′-linked oligophospholes and polyphosphole by using Pd−CuI-promoted Stille-type coupling and their optical/electrochemical properties.

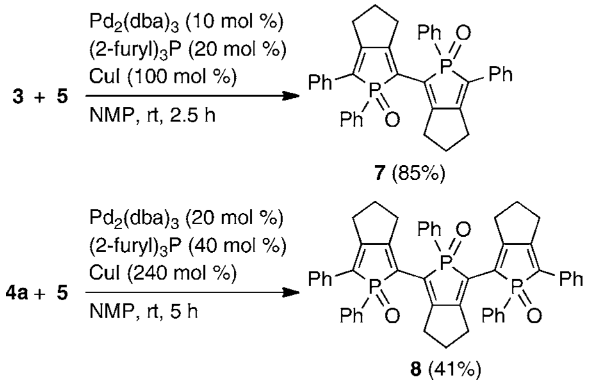
α-Stannylphosphole **3**[10] and α,α′-distannylphosphole **4a**, which are prerequisite constituents for Stille coupling, were prepared from the corresponding diynes **1** and **2** by utilizing a Ti(II)-mediated cyclization method as a key step (Scheme 1).[4f,8,11] To prevent undesirable side reactions in the following steps, the phosphorus center was oxygenated at this stage. The ^{31}P peaks of **3** and **4a** appeared at δ_P 64.9 and 78.2, respectively, with characteristic coupling patterns arising from α-tin atoms ($^2J_{P-Sn} = 116-122$ Hz). Treatment of **3** and **4a** with stoichiometric amounts of *N*-iodosuccinimide (NIS) afforded α-iodophosphole **5** (δ_P 51.5) and α,α′-diiodophosphole **6a** (δ_P 48.4), respectively. This protocol enabled us to introduce tributylstannyl and iodo groups to α,α′ positions of the phosphole ring in three to four steps from commercially available reagents. With these precursors in hand, we first evaluated the efficiency of a Stille coupling method for the synthesis of α,α′-biphosphole. In the presence of $Pd_2(dba)_3$, tris(2-furyl)phosphine, and CuI,[12] Stille-type cross coupling between **3** and **5** proceeded smoothly at room temperature to give α,α′-biphosphole **7** in 85% yield (Scheme 2). It should be noted that both the Pd catalyst and CuI are indispensable for producing **7** with high efficiency. Under the same reaction conditions, homocoupling of **3** also proceeded, albeit more slowly than Stille-type coupling, to give **7**.[13] When **4a** was reacted with **5**, terphosphole **8** was obtained as the major product. The relatively low-yield formation of **8** is attributable to a competitive homocoupling of **4a**, which led to small amounts of quaterphosphole (detected by MS) and other uncharacterized oligophospholes. Compounds **7** and **8** were characterized by standard spectroscopic techniques. The ^{31}P NMR spectra indicated the presence of two diastereomers for **7** and three diastereomers for **8**.[14]

Scheme 1. Synthesis of α-Stannyl- and α-Iodophospholes



1 (R = Ph)
2 (R = SnBu$_3$)
3 (R = Ph; 56%)
4a (R = SnBu$_3$; 22%)
5 (R = Ph; 98%)
6a (R = I; 90%)

Scheme 2. Synthesis of Diphosphole **7** and Terphosphole **8**



7 (85%)

8 (41%)

Next, we attempted to synthesize polyphosphole from **4a** and **6a** by using the Pd−CuI-promoted Stille-type coupling. Judging from gel permeation chromatography (GPC) analysis, however, only low-molecular-weight polymer was obtained probably due to its low solubility. Hence, phosphole monomers **4b** (δ_P 78.7, $^2J_{P-Sn} = 116$ Hz) and **6b** (δ_P 49.8) bearing a *p*-dodecyloxyphenyl group as a solubilizing function were newly synthesized according to the titanacycle protocol (Scheme S1, Supporting Information) and applied to the Stille-type coupling (Scheme 3).[15] As expected, the

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(4) Conjugated copolymers containing phosphole units have been reported by several groups. For example, see: (a) Mao, S. S. H.; Tilley, T. D. *Macromolecules* **1997**, *30*, 5566. (b) Lucht, B. L.; Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 4354. (c) Morisaki, Y.; Aiki, Y.; Chujo, Y. *Macromolecules* **2003**, *36*, 2594. (d) Tomita, I.; Ueda, M. *Macromol. Symp.* **2004**, *209*, 217. (e) Sebastian, M.; Hissler, M.; Fave, C.; Rault-Berthelot, J.; Odin, C.; Réau, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 6152. (f) de Talancé, V. L.; Hissler, M.; Zhang, L.-Z.; Kárpáti, T.; Nyulászi, L.; Caras-Quintero, D.; Bäuerle, P.; Réau, R. *Chem. Commun.* **2008**, 2200.

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(8) Matano, Y.; Nakashima, M.; Imahori, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 4002.

(9) Very few attempts were reported for cross coupling of α-halophospholes. Holand, S.; Gandolfo, F.; Ricard, L.; Mathey, F. *Bull. Soc. Chim. Fr.* **1996**, *133*, 33.

(10) 2-Stannylphosphole was previously reported. Deschamps, B.; Mathey, F. *Bull. Soc. Chim. Fr.* **1996**, *133*, 541.

(11) (a) Matano, Y.; Miyajima, T.; Nakabuchi, T.; Imahori, H. *J. Org. Chem.* **2006**, *71*, 5792. (b) Matano, Y.; Miyajima, T.; Imahori, H.; Kimura, Y. *J. Org. Chem.* **2007**, *72*, 6200. (c) Sanji, T.; Shiraishi, K.; Tanaka, M. *Org. Lett.* **2007**, *9*, 3611.

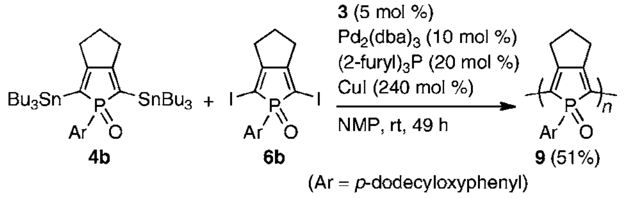
(12) Devreux, V.; Wiesner, J.; Jomaa, H.; Rozenski, J.; der Eycken, J. V.; Calenbergh, S. V. *J. Org. Chem.* **2007**, *72*, 3783.

(13) Pd-catalyzed homocoupling of stannylarenes was reported previously. For example, see: (a) Liebeskind, L. S.; Riesinger, S. W. *J. Org. Chem.* **1993**, *58*, 408. (b) Farina, V.; Krishnan, B.; Marshall, D. R.; Roth, G. P. *J. Org. Chem.* **1993**, *58*, 5434. (c) Liebeskind, L. S.; Yu, M. S.; Wang, J.; Hagen, K. S. *J. Am. Chem. Soc.* **1993**, *115*, 9048.

(14) Density functional theory (DFT) calculations (B3LYP/6-31G*) on **7** showed that there was little difference in free energies between the respective diastereomers. For details, see the Supporting Information.

(15) In this polymerization, a small amount of **3** (5 mol % per **4b**) was added as an end-cap unit for the purpose of controlling the molecular weight.

Scheme 3. Synthesis of α,α′-Polyphosphole **9**



polymerization occurred efficiently at room temperature to give α,α′-linked polyphosphole **9** as a dark blue powder in 51% yield after filtration through a 0.45-μm membrane filter and repeated precipitations from CH_2Cl_2−hexane and CH_2Cl_2−MeOH. The number average molecular weight (M_n) and polydispersity index (PDI) of **9** were determined by GPC (relative to polystyrene standard) as 13000 and 2.3, respectively.[16] Polyphosphole **9** showed a group of rather broad ^{31}P peaks at δ_P 51.6−56.4, which covers the region observed for **7** (δ_P 54.0−55.1) and **8** (δ_P 51.9−55.5). Unfortunately, treatment of **9** with $HSiCl_3$ did not proceed cleanly, and we have not succeeded in obtaining polyphosphole of the σ^3-P type.

The average polymerization degree of **9** (n = 32) is sufficiently large for discussing the optical and electrochemical properties of α,α′-linked polyphosphole by comparison with those of polythiophenes. The observed data for **7**−**9** and monomer **10**[17] are summarized in Figure 1 and Table 1.

Table 1. Optical Data and Redox Potentials of **7**−**10** in CH_2Cl_2

compd	λ_{ab}/nm (log ε)	$\lambda_{em}{}^{a}$/nm (Φ_F)^{b}	$E_{ox}{}^{c}$/V	$E_{red}{}^{c}$/V
7	463 (4.35)	583 (0.02)	+0.76	−1.75
8	511 (4.40)	605 (<0.01)	+0.64	−1.62
9	655 (3.80)^{d}	*e*	+0.30^{f,g}	−1.20^{f}
10	386 (4.15)	491 (0.19)	+1.19	−2.02

[a] λ_{ex} = 440 nm for **7** and **10**, 510 nm for **8**. [b] Relative fluorescence quantum yields. [c] Determined by DPV (0.1 M $n$$Bu_4N^+PF_6^-$; Ag/Ag$^+$). First oxidation ($E_{ox}$) and reduction ($E_{red}$) potentials vs Fc/Fc$^+$. [d] Calculated per repeating unit. [e] Nonfluorescent. [f] E_{onset}. [g] A broad and weak peak was observed for the first oxidation process.

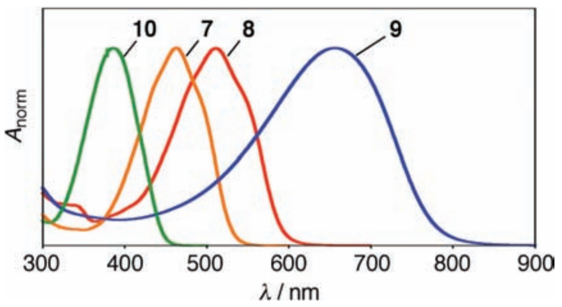


Figure 1. UV/vis absorption spectra of **7**−**10** in CH_2Cl_2.

The absorption maxima (λ_{ab}) shift to longer wavelength with increasing the number of phosphole units, which is commonly seen for α,α′-linked heteroles. The λ_{ab} values of **7**, **8**, and **9** are significantly red-shifted ($\Delta\lambda_{ab}$ = 90−110 nm) relative to the respective values reported for bithiophene **11a**[18] (λ_{ab} = 376 nm), terthiophene **11b**[18] (λ_{ab} = 404 nm), and polythiophene (36-mer) **12**[19] (λ_{ab} = 546.3 nm) (Figure 2). Notably, the onset of **9** reaches around 850 nm (E_g = 1.46 eV), indicating that the polymerization at the α,α′ positions expands conjugation of the phosphole π-system quite effectively. While **7** and **8** are weakly fluorescent, **9** is nonfluorescent in solution.

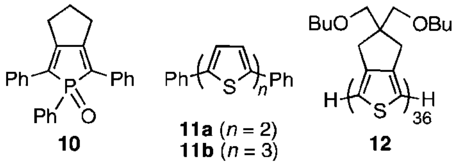


Figure 2. Monomer reference **10**, oligothioiphenes **11a**,**b**, and polythiophene **12**.

Redox potentials of **7**−**9** were determined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The polymer **9** showed a broad first reduction process at E_{onset} = −1.20 V (vs Fc/Fc$^+$), which is less negative than E_{red} of monomer **10** (−2.02 V), dimer **7** (−1.75 V), and trimer **8** (−1.62 V). It is evident that the electron-accepting ability of the phosphole π-system is largely enhanced by polymerization. The redox behavior of **9** is in marked contrast to that of polythiophene and polypyrrole.

In summary, we have established convenient methods for the synthesis of α-stannyl- and α-iodophospholes. With these precursors available, the first example of α,α′-linked polyphosphole as well as related oligophospholes was successfully prepared by using the Stille-type coupling. Notably, polyphosphole possesses an extremely narrow band gap and a high electron-accepting ability. The present monomers are applicable to the synthesis of phosphole-containing conjugated copolymers, and further studies on this project are now in progress.

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Supporting Information Available: Experimental details and DFT calculation results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Attempts to prepare **9** by the homocoupling of **4b** resulted in failure probably due to its inefficiency compared to the heterocoupling of **4b**/**6b**.

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