



Poly(*p*-phenylenediethynylene phosphane): A Phosphorus-Containing Macromolecule that Displays Blue Fluorescence Upon Oxidation**

Benjamin W. Rawe and Derek P. Gates*

Dedicated to Dr. Howard C. Clark

Abstract: Despite the challenges associated with their synthesis, hybrid inorganic–organic polymers featuring heavier main-group elements spaced by π -conjugated organic functionalities have garnered considerable recent attention due to their chemical functionality and novel photophysical properties. We have succeeded in the preparation of an unprecedented organophosphorus polymer possessing functional phosphane-di-yne moieties in the main chain. Namely, poly(*p*-phenylenediethynylene phosphane) (PPYP) is prepared using a nickel(II)-catalyzed P–C bond-forming reaction. The hexyl-substituted PPYPs are solution processible and have been thoroughly characterized (molecular weight, M_w , ca. 10^4 Da vs. polystyrene; degree of polymerization, DP, ca. 10). Remarkably, although PPYP shows very weak emission upon irradiation with UV light, its oxide shows blue “turn-on” fluorescence. The present discovery bridges the areas of main-group and polymer science and opens the door to a new class of σ - π -conjugated macromolecules with unique chemical functionality.

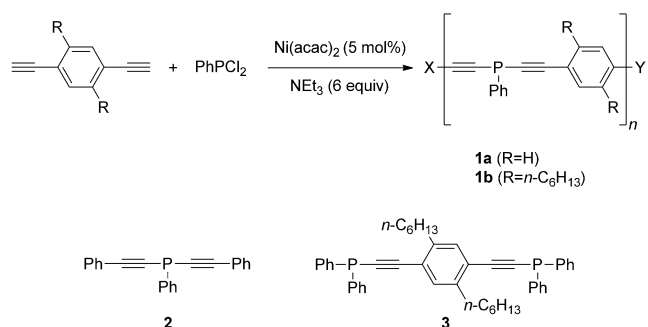
The development of phosphorus-containing macromolecules is a highly active research area lying at the interface of main-group chemistry and polymer science. Inspired by the prospect of finding materials with novel chemical functionality and properties, researchers are attracted by the wide range of coordination numbers, oxidation states and bonding environments that are uniquely provided by phosphorus.^[1] Perhaps resulting from the synthetic difficulty to incorporate phosphorus atoms into long chains, the major classes of organophosphorus polymers remain limited to polyphosphazenes,^[1f] poly(phosphole)s,^[2] poly(*p*-phenylene phosphalkene/diphosphene)s,^[3] poly(arylene/vinylene phosphane)s,^[4] poly(ferrocenylphosphane)s,^[5] polyphosphinoboranes,^[6] and poly(methylenephosphane)s.^[7] A major thrust in this area has involved incorporating phosphorus moieties within extended π -conjugated organic frameworks. The ready oxidation or

coordination of the phosphorus moiety has the potential to finely tune or modulate the electronic properties.

Poly(*p*-phenyleneethynylene)s represent a widely studied organic π -conjugated polymer possessing useful photophysical properties and potential applications as sensors.^[8] There has been growing interest in combining alkyne functionalities with phosphane or phosphalkene moieties as building blocks in molecular chemistry.^[9] Although researchers have proposed more extended structures, polymers possessing P-alkyne functionalities in the main chain have not been realized until now.

Herein, we provide an efficient synthetic route to a fascinating class of “turn-on” luminescent and chemically functional phosphorus-containing macromolecule. Namely, we report the synthesis and characterization of poly(*p*-phenylenediethynylene phosphane) (PPYP, **1**) the first di-yne-substituted phosphane macromolecule (Scheme 1).

A modified nickel(II)-catalyzed coupling procedure^[10] was adopted for the synthesis of the title poly(*p*-phenylenediethynylene phosphane)s (PPYPs) (**1a** and **1b**) and model compounds **2** and **3**. To a solution of 1,4-diethynylbenzene and PhPCL_2 (1:1) in toluene was added $\text{Ni}(\text{acac})_2$ (5 mol%; acac = acetylacetonato) in the presence of excess triethylamine (6 equiv). The reaction mixture was heated to 85 °C for several hours whereupon the initially colorless solution turns dark red-brown and a precipitate is formed. Analysis of the soluble fraction by ^{31}P NMR spectroscopy revealed signals assigned to monomer PhPCL_2 ($\delta = 161.2$) and to oligomer/polymer **1a** ($\delta = -60.6$; cf. **2**: $\delta = -60.4$). Unfortunately, the majority of the macromolecular product



Scheme 1. Synthetic procedure to poly(*p*-phenylenediethynylene phosphane)s (PPYPs) **1a** and **1b**. Analogous procedures are used to prepare model compounds **2** and **3**. For each model and polymer, the corresponding phosphane oxide has also been prepared and fully characterized (e.g. **1b**-O, **2**-O and **3**-O).

[*] B. W. Rawe, Prof. Dr. D. P. Gates
Department of Chemistry, University of British Columbia
2036 Main Mall, Vancouver, BC, V6T 1Z1 (Canada)
E-mail: dgates@chem.ubc.ca

[**] The authors are grateful to the Natural Sciences and Engineering Research Council (NSERC) of Canada for Discovery and Research Tools grants to D.G. in support of this work. We thank Dr. S. Kamal (UBC-LASIR) for assistance with excited-state lifetime measurements, and Mr. S. C. Serin and Dr. B. O. Patrick for assistance with crystal structure determinations.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201504464>.

was insoluble in common organic solvents (such as toluene, CH_2Cl_2 , THF = tetrahydrofuran, diethyl ether, DMSO = dimethyl sulfoxide, hexanes). MALDI-TOF MS (DHB matrix) of the solid provided strong evidence for its formulation as PPYP **1a**. Importantly, a series of ions were observed spaced by the mass of the monomer unit (233 Da) in **1a** that could be assigned to fragments of the protonated molecular ion. Due to its poor solubility, we are unable to obtain additional information about this new material at the present time.

A common strategy to solubilize π -conjugated polymers involves attaching long chain alkyl-substituents in the 2- and/or 5-positions of the arylene spacer. Thus, the di-*n*-hexyl-substituted polymer **1b** was prepared from 1,4-diethynyl-2,5-di-*n*-hexylbenzene^[11] and PhPCl_2 (1:1) under otherwise identical catalytic conditions to those described above. Two trials were conducted with the only difference being the monomer concentrations in the toluene reaction mixture (trial 1: 0.11 M; trial 2: 0.24 M). For trial 1, the reaction progress was monitored by ^{31}P NMR spectroscopy (Figure 1a). Within the first hour, several new major signals ($\delta = -61$) and two new minor signals ($\delta = 51.2$ and -0.5) were observed along with residual monomer PhPCl_2 ($\delta = 161.2$). The overlapping signals at -61 ppm, assigned to PPYP (**1b**), continued to grow and broaden over the next several hours as PhPCl_2 was slowly consumed. In contrast to that observed for a typical step polymerization, where the monomer is entirely consumed at early stages of the polymerization, PhPCl_2 remains until late in the reaction. Moreover, the intensity of the signal attributed to $-\text{C}\equiv\text{C}-\text{P}(\text{Ph})\text{Cl}$ end groups ($\delta = 51.2$)^[12] appears to reach a steady state and is only depleted at very late stages of the polymerization. These observations are consistent with a polymerization where one end group ($-\text{P}(\text{Ph})\text{Cl}$) has a significantly higher reactivity than the other ($-\text{C}\equiv\text{CH}$).

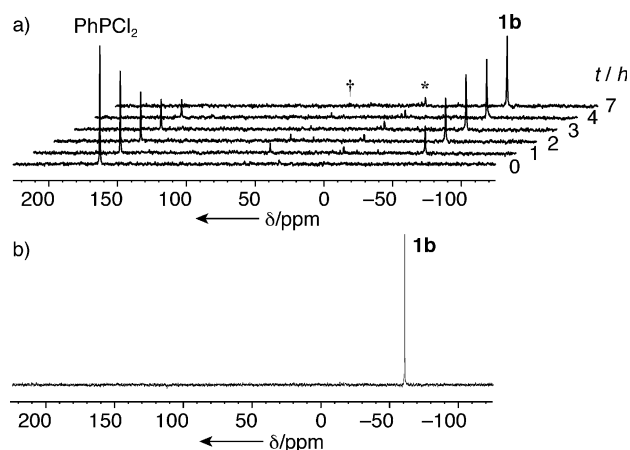


Figure 1. a) Selected ^{31}P NMR spectra (121.5 MHz, toluene, 358 K) showing: the progress of the polymerization of PhPCl_2 and 1,4-diethynyl-2,5-*n*-diethylbenzene using $\text{Ni}(\text{acac})_2$ (5 mol %) as catalyst and NEt_3 (6 equiv) as base (trial 1). The measurement times are given in hours. $\dagger$ indicates signals assigned to $-\text{P}(\text{Ph})\text{Cl}$ moieties. We speculate that the signals marked with $*$ result from hydrolysis of PhPCl_2 by traces of water found in the nickel(II) catalyst. b) ^{31}P NMR spectrum (121.5 MHz, CDCl_3 , 358 K) of isolated polymer **1b** after precipitation.

Thus, polymer (**1b**) is expected to consist primarily of alkyne end-groups (i.e. $\text{X} = \text{H}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_2\text{R}_2-$; $\text{Y} = -\text{C}\equiv\text{C}-\text{H}$) and all characterization data obtained for the polymer suggests this is the case (vide infra).

Soluble PPYP (**1b**) may be isolated as a dark red gum after precipitation ($\times 3$) of a THF solution of the crude polymer with degassed methanol. The isolated material slowly oxidizes in air or can be oxidized with hydrogen peroxide to afford an air-stable film-forming phosphane oxide **1b**-O (this has also been fully characterized—for details, see the Supporting Information). Unoxidized **1b** was characterized by using ^{31}P , ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, MALDI-TOF MS, GPC, UV/Vis spectroscopy (absorption and emission), and elemental analysis. The ^{31}P NMR spectrum of precipitated **1b** (CDCl_3) reveals a broad resonance at -61 ppm with no detectable signals attributed to $\text{P}-\text{Cl}$ end groups [Figure 1(b)]. Importantly, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1b** (CDCl_3) shows broad resonances assigned to alkyne carbon atoms of a $\text{P}-\text{C}_A\equiv\text{C}_B-$ functionality ($\delta = 87.6$ and 104.9). For comparison, model **2** shows similar spectral features for the $\text{P}-\text{C}_A\equiv\text{C}_B-$ moiety [$\delta = 82.8$ ($^1J_{\text{PC}} = 3$ Hz), 106.3 ($^2J_{\text{PC}} = 7$ Hz)]. In addition to showing the expected signals with the proper integration for the aliphatic and aromatic protons within **1b**, the ^1H NMR spectrum shows a resonance attributed to $\text{C}\equiv\text{C}-\text{H}$ end groups ($\delta = 3.3$). Integration of this signal against those assigned to the *n*-hexyl substituents allows for the estimation of the degree of polymerization (trial 1: $\text{DP}_n = 7$; trial 2: $\text{DP}_n = 10$; DP = degree of polymerization). ^{13}C APT, ^{13}C DEPT135 and $^1\text{H}-^{13}\text{C}$ HSQC NMR experiments permitted the assignment of the $-\text{C}_A\equiv\text{C}_B-\text{H}$ end groups of polymer **1b** (C_A : $\delta = 82.2$, C_B : $\delta = 81.8$; cf. 1,4-diethynyl-2,5-di-*n*-hexylbenzene: C_A : $\delta = 82.3$, C_B : $\delta = 81.5$).

PPYP (**1b**) and the MeOH soluble fraction containing oligomers were further characterized by using gel permeation chromatography (GPC, see Figure 2). As expected for a step

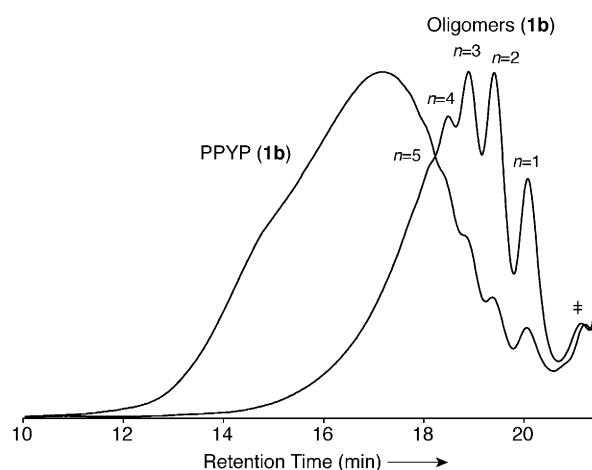


Figure 2. Gel permeation chromatography (GPC) traces of PPYP (**1b**) [trial 1: $M_w = 10,000$ Da; $\text{PDI} = 2.0$, vs. polystyrene standards] and the methanol-soluble fraction containing oligomers of **1b** ($n = 1-5$ are resolved; $\text{X} = \text{H}-\text{C}\equiv\text{C}-$; $\text{Y} = -\text{C}_6\text{H}_2\text{R}_2-\text{C}\equiv\text{C}-\text{H}$). The assignments are tentative. $[\dagger]$ assigned to monomer 1,4-diethynyl-2,5-di-*n*-hexylbenzene by comparison to the GPC trace of an authentic sample.

growth polymerization, PPYP **1b** was of modest molecular weight (trial 1: $M_w = 10000$ Da; trial 2: $M_w = 12000$ Da vs. polystyrene standards) with an expectedly moderate polydispersity index (trial 1: PDI = 2.0; trial 2: PDI = 1.8).^[13] Strikingly, the GPC chromatogram shows several partially resolved peaks at the low M_w end (i.e. long retention time). These peaks were significantly more prominent in the GPC trace of the methanol-soluble material separated during the precipitation of **1b** (Figure 2). Speculating that these signals were attributable to oligomers with formulation **1b** bearing alkyne end-groups [MALDI-TOF analysis shows ions for **1b** ($n = 1$ and 2 ; $X = H-C \equiv C-C_6H_2R_2^-$; $Y = -C \equiv C-H$)], the peak maximum for each GPC signal was used to estimate the molecular weight (vs. polystyrene) of each oligomer (necessarily, each oligomer would be monodisperse). On that basis, each peak in the chromatogram could be tentatively assigned to a specific oligomer **1b** ($n = 1-5$). Although the GPC molecular weights (vs. polystyrene) were significantly overestimated [for example, $n = 5$: 3290 (GPC); 2297 (FW)], a plot of formula weight vs. GPC molecular weight was linear with a near-zero intercept (see the Supporting Information). Importantly, such an observation not only suggests that the assignments are correct but is consistent with the expected overestimation of MW by GPC (vs. polystyrene) for a rigid linear polymer such as PPYP.^[14]

To gain insight into any possible conjugative effects within PPYPs, the X-ray crystal structures for model compounds **2-O** and **3-O** were determined. Molecular structures are shown in Figure 3.^[15] Particularly interesting is that the $C \equiv C$ bond lengths [**2-O**: 1.203(6) Å; **3-O**: 1.196(4) Å] are at the long end of the normal range for alkynes (ca. 1.18 Å).^[16] The $P-C_{sp}$ bonds (**2-O**: 1.750(4) Å; **3-O**: 1.746(3) Å) are shorter than the $P-C_{Ar}$ bonds [**2-O**: 1.793(3) Å; **3-O**: 1.800(4) Å] but both are significantly shorter than a typical P-C single bond (1.84 Å).^[16] Similar trends have been observed for related alkynylphosphanes [for example, $Ph_2P(O)(C \equiv CPh)$,^[17] $Mes_2P(C \equiv CPh)$,^[9f] and $P(CCPh)_3$.^[18] In addition, the aryl rings bearing alkyne moieties are fairly close to coplanar (angle between planes: 9.1°). Similarly, in **3-O** the angle between the central arylene ring and one of the P-Ph rings is 23.6°. The slight shortening of P-C and slight lengthening of $C \equiv C$ bonds combined with the tendency for towards coplanarity of the aryl groups in **2-O** and **3-O** may be reflective of conjugative effects through the phosphorus moieties. Although crystal packing effects could also contribute to the relative orientations of the aryl rings, intermolecular pi-stacking does not appear to be significant since there are no close contacts between the aryl or arylene moieties of adjacent molecules. The closest intermolecular contacts are between the oxygen and the P-phenyl hydrogens in **2-O** ($O1 \cdots H3 = 2.39$ Å) and between the oxygen and the C16-CH₂ hydrogen of the hexyl substituent in **3-O** ($O1 \cdots H = 2.49$ Å).

Further insight into the electronic properties of PPYPs may be gained by examining their photophysical properties. The UV/Vis absorption spectra of polymers **1b** and **1b-O** were recorded along with models **2**, **2-O** and **3-O**. Each species shows four characteristic bands in the UV region as does 1,4-diethynyl-2,5-di-*n*-hexylbenzene. The absorption spectra for the polymers are shown in Figure 4 (top). Importantly, the

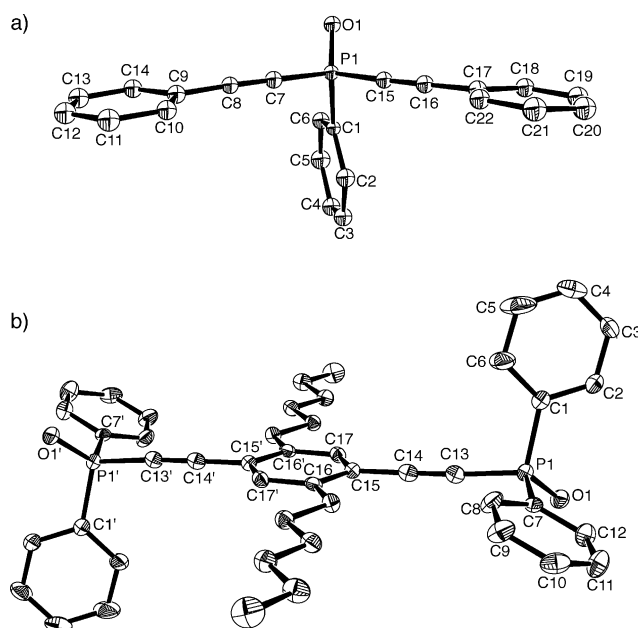


Figure 3. Molecular structures of **2-O** (a) and **3-O** (b) (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): **2-O** (a): P1-O1 1.481(2), P1-C1 1.793(3), P1-C7 1.751(3), P1-C15 1.750(3), C7-C8 1.201(4), C8-C9 1.443(4), C15-C16 1.204(4), C16-C17 1.439(4); C1-P1-C7 105.57(13), C1-P1-C15 105.30(13), C1-P1-O1 113.22(13), C7-P1-O1 115.08(12), C15-P1-O1 112.64(12), P1-C7-C8 173.6(3), C7-C8-C9 178.0(3), P1-C15-C16 173.4(3), C15-C16-C17 178.1(3); **3-O** (b): P1-O1 1.480(2), P1-C1 1.802(3), P1-C7 1.797(3), P1-C13 1.746(3), C13-C14 1.196(4), C14-C15 1.441(4); C1-P1-C7 107.3(1), C1-P1-C13 104.6(1), C1-P1-O1 112.5(1), C7-P1-O1 111.1(1), C13-P1-O1 116.0(1), C7-P1-C13 104.6(1), P1-C13-C14 176.5(3), C13-C14-C15 178.7(3). Angles between planes (°): **2-O** (a): C9-C14 and C17-C22 9.1, C1-C6 and C9-C14 79.9, C1-C6 and C17-C22 88.5; **3-O** (b): C15-C17' and C7-C12 23.6, C15-C17' and C1-C6 82.3.

two highest energy bands are significantly bathochromically shifted for polymer **1b** ($\lambda_{max} = 289$ and 305 nm; $\epsilon \approx 2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) relative to model **2** ($\lambda_{max} = 257$ and 267 nm; $\epsilon \approx 4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 1,4-diethynyl-2,5-di-*n*-hexylbenzene ($\lambda_{max} = 265$ and 274 nm; $\epsilon \approx 3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The two lower energy bands of **1b** ($\lambda_{max} = 317$, 330 nm; $\epsilon \approx 2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) are significantly more intense but less red-shifted than in **2** ($\lambda_{max} = 306$, 328 nm; $\epsilon \approx 4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and 1,4-diethynyl-2,5-di-*n*-hexylbenzene ($\lambda_{max} = 297$, 308 nm; $\epsilon \approx 6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). A significant red shift in the absorbance maxima is also observed for the oxidized PPYP (**1b-O**) when compared to models (**2-O** and **3-O**). Consistently, a low energy tail that extends into the visible region is observed for the PPYPs. In addition, each displays an additional weak absorption (**1b**: 384 nm, **1b-O**: 382 nm). A similar feature has also been observed for poly(*p*-phenylene phosphane)s.^[4g]

We have also investigated the emission properties for these new PPYPs. Perhaps most striking is that a THF solution of **1b-O** shows a strong blue emission under a black (UV) light whilst no such emission is observed for **1b**.^[19] For **1b-O**, irradiation at 318 nm gives a broad emission spectrum ($\lambda_{em} = 339$ nm) that extends well into the visible region (Figure 4, bottom). Interestingly, model **2-O** is not fluorescent

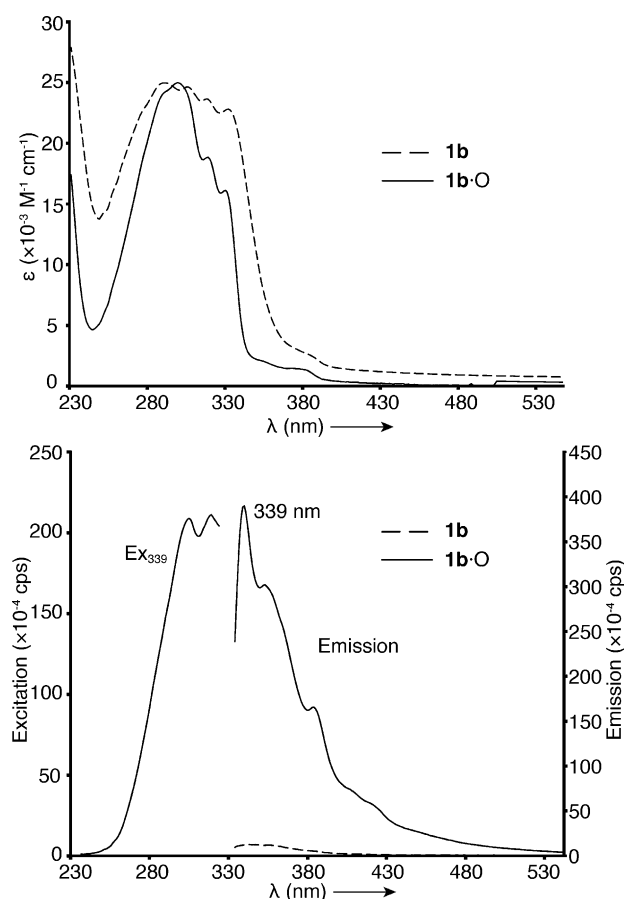


Figure 4. UV/Vis absorption spectra (top); emission and excitation spectra (bottom) of **1b** and **1b-O** in THF solution (10^{-5} M). The excitation spectrum labelled Ex₃₃₉ was recorded for the emission maxima at 339 nm, respectively. The emission spectra were recorded with excitation wavelength 318 nm. The abbreviation cps stands for counts per second.

whereas **3-O** is. Importantly, the emission spectrum of **1b-O** does not change with excitation wavelength (range: 260–330 nm). Moreover, the excitation spectrum of **1b-O** in THF at the emission maximum (339 nm) shows similar features to the absorbance spectrum. The excited state lifetime ($\tau = 0.34$ ns) is consistent with a fluorescence mechanism of emission.^[20] The quantum yield (ϕ) for the emission was 0.12 relative to that of anthracene ($\phi = 0.27$).^[21] Comparisons are difficult to find since most P-containing polymers are either not fluorescent or the quantum yield has not been measured. Of note, the quantum yields for several phosphole polymers with biphenyl spacers ($\phi = 0.08$ – 0.12 in solution)^[22] are similar to that obtained herein for PPYP **1b-O**.

Taken together, the molecular structures of the model compounds and the photophysical properties of the PPYPs **1b** and **1b-O** are consistent with π -conjugation within the *p*-phenylene-di-yne moieties in combination with hyperconjugation with phosphorus. Such effects are known with polysilanes^[22] and polymers containing organic π -systems and saturated heavier main-group element centers (e.g. silicon and phosphorus) in the main chain.^[1e,23] In addition, a low barrier to inversion at P has been observed spectroscopically

for phosphanes bearing alkyne substituents;^[9] this low barrier may be a consequence of some conjugation.

In summary, we have disclosed the synthesis and characterization of the first examples of poly(*p*-phenylenedi-yne phosphane)s and their respective molecular model compounds. PPYPs are an exciting new class of phosphorus-containing macromolecule bearing functional phosphane and alkyne groups. Although the study of the fascinating photo-physical properties is at an early stage, preliminary evidence for σ - π -conjugation within the polymer backbone has been obtained. Future work will further explore the novel electronic properties of PPYPs and their potential application as sensor materials. Additionally, we will attempt to explore the possibility of post-polymerization modification of PPYPs at either the alkyne and/or the phosphane functional groups.

Keywords: alkynes · conjugated polymers · inorganic polymers · phosphanes · phosphorus

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 11438–11442
Angew. Chem. **2015**, *127*, 11600–11604

- [1] For reviews, see: a) X. He, T. Baumgartner, *RSC Adv.* **2013**, *3*, 11334; b) J. I. Bates, J. Dugal-Tessier, D. P. Gates, *Dalton Trans.* **2010**, 39, 3151; c) P. W. Siu, D. P. Gates in *π -Conjugated Polymer Synthesis* (Ed.: Y. Chujo), Wiley-VCH, Weinheim, **2010**, Chap. 8; d) T. Baumgartner, R. Réau, *Chem. Rev.* **2006**, *106*, 4681; e) M. Hissler, P. W. Dyer, R. Réau, *Coord. Chem. Rev.* **2003**, *244*, 1; f) H. R. Allcock, *Chemistry and Applications of Polyphosphazenes*, Wiley-Interscience, New Jersey, **2003**.
- [2] See, for example: a) Y. Matano, H. Ohkubo, T. Miyata, Y. Watanabe, Y. Hayashi, T. Umeyama, H. Imahori, *Eur. J. Inorg. Chem.* **2014**, 1620; b) X. M. He, A. Y. Y. Woo, J. Borau-Garcia, T. Baumgartner, *Chem. Eur. J.* **2013**, *19*, 7620; c) M. Stolar, T. Baumgartner, *New J. Chem.* **2012**, *36*, 1153; d) O. Fadhel, Z. Benkö, M. Gras, V. Deborde, D. Joly, C. Lescop, L. Nyulészi, M. Hissler, R. Réau, *Chem. Eur. J.* **2010**, *16*, 11340; e) A. Saito, Y. Matano, H. Imahori, *Org. Lett.* **2010**, *12*, 2675; f) M. Sebastian, M. Hissler, C. Fave, J. Rault-Berthelot, C. Odin, R. Réau, *Angew. Chem. Int. Ed.* **2006**, *45*, 6152; *Angew. Chem.* **2006**, *118*, 6298; g) H. C. Su, O. Fadhel, C. J. Yang, T. Y. Cho, C. Fave, M. Hissler, C. C. Wu, R. Réau, *J. Am. Chem. Soc.* **2006**, *128*, 983; h) T. Baumgartner, T. Neumann, B. Würges, *Angew. Chem. Int. Ed.* **2004**, *43*, 6197; *Angew. Chem.* **2004**, *116*, 6323; i) Y. Morisaki, Y. Aiki, Y. Chujo, *Macromolecules* **2003**, *36*, 2594; j) C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulészi, R. Réau, *Chem. Eur. J.* **2001**, *7*, 4222; k) C. Hay, C. Fischmeister, M. Hissler, L. Toupet, R. Réau, *Angew. Chem. Int. Ed.* **2000**, *39*, 1812; *Angew. Chem.* **2000**, *112*, 1882; l) S. S. H. Mao, T. D. Tilley, *Macromolecules* **1997**, *30*, 5566.
- [3] See, for example: a) V. A. Wright, B. O. Patrick, C. Schneider, D. P. Gates, *J. Am. Chem. Soc.* **2006**, *128*, 8836; b) R. C. Smith, J. D. Protasiewicz, *J. Am. Chem. Soc.* **2004**, *126*, 2268; c) R. C. Smith, J. D. Protasiewicz, *Eur. J. Inorg. Chem.* **2004**, 998; d) R. C. Smith, X. F. Chen, J. D. Protasiewicz, *Inorg. Chem.* **2003**, *42*, 5468; e) V. A. Wright, D. P. Gates, *Angew. Chem. Int. Ed.* **2002**, *41*, 2389; *Angew. Chem.* **2002**, *114*, 2495.
- [4] See, for example: a) S. Greenberg, G. L. Gibson, D. W. Stephan, *Chem. Commun.* **2009**, 304; b) S. Greenberg, D. W. Stephan, *Inorg. Chem.* **2009**, *48*, 8623; c) K. Naka, T. Umeyama, A. Nakahashi, Y. Chujo, *Macromolecules* **2007**, *40*, 4854; d) L. A. Vanderark, T. J. Clark, E. Rivard, I. Mannes, J. C. Sloatweg, K. Lammertsma, *Chem. Commun.* **2006**, 3332; e) Z. Jin, B. L. Lucht, *J. Am. Chem. Soc.* **2005**, *127*, 5586; f) Z. Jin, B. L. Lucht, *J.*

- Organomet. Chem.* **2002**, 653, 167; g) B. L. Lucht, N. O. St Onge, *Chem. Commun.* **2000**, 2097; h) H. Ghassemi, E. McGrath, *Polymer* **1997**, 38, 3139.
- [5] See, for example: a) X. S. Wang, K. Cao, Y. B. Liu, B. Tsang, S. Liew, *J. Am. Chem. Soc.* **2013**, 135, 3399; b) S. K. Patra, G. R. Whittell, S. Nagiah, C. L. Ho, W. Y. Wong, I. Manners, *Chem. Eur. J.* **2010**, 16, 3240; c) L. Cao, I. Manners, M. A. Winnik, *Macromolecules* **2001**, 34, 3353; d) T. Mizuta, M. Onishi, K. Miyoshi, *Organometallics* **2000**, 19, 5005.
- [6] See, for example: a) A. Schäfer, T. Jurca, J. Turner, J. R. Vance, K. Lee, V. A. Du, M. F. Haddow, G. R. Whittell, I. Manners, *Angew. Chem. Int. Ed.* **2015**, 54, 4836; *Angew. Chem.* **2015**, 127, 4918; b) H. Dorn, J. M. Rodezno, B. Brünhofer, E. Rivard, J. A. Massey, I. Manners, *Macromolecules* **2003**, 36, 291; c) H. Dorn, R. A. Singh, J. A. Massey, J. M. Nelson, C. A. Jaska, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2000**, 122, 6669.
- [7] See, for example: a) B. W. Rawe, C. P. Chun, D. P. Gates, *Chem. Sci.* **2014**, 5, 4928; b) P. W. Siu, S. C. Serin, I. Krummenacher, T. W. Hey, D. P. Gates, *Angew. Chem. Int. Ed.* **2013**, 52, 6967; *Angew. Chem.* **2013**, 125, 7105; c) J. Dugal-Tessier, S. C. Serin, E. B. Castillo-Contreras, E. D. Conrad, G. R. Dake, D. P. Gates, *Chem. Eur. J.* **2012**, 18, 6349; d) K. J. T. Noonan, B. H. Gillon, V. Cappello, D. P. Gates, *J. Am. Chem. Soc.* **2008**, 130, 12876; e) B. H. Gillon, B. O. Patrick, D. P. Gates, *Chem. Commun.* **2008**, 2161; f) K. J. T. Noonan, D. P. Gates, *Angew. Chem. Int. Ed.* **2006**, 45, 7271; *Angew. Chem.* **2006**, 118, 7429; g) C. W. Tsang, B. Baharloo, D. Riendl, M. Yam, D. P. Gates, *Angew. Chem. Int. Ed.* **2004**, 43, 5682; *Angew. Chem.* **2004**, 116, 5800; h) C. W. Tsang, M. Yam, D. P. Gates, *J. Am. Chem. Soc.* **2003**, 125, 1480.
- [8] For an excellent overview of poly(aryleneethynyls), see: U. H. F. Bunz, *Macromol. Rapid Commun.* **2009**, 30, 772, and references therein.
- [9] See, for example: a) A. Kreienbrink, M. B. Sárosi, R. Kuhnert, P. Wonneberger, A. I. Arkhypchuk, P. Lönnecke, S. Ott, E. Hey-Hawkins, *Chem. Commun.* **2015**, 51, 836; b) E. Öberg, A. Orthaber, C. Lescop, R. Réau, M. Hissler, S. Ott, *Chem. Eur. J.* **2014**, 20, 8421; c) J. Möbus, Q. Bonnin, K. Ueda, R. Fröhlich, K. Itami, G. Kehr, G. Erker, *Angew. Chem. Int. Ed.* **2012**, 51, 1954; *Angew. Chem.* **2012**, 124, 1990; d) C. Appelt, H. Westenberg, F. Bertini, A. W. Ehlers, J. C. Slootweg, K. Lammertsma, W. Uhl, *Angew. Chem. Int. Ed.* **2011**, 50, 3925; *Angew. Chem.* **2011**, 123, 4011; e) X. L. Geng, S. Ott, *Chem. Eur. J.* **2011**, 17, 12153; f) O. Ekkert, G. Kehr, R. Fröhlich, G. Erker, *Chem. Commun.* **2011**, 47, 10482; g) E. Öberg, X. L. Geng, M. P. Santoni, S. Ott, *Org. Biomol. Chem.* **2011**, 9, 6246; h) X. L. Geng, Q. Hu, B. Schäfer, S. Ott, *Org. Lett.* **2010**, 12, 692; i) H. Westenberg, J. C. Slootweg, A. Hepp, J. Kösters, S. Roters, A. W. Ehlers, K. Lammertsma, W. Uhl, *Organometallics* **2010**, 29, 1323; j) B. Schäfer, E. Öberg, M. Kritikos, S. Ott, *Angew. Chem. Int. Ed.* **2008**, 47, 8228; *Angew. Chem.* **2008**, 120, 8352; k) S. G. A. van Assema, P. B. Kraikivskii, S. N. Zelinskii, V. V. Saraev, G. B. de Jong, F. J. J. de Kanter, M. Schakel, J. C. Slootweg, K. Lammertsma, *J. Organomet. Chem.* **2007**, 692, 2314; l) G. Märkl, T. Zollitsch, P. Kreitmeier, M. Prinzhorn, S. Reithinger, E. Eibler, *Chem. Eur. J.* **2000**, 6, 3806; m) V. Huc, A. Balueva, R. M. Sebastian, A. M. Caminade, J. P. Majoral, *Synthesis* **2000**, 726; n) L. T. Scott, M. Unno, *J. Am. Chem. Soc.* **1990**, 112, 7823.
- [10] I. P. Beletskaya, V. V. Afanasiev, M. A. Kazankova, I. V. Efimova, *Org. Lett.* **2003**, 5, 4309.
- [11] H. Y. Gao, H. Wagner, D. Zhong, J. H. Franke, A. Studer, H. Fuchs, *Angew. Chem. Int. Ed.* **2013**, 52, 4024; *Angew. Chem.* **2013**, 125, 4116.
- [12] Although $\text{PhP}(\text{C}\equiv\text{CPh})\text{Cl}$ has not been reported previously, we have gained evidence for it by adding a THF solution of $\text{PhC}\equiv\text{CLi}$ dropwise to a solution of PhPCl_2 (4 equivs) in THF at -78°C . Specifically, the ^{31}P NMR spectrum of the reaction mixture showed singlet resonances at 53.0 ppm and -60.1 ppm in a 5:6 ratio and assigned to $\text{PhP}(\text{C}\equiv\text{CPh})\text{Cl}$ and previously known $\text{PhP}(\text{C}\equiv\text{CPh})_2$, respectively (See the Supporting Information).
- [13] Attempts to analyze **1b** (and **1b-O**) using GPC equipped with multi-angle light scattering (MALS) were unsuccessful since the absorption and/or emission properties of the PPYP seemed to interfere with light-scattering analysis.
- [14] A similar analysis showing overestimation of molecular weight by GPC for a rigid polyarylene has been performed. See, for example: K. Becker, G. Gaefke, J. Rolfs, S. Höger, J. M. Lupton, *Chem. Commun.* **2010**, 46, 4686.
- [15] CCDC 1400994 (**2-O**) and 1400995 (**3-O**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
- [16] "Characteristic Bond Lengths in Free Molecules" *CRC Handbook of Chemistry and Physics*, 84th Ed., CRC, Boca Raton, FL, **2003**.
- [17] J. Hu, N. Zhao, B. Yang, G. Wang, L. N. Guo, Y. M. Liang, S. D. Yang, *Chem. Eur. J.* **2011**, 17, 5516.
- [18] D. Mootz, G. Sassmannshausen, *Z. Anorg. Allg. Chem.* **1967**, 355, 200.
- [19] It is well established that organophosphines bearing fluorescent substituents are usually not strongly emissive. See, for example: a) S. T. Cai, Y. Lu, S. He, F. F. Wei, L. C. Zhao, X. S. Zeng, *Chem. Commun.* **2013**, 49, 822; b) M. Osawa, M. Hoshino, M. Akita, T. Wada, *Inorg. Chem.* **2005**, 44, 1157; c) S. Yamaguchi, S. Akiyama, K. Tamao, *J. Organomet. Chem.* **2002**, 652, 3; d) K. Akasaka, H. Ohru, *J. Chromatogr. A* **2000**, 881, 159; e) K. Akasaka, T. Suzuki, H. Ohru, H. Meguro, *Anal. Lett.* **1987**, 20, 731; f) J. Bourson, L. Oliveros, *Phosphorus Sulfur Silicon Relat. Elem.* **1986**, 26, 75; g) D. J. Fife, K. W. Morse, W. M. Moore, *J. Photochem.* **1984**, 24, 249; h) N. A. Rozanelskaya, A. I. Bokanov, B. M. Uzhinov, B. I. Stepanov, *Zh. Obshch. Khim.* **1975**, 45, 277; i) H. Schindlbauer, H. Hagen, *Monatsh. Chem.* **1965**, 96, 285.
- [20] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, New York, **2006**.
- [21] W. H. Melhuish, *J. Phys. Chem.* **1961**, 65, 229.
- [22] J. E. Mark, H. R. Allcock, R. West, *Inorganic Polymers*, 2nd ed., Oxford University Press, New York, **2005**.
- [23] See, for example: a) S. Yamaguchi, K. Tamao, *Chem. Lett.* **2005**, 34, 2; b) C. Fave, M. Hissler, T. Kárpáti, J. Rault-Berthelot, V. Deborde, L. Toupet, L. Nyulászi, R. Réau, *J. Am. Chem. Soc.* **2004**, 126, 6058; c) H. Li, R. West, *Macromolecules* **1998**, 31, 2866; d) M. I. Kabachnik, T. A. Mastryukova, T. A. Melent'eva, A. V. Dombrovskii, M. I. Shevchuk, *Theor. Exp. Chem.* **1965**, 1, 174; e) J. Kapp, C. Schade, A. M. El-Nahasa, P. V. R. Schleyer, *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 2236; *Angew. Chem.* **1996**, 108, 2373; f) D. E. Cabelli, A. H. Cowley, M. J. S. Dewar, *J. Am. Chem. Soc.* **1981**, 103, 3286.

Received: May 17, 2015

Revised: January 0, 0000

Published online: July 14, 2015