

Cationic Dithieno[3,2-*b*:2',3'-*d*]phospholes: A New Building Block for Luminescent, Conjugated Polyelectrolytes

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ABSTRACT



Cationic dithieno[3,2-*b*:2',3'-*d*]phospholes are accessible very efficiently by methylation of the phosphorus center. Further functionalization with bromo substituents in 2,6-positions affords a polymerizable monomer that can be copolymerized with a difunctionalized fluorene in a Suzuki–Miyaura-type cross-coupling protocol. The monomers as well as the resulting conjugated polyelectrolyte based on the phospholium units show very intriguing photoluminescence properties, even in the solid state.

Conjugated polyelectrolytes (CPEs) are currently the focus of several research groups due to their intriguing features that span a broad range of electrical, mechanical, solubility, and self-assembly properties.¹ These features allow them to be considered for a variety of applications including sensing of biomolecules^{1b,d} or inorganic ions,^{1f} as well as organic electronics,^{1e} e.g., as components in multilayer organic devices.² Several methods toward conjugated polyelectrolytes

have been developed to date, most of them introducing the ionic centers as pendent side chains.¹ The number of CPEs containing ionic centers as part of the backbone, however, is fairly limited, likely due to the restricted synthetic accessibility of these materials. The incorporation of organophosphorus building blocks such as phospholes into π -conjugated materials, on the other hand, is an intriguing perspective for organic electronics and optoelectronics due to their unique electronic structure as well as the versatile reactivity of the phosphorus center.^{3,4} The latter allows for

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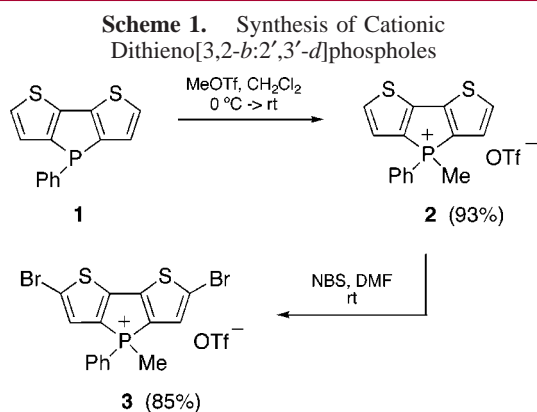
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the efficient fine tuning of the electronic properties of the materials by very simple chemical modifications. These can include oxidation or complexation reactions via Lewis acids or transition-metal complexes.^{3–5} In the context of our research on phosphoorganic materials, 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.⁶

Here, we report on the new modification of the phosphorus center in dithieno[3,2-*b*:2',3'-*d*]phospholes through methylation to generate the corresponding cationic phospholium compounds. Their functionalization toward polymerizable monomers as well as the synthesis of the first CPE with cationic phosphorus centers in the backbone are also discussed. Furthermore, the photophysical properties of the monomers and the polymer are presented in detail.

The methylated phospholium species **2** is accessible almost quantitatively (isolated yield of 93%) by treatment of the dithienophosphole **1** with methyl triflate in dichloromethane at 0 °C and stirring the solution for 2 h at that temperature (Scheme 1). The progression of the reaction can be monitored



by the fluorescence emission of the solution changing from blue to green. The ³¹P NMR spectrum of **2** shows a single resonance at $\delta = 12.2$ ppm that is significantly shifted downfield from that of the starting material **1** ($\delta = -21.5$ ppm).^{6a} The ¹H NMR spectrum of **2** exhibits an additional, characteristic signal for the methyl group at $\delta = 2.7$ ppm with a ²J(H,P) coupling constant of 15.3 Hz.^{5a} We were able to obtain single crystals of **2** that were suitable for an X-ray structure analysis from a concentrated chloroform/heptane (4:1) solution at room temperature.⁷

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The molecular structure of **2** in the solid state (Figure 1) shows features similar to related dithienophospholes with

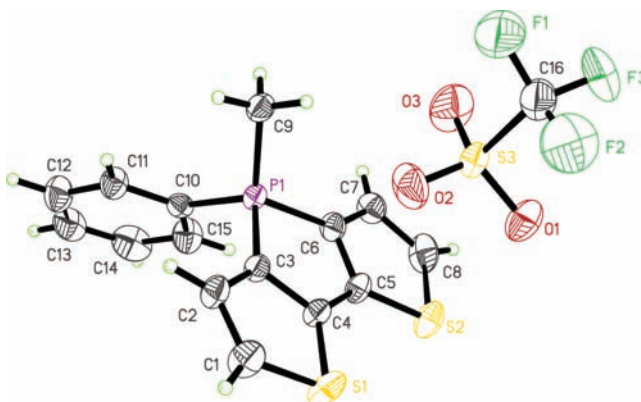


Figure 1. Molecular structure of **2** in the solid state (40% probability level).

elongated C=C and shortened C–C bonds of the planar framework, indicating a high degree of π -conjugation within the system.^{6a–c} Because of the cationic nature of the phosphonium center, the P–C bonds are significantly shortened (P–C_{Ar} = 1.778(4)–1.785(4) Å; cf. **1**, P–C_{Ar} = 1.819(1)–1.837(1) Å).^{6a} The P–C_{Me} bond of 1.769(4) Å is also slightly shorter than that of other structurally characterized phospholium salts (1.775(3)–1.787(5) Å).⁸ It is also noteworthy that the two ions are well separated in the solid state.

As already mentioned, the phospholium salt **2** shows a strong fluorescence intensity in solution (Table 1), similar

Table 1. Photoluminescence Data of the Dithienophospholes **2**, **3**, and **7** under Varying Conditions

compound	λ_{ex} [nm] ^a	λ_{em} [nm] ^b	ϕ_{PL}
1 (CH ₂ Cl ₂) ^{6a}	338	415	0.78 ^c
2 (CH ₂ Cl ₂)	276, 376	467	0.53 ^c
2 (H ₂ O, pH 7)	273, 370	466	0.57 ^c
2 (H ₂ O, pH 0)	273, 365	465	0.56 ^c
2 (H ₂ O, pH 14)	296	410	–11
3 (CH ₂ Cl ₂)	279, 411	495	0.71 ^c
5 (CH ₂ Cl ₂)	345, 485	509, 540	0.47 ^d
5 (solid state)	527	556	–

^a Maximum wavelength of absorption. ^b Maximum wavelength of emission. ^c Relative to quinine sulfate (0.1 M H₂SO₄ solution) \pm 10%. ^d Relative to rhodamine101 (10^{–4} M in EtOH) \pm 10%.¹⁰

to all known dithienophospholes,⁶ however, in the green region of the optical spectrum ($\lambda_{\text{ex}}(\pi-\pi^*) = 376$ nm; $\lambda_{\text{em}} = 467$ nm), with a significant photoluminescence (PL) quantum yield efficiency of $\phi_{\text{PL}} = 0.53$ (cf. **1**, $\lambda_{\text{ex}}(\pi-\pi^*) = 338$ nm; $\lambda_{\text{em}} = 415$ nm; $\phi_{\text{PL}} = 0.78$).^{6a} Because of the ionic nature of **2**, it is soluble in aqueous solutions allowing us to also determine potential pH effects on the photophysical

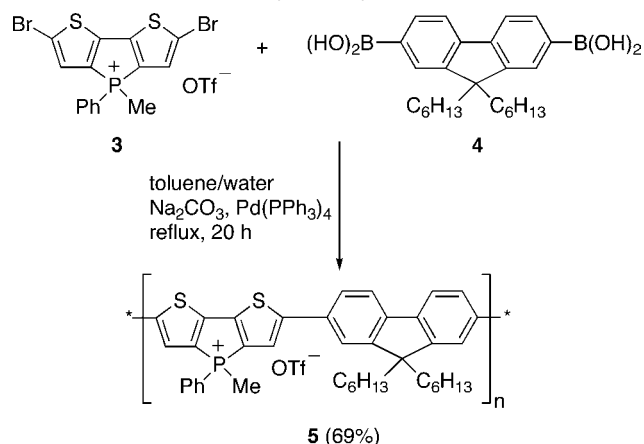
properties of the material. At neutral pH (7), the observed wavelengths for absorption and emission for **2** in water are almost identical with the values obtained from CH₂Cl₂ ($\lambda_{\text{ex}}(\pi-\pi^*) = 370 \text{ nm}$; $\lambda_{\text{em}} = 466 \text{ nm}$; $\phi_{\text{PL}} = 0.57$, Table 1).

The slight differences in the absorption values could be explained by solvation effects leading to a more separated ion pair for **2** in aqueous solution. Acidification of the solution with HCl (pH 0) effects only minor changes in its optoelectronic properties ($\lambda_{\text{ex}}(\pi-\pi^*) = 365 \text{ nm}$; $\lambda_{\text{em}} = 465 \text{ nm}$; $\phi_{\text{PL}} = 0.57$) that could be connected to anion exchange processes in solution. In a strongly basic environment (pH 14), however, the fluorescence intensity of the solution drops significantly.¹¹ Because the almost complete disappearance of the fluorescence is also accompanied by a significant blue shift ($\lambda_{\text{ex}} = 296 \text{ nm}$; $\lambda_{\text{em}} = 410 \text{ nm}$), decomposition of **2** is very likely to occur. The observed fluorescence can be attributed to a bithienyl group ($\lambda_{\text{ex}} = 302 \text{ nm}$; $\lambda_{\text{em}} = 362 \text{ nm}$; $\phi_{\text{PL}} = 0.017$),¹² generated by a nucleophilic attack of hydroxide at the phosphorus center, as reported for related phospholes, leading to the degeneration of the phosphole ring.⁴

To be able to incorporate the phospholium species **2** into polymers, further functionalization with suitable groups was necessary. According to an established procedure for dithieno[3,2-*b*:2',3'-*d*]thiophene dioxides,¹³ dibromination of **2** could be achieved by treatment with NBS in DMF in the dark at room temperature over 18 h affording the 2,6-dibrominated phospholium salt **3** in 85% isolated yield (Scheme 1). Its ³¹P NMR resonance of $\delta = 15.7 \text{ ppm}$ is shifted downfield compared to that of **2**, supporting the successful functionalization. Dibromination also leads to a significant red shift of the absorption and emission maxima of **3** in dichloromethane due to the acceptor character of the bromo functionalities, as expected, now showing a maximum wavelength of absorption at $\lambda_{\text{ex}}(\pi-\pi^*) = 411 \text{ nm}$ ($\Delta\lambda_{\text{ex}} = 35 \text{ nm}$) and a maximum wavelength of emission at $\lambda_{\text{em}} = 495 \text{ nm}$ ($\Delta\lambda_{\text{em}} = 28 \text{ nm}$). Furthermore, a significant increase of the PL quantum yield efficiency to $\phi_{\text{PL}} = 0.71$ can also be observed for **3**.

The 2,6-dibrominated phospholium salt **3** was then successfully incorporated in the CPE **5** by a Suzuki–Miyaura-type protocol via copolymerization with a suitable fluorene-bis(boronic acid) (**4**) (Scheme 2).^{14,15} The reaction conditions further involved a biphasic medium (toluene/water) with

Scheme 2. Synthesis of the Conjugated Phospholium Polyelectrolyte **5**



Na_2CO_3 and $\text{Pd}(\text{PPh}_3)_4$ added as (co)catalysts. The reaction mixture was refluxed for 20 h, upon which the fluorescence of the solution noticeably changed from green to yellow and the product started to precipitate out of the mixture. The polyelectrolyte **5** was purified by extraction of its CH₂Cl₂ solution with NaHCO₃-containing water (yield of 69%). It should be mentioned in this context that the yellow polymer **5** is not soluble in water, likely due to the organic nature of the hexyl-substituted fluorene comonomer. The material is, however, soluble in polar solvents such as chloroform, dichloromethane, and THF. The ³¹P NMR spectrum of **5** shows a single, downfield shifted, but broad, resonance at $\delta = 23.2 \text{ ppm}$ supporting its polymeric nature. The same is true for its ¹H and ¹³C NMR spectra exhibiting all the necessary, broadened signals. Analysis by gel permeation chromatography (GPC) indicated a molecular weight of $M_w = 9800 \text{ g/mol}$ with a chain-length distribution (PDI) of 1.70 that is sufficient to allow for the formation of thin films of **5** via dropcasting from a concentrated dichloromethane solution.

The photophysical data of the polyelectrolyte **5** in dichloromethane show strongly red-shifted values for absorption and emission maxima compared to the monomers **2** and **3** (Table 1). This supports the extension of the π -conjugated system along the polymer backbone now showing greenish–yellow fluorescence, as already mentioned. The photoluminescence spectrum of **5** (Figure 2) in CH₂Cl₂ exhibits a feature that is commonly observed for fluorene-based polymers:¹⁶ a vibronic sideband ($\lambda_{\text{em}} = 540 \text{ nm}$), slightly red-shifted from the emission maximum at $\lambda_{\text{em}} = 509 \text{ nm}$.

Remarkably, the emission and absorption ($\lambda_{\text{ex}}(\pi-\pi^*) = 485 \text{ nm}$) maxima of CPE **5** are also strongly red-shifted from those of the corresponding 9,9-dihexyl-fluorene homopolymer ($\lambda_{\text{ex}} = 388 \text{ nm}$; $\lambda_{\text{em}} = 445 \text{ nm}$)^{16a} and related fluorene copolymers containing 2,2'-bithienyl ($\lambda_{\text{ex}} = 398 \text{ nm}$; $\lambda_{\text{em}} = 483, 520 \text{ nm}$)^{16b} or dithieno[3,2-*b*:2',3'-*d*]silole ($\lambda_{\text{ex}} = 386 \text{ nm}$; $\lambda_{\text{em}} = 486, 515 \text{ nm}$)^{16c} moieties. This indicates a strong

(7) Crystallographic data for the structure of **2** have been deposited in the Cambridge Crystallographic Data Centre (deposition number: CCDC 622319). Copies of these data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.; fax (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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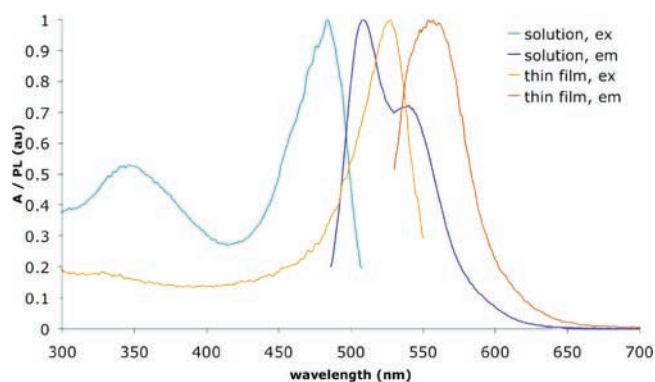


Figure 2. Fluorescence spectra of **5** in solution and in the solid state.

impact by the dithienophospholium moiety on the electronic structure of the polymer **5**, most likely due to a significantly lowered LUMO level, as derived from related dithienophosphole monomers.^{6b} It should also be mentioned that the Stokes shift for **5** is exceptionally small amounting to only 15 nm, which indicates a fairly rigid molecular structure; in the related fluorene-based polymers, it ranges from 50 to 100 nm.¹⁶

The thin film of **5** shows even further red-shifted absorption and emission values at $\lambda_{\text{ex}}(\pi-\pi^*) = 527$ nm and $\lambda_{\text{em}} = 556$ nm that are indicative of intermolecular (π -stacking) interactions in the solid state.^{15,16} The PL emission spectrum is featureless. It is, however, surprising that the fluorescence emission of **5** is still fairly intense in the solid state,

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particularly in the presence of these intermolecular interactions. As observed for many “classic” polyelectrolytes, solid-state interactions often lead to a complete quenching of the fluorescence, a phenomenon that is also referred to as “superquenching”.^{1b} The strikingly strong fluorescence of **5**, on the other hand, could be attributed to the steric bulk around the cationic phosphorus atoms that reduces the accessibility of these centers for potential quenchers in the solid state.

In conclusion, we have efficiently synthesized newly functionalized cationic dithieno[3,2-*b*:2',3'-*d*]phospholes that can successfully be built into the backbone of a conjugated polyelectrolyte. The photoluminescence properties of the model compounds/monomers as well as the polymer are remarkable in terms of emission intensities with high quantum yield efficiencies—as typically observed for dithienophospholes—suggesting a potential application in polymer-based, multilayer optoelectronic devices. Current investigations include the further modification of the comonomers to eventually access water-soluble polyelectrolytes as well as their potential for optoelectronic PLED applications.

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

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