

Conjugated Polymers Featuring Heavier Main Group Element Multiple Bonds: A Diphosphene-PPV

Rhett C. Smith and John D. Protasiewicz*

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio, 44106-7078

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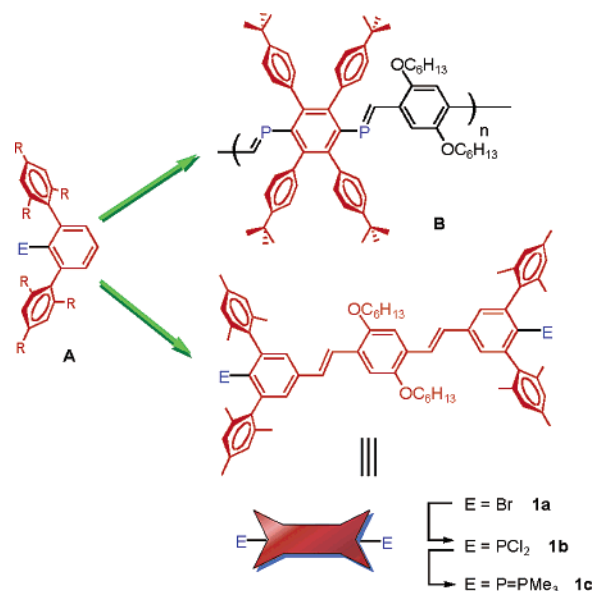
Organic π -conjugated polymers are of much current academic and significant technological interest due to their optical and electronic properties. Of these materials, poly(phenylenevinylene)s (PPVs) have attracted the most attention and found greatest utility in devices.¹ This particular architectural framework thus serves as an attractive platform upon which one may consider systematic isolobal replacements of the constituent carbene (CR_2) fragments for other main group fragments having available a p orbital capable of participating in p-p π conjugation with carbon-carbon double bonded systems. Phosphinidenes (PR) are fragments capable of replacing carbene units within molecules and providing a wide array of molecules containing P=C and P=P functional groups.² While phosphorus has long been an important component of polymers,³ materials engaging the phosphorus atom in extended linear p-p π conjugation have only recently been realized.^{4,5} Hybrid inorganic-organic conjugated systems promise novel electronic properties and the processability and tunability typical of many organic polymers.

A key challenge to the incorporation of heavier elements into extended conjugated systems is the need for steric protection to promote stability for more reactive multiple bonds.⁶ A general bifunctional sterically demanding platform that would stabilize conjugated systems for a variety of EE multiple bonds is lacking. In this report we present a new type of bifunctional sterically demanding ligand and demonstrate its general applicability for synthesis of polymers having phosphorus centers engaged in p-p π conjugation along the main chain.

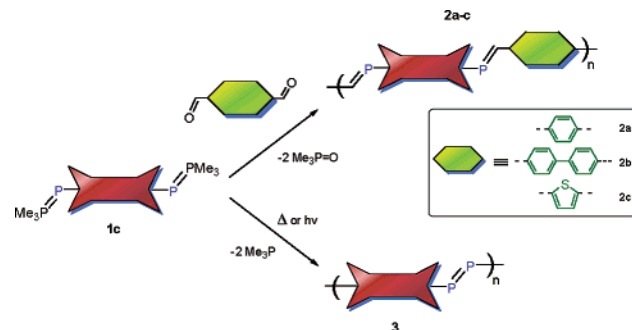
As a class of sterically demanding ligands, *m*-terphenyl ligands (Chart 1, **A**) have proven highly successful for stabilizing a plethora of compounds featuring multiply bonded main group elements.⁷ Our initial strategy using 2,3,5,6-tetrarylbenzenes (Chart 1, red portion of **B**) as bifunctional mimics of *m*-terphenyls to confer simultaneous steric protection to two low-coordinate phosphorus centers in conjugated polymers met with two major difficulties. First, tetrarylbenzenes having steric protection comparable to the bulky aryl Dmp (Dmp = 2,6-Mes₂C₆H₃) were not readily accessible,^{8b} and thus the possibilities for isolating polymers having the broadest range of element-element π -bonds were limited to materials such as poly(phosphaalkenes) (**B**).^{8a} Second, such polymers were relatively insoluble unless solubilizing groups such as 2,5-dihexyloxybenzene were introduced. These findings led to development of the second-generation bifunctional bulky ligand **1** (Chart 1). It was anticipated that this ligand would finally allow access to polymers containing a variety of E=E units, as the steric bulk afforded at each end of **1** is identical to that of Dmp, a ligand that has been previously demonstrated to support E=E bonds all the way from E = P through As, Sb, to Bi.⁹ In addition, the polymers should be soluble due to the 2,5-dihexyloxybenzene core that has been integrated into the bulky ligand.

Compound **1a** was conveniently prepared in multigram quantities from readily available starting materials in only a few steps.¹⁰

Chart 1



Scheme 1



Preparation of the organophosphorus derivatives **1b** and **1c** followed reported procedures.^{8a,c,10} The greater steric protection conferred by **1** over **B** allows successful isolation of the stable (in the absence of air and water) diphospha-Wittig reagent **1c** and a diphosphene-containing polymer. Thus, deployment of **1c** for synthesis of phosphoalkene polymers **2a-c** (Scheme 1) was easily achieved upon addition of 1.005 equiv of various conjugated dialdehydes (excess of dialdehyde provides stable end groups). This variation of the phospho-Wittig reaction proceeds in essentially quantitative yields at room temperature, forming phosphoalkenes exclusively in the *E* conformation.¹² Polymers **2a-c** were thus produced in 76–85% isolated yields as orange (**2a, b**) or violet (**2c**) freely soluble materials that are fairly thermally stable in the absence of air or water.¹⁰ Solid samples of **2a** and **2b**, for example, are unaffected by heating at 140 °C for 6 h under N₂. Solutions of **2a-c** in C₆D₆ remain unchanged upon heating at 120° for 4 h.

Table 1. Properties of Select Materials

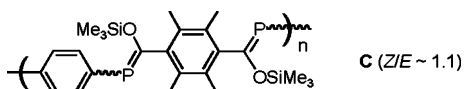
	χ_n	M_n (g mol ⁻¹)	UV/vis (nm) $\lambda_{\pi-\pi^*}$ (log ϵ)	UV/vis (nm) $\lambda_{n-\pi^*}$ (log ϵ)	PL max (nm)	PL intens ^b (%)	PDI
1a	(na)	1175	399 (4.63)	(na)	460	620	(na)
2a	4.5	5000	435 (4.76)	(na)	481	80	2.3
2b	6	7200	427 (4.87)	(na)	486	130	2.2
2c	6.5	7300	416 (4.65)	473 (4.54)	481	110	1.9
3	5.8	5900	435 (4.63)	481 (4.42)	(na)	~0	2.1
B	6	6500	445 (4.03)	(na)	545	8	(na)

^a UV/vis and PL spectra in CHCl₃. ^b Relative to (*E*)-stilbene.

Previous studies of DmpP=PMe₃ showed that the diphosphene DmpP=PDmp is produced in high yields by photolytic extrusion of PME₃.¹³ Photolysis (C₆D₆, rt) of bifunctional analogue **1c** does indeed result in extrusion of two equivalents of volatile PME₃ and formation of desired red polymer **3** in near quantitative yield (Scheme 1).¹⁰ Thermolysis of **1c** (neat, 250 °C) also effects the same transformation and is the preferred method as it is very rapid (ca. 2 min), is readily applied to larger quantities, and leads to fewer side products. While reduction of ArPCL₂ using magnesium or other metals is a classic avenue to diphosphenes (ArP=PAR),¹⁴ low yields rendered this route inappropriate for achieving polymers. To the best of our knowledge, **3** is the first example of a polymer featuring multiple bonds between two heavier main group elements along a polymer backbone. More importantly, the successful stabilization of diphosphene units by **1** suggests its viability in stabilizing other E–E multiple bonds which may be incorporated into conjugated polymer backbones.¹⁵

The degree of polymerization and molecular weights of polymers **2** and **3** were determined by end group analysis (¹H NMR integration) in conjunction with GPC (Table 1). Despite the modest degree of polymerization, fairly high molecular weights are attained due to the very large monomeric units. More importantly, each repeat unit contains four phenylenevinylene-type repeat units, so that the total number of units in a chain ranges from 18 to 26. Many of the optical/electronic properties in organic PPV derivatives level off at a length of around 10 repeat units,¹⁶ and a similar trend may be expected of polymers **2** and **3**.

Key spectroscopic data for **1–3** are also summarized in Table 1. The absorption spectra of **1–3** feature characteristic $\pi-\pi^*$ bands. Polymer **3** also shows an $n-\pi^*$ band typical of diphosphenes, and thiophene lone pairs in **2c** participate in $n-\pi^*$ transitions, which give rise to a shoulder at 473 nm in its absorption spectrum. One of the key features of interest in π -conjugated materials is the $\pi-\pi^*$ gap. Comparison of this value for **2** and **3** can be made to organic systems such as unsubstituted (*E*)-PPV, ($\lambda_{\pi-\pi^*}$ = 426 nm),^{17a} and to structurally more similar poly(phenylenevinylene-*alt*-2,5-dihexyloxyphenylenevinylene) ($\lambda_{\pi-\pi^*}$ = 459 nm).^{17b} The $\lambda_{\pi-\pi^*}$ values for **2** and **3** fall between the values. Comparison can also be drawn to **C** ($\lambda_{\pi-\pi^*}$ = 338 nm)⁵ and **B** ($\lambda_{\pi-\pi^*}$ = 445 nm) (Chart 1).^{8a} Phosphaalkene units in **C** are a mixture of *Z* and *E* conformations, complicating direct comparison. The red shift of **B** versus **2** may be due to structural differences or due to replacement of all of the vinylene fragments in **B** by phosphaalkenes while only half are replaced in **2**. This latter hypothesis agrees with studies on oligomeric models.¹⁸



The photoluminescence (PL) intensity of these materials drops off as phosphorus atoms are substituted for olefinic carbons. The PL intensities of **2a–c** are approximately equal to that of (*E*)-stilbene, while that of **B** is only 8% that of (*E*)-stilbene, and diphosphene-containing **3** does not exhibit appreciable PL. This may be due to fluorescence quenching by interaction with phosphorus lone pairs.^{8a}

In conclusion, a conveniently synthesized bifunctional ligand capable of simultaneously supporting two heavier main group multiple bonds has been reported. This ligand was employed in the synthesis of new *phospha*-PPVs including the first conjugated polymer incorporating P=P linkages along the polymer backbone. Ligand **1** should allow access to a variety of linear conjugated materials having multiply bonded elements previously excluded for polymer synthesis.

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Note Added after ASAP: In the version published on the Web 2/4/2004, two asterisks were missing from the column headings in Table 1. The version posted 2/6/2004 and the print version are correct.

Supporting Information Available: Details for synthesis and characterization of **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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