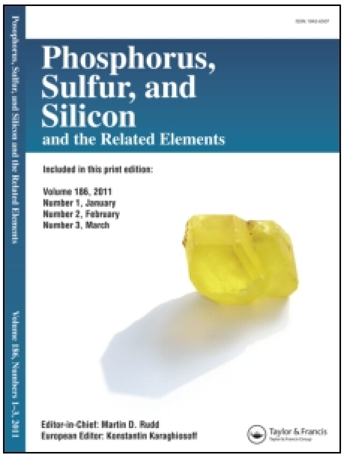

**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# New Conjugated π-Systems Incorporating Phosphole Rings

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**To cite this Article** Hay, Caroline , Sauthier, Mathieu , Hissler, Muriel , Nyulaszi, Laszlo and Reau, Regis(2002) 'New Conjugated π-Systems Incorporating Phosphole Rings', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 6, 1423 — 1425

**To link to this Article: DOI:** 10.1080/10426500212290

**URL:** http://dx.doi.org/10.1080/10426500212290

*Phosphorus, Sulfur and Silicon*, 2002, Vol. 177:1423–1425

1042-6507/02 \$12.00 + .00
DOI: 10.1080/10426500290093072

# NEW CONJUGATED π-SYSTEMS INCORPORATING PHOSPHOLE RINGS

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(Received July 29, 2001; accepted December 25, 2001)

*The synthesis and photophysical properties of mixed thiophene-phosphole oligomers and polymers are described.*

*Keywords:* π-conjugated systems; electropolymerization; phosphole

## INTRODUCTION

π-conjugated oligomers and polymers based on aromatic heterocyclopentadienes have attracted increasing interest in recent years owing to their potential application for electronic devices.[1] The possibility of incorporating building blocks with different aromatic character and electronic nature allows for molecular engineering. Although the chemistry of phospholes is well developed,[2] these P-heterocyclopentadienes have received little attention as building blocks for π-conjugated systems.[3] Herewith, we describe the synthesis and physical properties of model molecules possessing pyridyl-phosphole or thienyl-phosphole units and of the corresponding oligomers and polymers.

## RESULTS AND DISCUSSION

Phospholes **1** (Scheme 1) can be prepared via intramolecular oxidative coupling of functionalized diynes with “zirconocene” followed by

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This work was financially supported by the Conseil Régional Bretagne, the Ministère de l’Education Nationale, de la Recherche et de la Technologie and the Centre National de la Recherche Scientifique.

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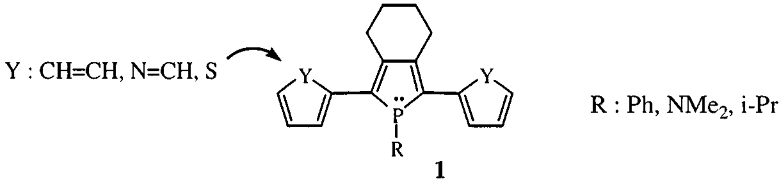
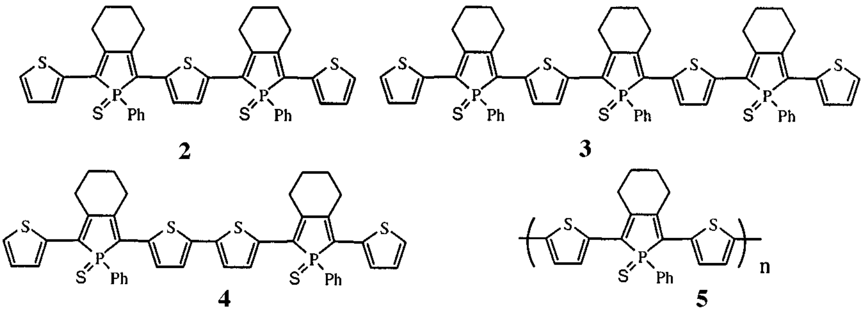


**1**

SCHEME 1

addition of dihalogenophosphines (Fagan-Nugent's route).[3,4] This versatile method allows us to vary the nature of the substitution pattern of the phosphole ring.

X-ray diffraction studies performed on 2,5-di(2-thienyl)- and 2,5-di(2-pyridyl)-phospholes clearly show that (1) the P-lone pair of the $\sigma^3,\lambda^3$-phospholes is not conjugated with the endocyclic dienic framework and (2) an extended delocalization pathway involving the dienic moiety of the phosphole rings and the two pyridyl or thienyl units takes place. According to UV-vis data and theoretical calculations, the delocalization of the $\pi$-system in model molecules **1** increases when replacing a phenyl with a pyridyl group and is maximum with the thienyl substituents. Furthermore, in the thienyl series oxidation of the P-atom of the phosphole ring with elemental sulfur led to a decrease of the HOMO-LUMO gap. These results prompted us to investigate the preparation of well-defined oligomers **2–4** and polymer **5** (Scheme 2).



**2** **3** **4** **5**

SCHEME 2

The oligomers **2–4** have been prepared via the Fagen-Nugent's route as a mixture of diastereoisomers. Polymer **5** was obtained by electro-oxidation of the corresponding 2,5-(dithienyl)-thioxophosphole monomer conducted at an optimum polymerization potential. Oligomers **2–4** are soluble in common polar solvent, and their absorption maximum in the UV-vis spectrum range is from 508 to

584 nm. These optical data show that oligomers **2–4** possess extended π-conjugated systems. No saturation of the delocalization is observed upon increasing the length of the oligomers up to seven units. Polymer **5** is insoluble and thin film absorption spectra were recorded in order to probe the electronic nature of this compound. The dedoped polymer exhibits one broad absorption band in the visible at about 529 nm with a $\lambda_{\text{onset}}$ at 750 nm. The $\lambda_{\text{onset}}$ ("optical band gap") is red-shifted in comparison with those observed for the corresponding monomers ($\Delta\lambda_{\text{onset}} = 254$ nm) and oligomers **3** ($\Delta\lambda_{\text{onset}} = 150$ nm), suggesting that **5** consists of rather long oligomers featuring 2,5-dithienylphosphole as the repeating unit.

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