ORGANIC
LETTERS

2006
Vol. 8, No. 3
503−506

Synthesis and Unexpected Reactivity of Si–H Functionalized Dithieno[3,2-*b*:2′,3′-*d*]phospholes

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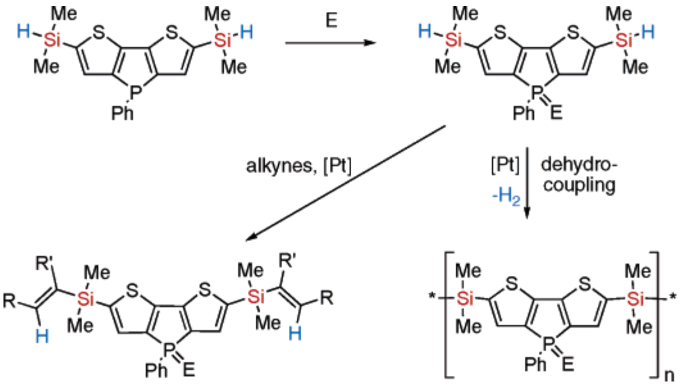
Received December 2, 2005

ABSTRACT



Si–H functionalized, blue light-emitting dithieno[3,2-*b*:2′,3′-*d*]phospholes are accessible by reaction of an appropriate bithiophene precursor with a dichlorophosphane. Subsequent functionalization of the central phosphorus center allows for a fine-tuning of the optoelectronic properties of the material. Pt-catalyzed reaction of the Si–H functionalities with alkynes affords the hydrosilation products including a polymer by reaction with 1,7-octadiyne. By contrast, the absence of any substrate leads to the exclusive formation of a polymer via dehydrogenative homocoupling.

The incorporation of phosphorus centers into π-conjugated materials for molecular electronics and optoelectronics is a young, emerging field of research.[1] Phosphole-based materials, in particular, are very intriguing candidates for respective applications owing to their unique electronic structure (e.g., low degree of lone-pair delocalization; low lying LUMO).[2] The versatile reactivity of the central phosphorus atom allows for an efficient fine-tuning of the electronic properties of the materials by very simple chemical modifications.[3,4] These can include oxidation or complexation reactions via Lewis acids or transition metal complexes. In this context, we have recently established the novel dithieno[3,2-*b*:2′,3′-*d*]phosphole system with very advantageous and readily tunable photophysical properties that can be attributed to the nature of the bridging phosphorus atom.[4]

To successfully utilize novel π-conjugated materials in optoelectronic applications, it appears necessary, however,

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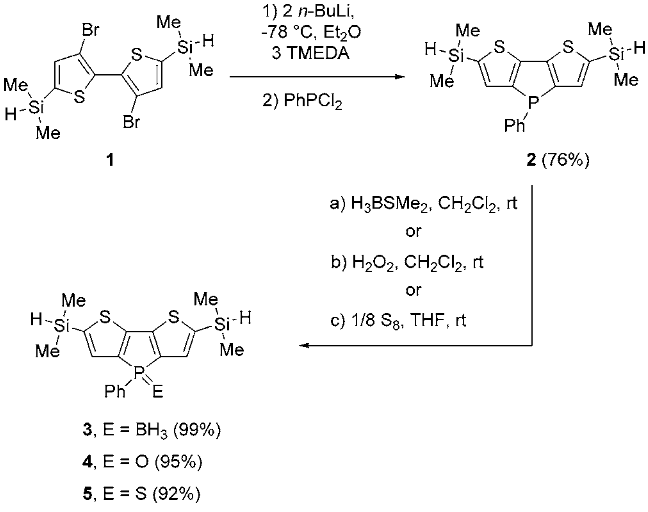
10.1021/ol0529288 CCC: $33.50

to be able to form very thin films of the respective materials.[5] One of the major strategies to approach this issue is the spin coating of a solution of the material onto a substrate, which is suitable for oligomeric/polymeric systems as they tend to form films easily upon removal of the solvent.[5a,6]

Here we report on the synthesis of Si−H functionalized dithieno[3,2-*b*:2′,3′-*d*]phospholes and the fine-tuning of their optoelectronic properties by simple chemical modifications performed at the phosphorus center. Their hydrosilation reactivity toward alkynes and the serendipitous dehydrogenative homocoupling to access polymeric dithienophosphole materials potentially suitable for optoelectronic applications are also presented.

The Si−H functionalized dithienophosphole **2** is accessible in good yield (76%) via a similar protocol as reported for other silylated dithienophospholes.[4] Reaction of 5,5′-bis-(dimethylsilyl)-3,3′-dibromo-2,2′-dithiophene[7] **1** with *n*-BuLi in the presence of TMEDA in Et_2O at −78 °C affords the product **2** after addition of phenyl(dichloro)phosphane (Scheme 1). The ^{31}P NMR spectrum of **2** shows a resonance at δ −24.1 ppm that is slightly downfield shifted compared to other related silyl-functionalized dithienophospholes (δ ^{31}P −25.0 to −28.2 ppm).[4a] The ^{1}H NMR spectrum exhibits the characteristic Si−H resonance at δ 4.54 ppm with the expected septet splitting due to the coupling to six equivalent methyl protons. Similar to all known dithienophospholes,[4] compound **2** also exhibits very pronounced optoelectronic properties with a maximum wavelength of absorption at λ_{ex} = 366 nm, a maximum wavelength of emission at λ_{em} = 420 nm (blue), and an exceptionally high photoluminescence quantum yield efficiency of $\phi_{PL} = 0.810$.[8]

Scheme 1. Synthesis and Functionalization of Si−H Substituted Dithienophospholes



As already indicated, the electronic nature of the phosphorus center has a significant impact on the optoelectronic properties of the dithienophosphole moiety. Chemical modifications performed at the trivalent phosphorus center in general lead to materials with significantly red-shifted absorption and emission wavelength maxima that are coherent with a lowered energy of the π^*-LUMO level.[4a] This is also observed with the chemically modified dithienophospholes **3**−**5** that are accessible in almost quantitative yields by reaction of **2** with borane (added as $H_3B{\cdot}SMe_2$), hydrogen peroxide, or sulfur, respectively (Scheme 1). Their downfield shifted ^{31}P NMR resonances at δ 12.5 (**3**), 17.1 (**4**), and 23.6 ppm (**5**) correlate well with those observed for related compounds[4a] and correspond to the increased electron acceptor character of the phosphorus center. The same applies to the optoelectronic properties of the three species showing red-shifted absorption and emission maxima, compared with the values for **2** (see Table 1). The presence of the Si−H resonance in the ^{1}H NMR spectra of the three compounds **3**−**5** indicates that this functionality is not affected by the reaction conditions applied and that it can be utilized in subsequent experiments.

Table 1. Photoluminescence Data of the Dithienophospholes **2**−**8** ($c = 1 \times 10^{-4}$ M in CH_2Cl_2)

compd	λ_{ex} [nm][a]	λ_{em} [nm][b]	ϕ_{PL}[8]
2	366	420	0.810
3	376	447	0.634
4	383	457	0.581
5	383	457	0.615
6	357 (sh), 399	459	0.548
7	378	460	0.562
8	353 (sh), 393	459	0.566

[a] Maximum wavelength of absorption. [b] Maximum wavelength of emission.

To probe the hydrosilation reactivity of the Si−H functionalized dithienophospholes, we first focused upon suitable model compounds to optimize the reaction conditions. The primary substrate for these reactions was 1,2-diphenylacetylene (tolane). Furthermore, all hydrosilation experiments were performed with the oxidized dithienophosphole **4** exclusively, to prevent potential poisoning of the employed catalyst (PtDVDS, “Karstedt catalyst”);[9] as shown recently by our group, the phosphorus center in dithienophospholes is an excellent ligand for corresponding platinum complexes.[4c]

The reaction of **4** with 2 equiv of tolane works best in dichloromethane at room temperature with a few drops of Karstedt catalyst solution[9] added (Scheme 2). These conditions afford a quantitative conversion to the desired product **6** overnight, which could be isolated in good yield (75%) as a light yellow, sticky oil. The successful generation of **6** is supported by the disappearance of the Si−H resonance in

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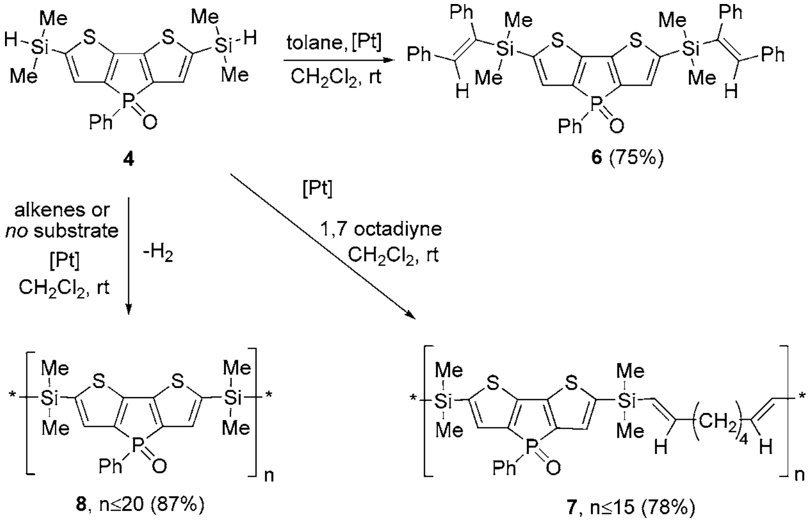
[8] Relative to quinine sulfate (0.1 M H_2SO_4 solution) ±10%; see: Demas, N. J.; Crosby, G. A. *J. Chem. Phys.* **1971**, *75*, 991.

[9] Solution in xylenes, ca. 2% metal.

Scheme 2. Synthesis of Extended Dithienophosphole Materials



the ^{1}H NMR spectrum and a slightly highfield-shifted ^{31}P NMR resonance at δ 14.7 ppm (cf. δ 17.1 ppm for **4**).

Compound **6** also exhibits very pronounced optoelectronic features with $\lambda_{ex} = 399$ nm, $\lambda_{em} = 459$ nm, and $\phi_{PL} = 0.548$.[8] As observed earlier, the modification of the substitution pattern of the silyl group only alters the absorption properties of the dithienophosphole moiety whereas its emission remains almost unaffected.[4a] The same holds true for the diphenylethylene-substituted species **6** ($\Delta\lambda_{ex} = 15$ nm, $\Delta\lambda_{em} = 2$ nm). The presence of a second, very strong transition at $\lambda_{ex} = 357$ nm appearing as a shoulder in the excitation spectrum could arise from a charge transfer from the diphenylethylene (dpe) moiety to the dithienophosphole (dtp) moiety ($\pi_{dpe} \rightarrow \pi^*_{dtp}$) indicating a potential extension of the π-conjugated system through the silicon centers; a corresponding transition is not commonly observed in the excitation spectra of dithienophospholes.[4] This finding, on the other hand, shows that the preservation of the intriguing blue light-emitting properties of the monomers would be possible in oligomeric/polymeric systems accessed via a similar strategy.

An extended, polymeric material can be generated by using a suitable α,ω-bis(alkyne) as substrate. Reaction of the oxidized dithienophosphole **4** with 1 equiv of 1,7-octadiyne in dichloromethane and a catalytic amount of Karstedt catalyst at room temperature afforded a polymeric material after 3 days (Scheme 2). The almost complete disappearance of the Si−H resonance at δ ^{1}H 4.54 ppm as well as the presence of two major olefinic ^{1}H resonances at δ ^{1}H 6.19 and 5.68 ppm with a vicinal trans coupling of ^3J(H,H) = 18.8 Hz support a cis-1,2-addition of silicon and hydrogen to the alkyne units to be favored.[10] Analysis by gel permeation chromatography (GPC) of the dark orange, glassy oil obtained after precipitation from CH_2Cl_2 into heptane indicated the generation of a polymeric material with molecular weights of up to 8000 ($n \leq 15$) supporting the successful hydrosilation step. The polymeric nature of the material was further confirmed by an end group analysis via ^{1}H NMR showing an integral ratio of ca. 13:1 for Ph vs SiH. The optoelectronic properties of the polymer **7** are comparable to those of the monomeric species **4** and **6** with $\lambda_{ex} = 378$ nm, $\lambda_{em} = 460$ nm, and $\phi_{PL} = 0.562$,[8] supporting the preservation of the photophysical features of the dithienophosphole monomers within the polymer **7**.

To further explore the reactivity of our system toward alkenes, we also performed hydrosilation experiments with *trans*-stilbene and cyclohexene, respectively, to access the corresponding model compounds. However, the reaction with *trans*-stilbene was found to be very slow. Even after prolonged reaction times (10 d) and increased temperatures only a minor portion (≤15%) of the dithienophosphole **4** was consumed. This could be attributed to the unfavorable trans geometry of the stilbene substrate employed. The reaction with cyclohexane present in the mixture, on the other hand, showed complete consumption of the starting material **4** after 3 d at room temperature, evident in the disappearance of the Si−H resonance in the ^{1}H NMR spectrum. However, to our surprise, the ^{1}H NMR spectrum of the product did not show the expected resonances of a cyclohexyl moiety suggesting a different reaction pathway being valid under these conditions. The generation of a polymeric material **8** (δ ^{31}P 14.6 ppm) instead of the targeted model compound was supported by the reduced solubility of the obtained product (insoluble in ether, pentane, heptane) and was confirmed by GPC analysis (molecular weight up to 10 000; $n \leq 20$). The presence of two sets of ^{29}Si satellites (J(H,Si) = 17.2, 25.4 Hz), detectable at the ^{1}H NMR resonance for the methyl groups attached to silicon, indicated that a dehydrogenative homocoupling occurred exclusively.

This finding was further supported by only one resonance at δ −4.7 ppm present in the ^{29}Si NMR. The fact that the alkene was indeed not involved in this reaction was confirmed by an experiment where a few drops of Karstedt

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(10) Multinuclear NMR data also indicate the presence of the 2,1-addition product in ca. 14% abundance.

catalyst solution were added to a dichloromethane solution of **4** without any substrate leading to a similar polymeric material after 4 d (molecular weight up to 10 000; $n \leq 20$). These results are intriguing insofar, since they represent the first case of a successful quantitative dehydrocoupling of a tertiary silane. Although there are some examples known in the literature, where tertiary silanes give a homocoupled product, they generally only occur as a side reaction to give a maximum of about 10% conversion. Furthermore, these reactions require very drastic conditions (e.g., $T \geq 100$ °C) to give notable amounts of dehydrocoupled products.[11] In the present case, a complete conversion is achieved at room temperature—with a catalyst that is known to be highly active for the hydrosilation of alkenes, even to access polymeric systems.[12] It is interesting to note that the observed dehydrocoupling process also seems to be a competitive reaction for the hydrosilation of alkynes, at least to some extend, as the ^{29}Si NMR of the polymer **7** also shows a corresponding resonance for a dehydrocoupled segment at δ −4.7 ppm of about 4% abundance. The emission properties of the dehydrocoupled polymer **8** are very similar to those of the monomer ($\lambda_{em} = 459$ nm), whereas the maximum wavelength of absorption experiences a red shift of about 10 nm now appearing at $\lambda_{ex} = 393$ nm, comparable to the value observed for compound **6**. The relation of the polymer **8** to the diphenylethylene-functionalized dithienophosphole **6** in terms of optoelectronic properties is also evident in a second, strong transition of the excitation spectrum at $\lambda_{ex} = 353$ nm, suggesting an interaction of the disilanylene linker with the dithienophosphole moiety ($\sigma_{SiSi} \rightarrow \pi^*_{dtp}$)[13] in the polymer **8** (see Figure 1).

In conclusion, we have synthesized the first Si−H functionalized dithieno[3,2-*b*:2′,3′-*d*]phospholes that can be fine-tuned conveniently by simple chemical modifications performed at the phosphorus center. Utilizing the Si−H functionality to access polymeric systems via a Pt-catalyzed hydrosilation protocol provides materials in the presence of suitable alkynes that possess the intriguing optoelectronic properties of the respective monomers. The absence of any substrate (or the presence of alkenes) affords a polymeric material via an unexpected, and for tertiary silanes unprecedented, Pt-catalyzed dehydrogenative homocoupling, with a quantitative conversion of the employed dithienophosphole. Further investigations will include a detailed study of this unusual dehydrocoupling process for future polymerization reactions to optimize the molecular weights of the materials. The fine-tuning of the optoelectronic properties of the polymers by regenerating the trivalent phosphorus center is also currently under detailed investigation.

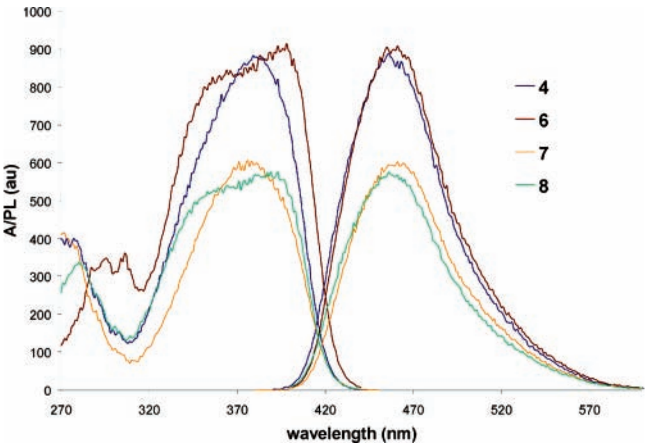

Figure 1. Fluorescence spectra (excitation, left; emission, right) of the dithienophospholes **4** and **6**−**8** ($c = 1 \times 10^{-4}$ M in CH_2Cl_2).

Acknowledgment. Financial support from the Fonds der Chemischen Industrie, the BMBF, the Deutsche Forschungsgemeinschaft (DFG), and Prof. Dr. J. Okuda is gratefully acknowledged. We thank K. Beckerle for his assistance with the polymer analysis.

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

OL0529288

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