Phospholes

DOI: 10.1002/anie.200900542

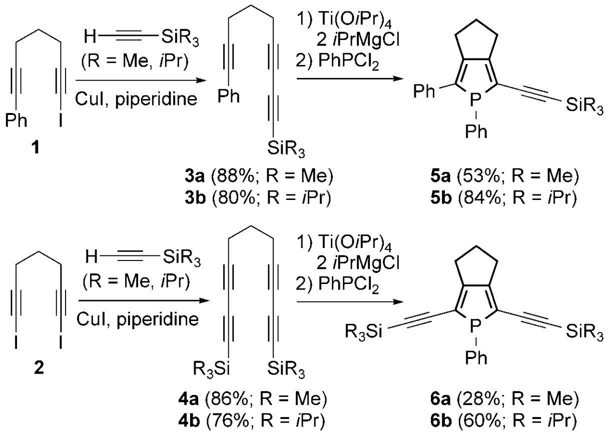
A Convenient Method for the Synthesis of α-Ethynylphospholes and Modulation of Their π-Conjugated Systems**

Yoshihiro Matano, Makoto Nakashima, and Hiroshi Imahori*

The carbon–carbon triple bond (acetylene group) is the simplest component for the construction of linear π networks. Numerous efforts have been devoted both to the establishment of a general method for the introduction of acetylene groups into π systems and the investigation of the optical and electrochemical properties of the resulting π-conjugated molecules.[1,2] Phospholes, that is, phosphorus-bridged 1,3-dienes, are now regarded as promising frameworks for the construction of new classes of π-conjugated organic materials.[3,4] Mathey and co-workers reported the first synthesis of phospholes bearing acetylene functions at the α positions. They prepared these α-alkynyl phospholes by the Sonogashira coupling of α-iodophospholes with terminal acetylenes as well as the S_N2 reaction of α-lithiophospholes with alkynyl sulfinates.[5] Except for these direct functionalization approaches, however, no methods leading to α-alkynyl phospholes have been reported, and only limited information is available about the fundamental reactivities and properties of this class of compounds.

During the course of our comparative study on phosphole-based π systems,[6] we aimed to establish a convenient method for the synthesis of a series of α-alkynyl phospholes and to reveal substituent effects on the optical and electrochemical properties of phosphole–acetylene π-conjugated systems. Herein, we report the first divergent synthesis of functionalized α-(arylethynyl) phospholes and a terphosphole, which are available from common α-ethynylphosphole precursors without a terminal substituent by cross-coupling and successive homocoupling/cyclization, respectively. The phosphole derivatives prepared exhibited the characteristic optical and electrochemical properties of phosphorus-bridged π systems.

We envisaged that metathesis reactions via titanacycles[7] would be applicable to the synthesis of α-ethynylphospholes in few steps. Scheme 1 illustrates the synthesis of the trialkylsilyl-capped 2-ethynylphospholes **5a**,**b** and the 2,5-diethynylphospholes **6a**,**b**. The precursors, silyl-capped triynes **3a**,**b** and tetraynes **4a**,**b**, were prepared by the copper-catalyzed heterocoupling of trialkylsilyl acetylenes with the corresponding iodinated 1,6-heptadiynes **1**[6c] and **2**[8] in 76–88% yield. The treatment of trimethylsilyl-capped oligoynes **3a** and **4a** with $[(\eta^2\text{-propene})\text{Ti}(\text{O}i\text{Pr})_2]$, generated in situ from $\text{Ti}(\text{O}i\text{Pr})_4$ and *i*PrMgCl (2 equiv),[6] followed by treatment with PhPCl_2, afforded the trimethylsilyl-capped 2-ethynyl-5-phenylphosphole **5a** (53%) and 2,5-diethynylphosphole **6a** (28%), respectively. After several attempts to improve the yield of the phospholes, we found that the triisopropylsilyl-capped acetylenes **3b** and **4b** were converted efficiently into the corresponding triisopropylsilyl-capped α-ethynylphospholes **5b** (84%) and **6b** (60%). Presumably, the bulky triisopropylsilyl groups protect the adjacent acetylene units sterically from undesirable titanium coordination.



Scheme 1. Synthesis of the silyl-capped α-ethynylphospholes **5** and **6**.

Compounds **5** and **6** were disilylated by treatment with tetra-*n*-butylammonium fluoride in THF to afford the 2-ethynyl-5-phenylphosphole **7** and 2,5-diethynylphosphole **8**, respectively, in high yield, as determined by NMR spectroscopy [Eq. (1)]. In contrast to **5** and **6**, however, **7** and **8** were difficult to purify completely, as they gradually decomposed in solution. Therefore, **7** and **8** were characterized only by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy and mass spectrometry (MS).

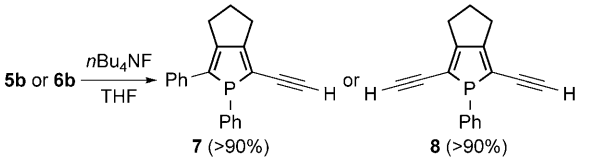
We examined cross-coupling reactions of **7** and **8** with iodoarenes for the synthesis of a series of acetylene-bridged phosphole–arene π-conjugated systems (Scheme 2). The addition of $n\text{Bu}_4\text{NF}$ to a solution in THF of **5b**, iodobenzene,

---

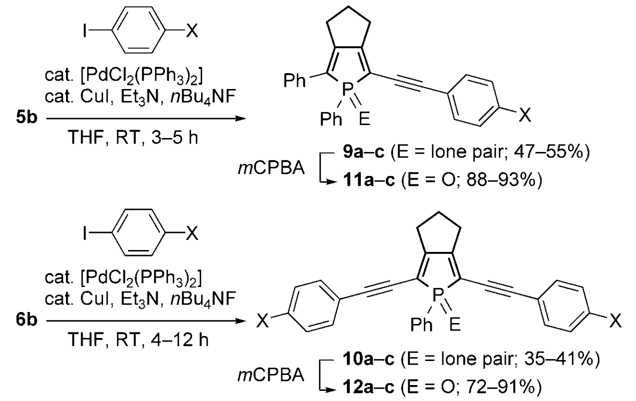
[*] Prof. Dr. Y. Matano, M. Nakashima, Prof. Dr. H. Imahori
Department of Molecular Engineering
Graduate School of Engineering, Kyoto University
Nishikyo-ku, Kyoto 615-8510 (Japan)
Fax: (+81) 75-383-2571
E-mail: matano@scl.kyoto-u.ac.jp
Prof. Dr. H. Imahori
Institute for Integrated Cell-Material Sciences (iCeMS)
Kyoto University, Nishikyo-ku, Kyoto 615-8510 (Japan)
and
Fukui Institute for Fundamental Chemistry, Kyoto University
Sakyo-ku, Kyoto 606-8103 (Japan)

[**] This research was partially supported by a research grant from The Murata Science Foundation.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200900542.



(1)



Scheme 2. Synthesis of **9**–**12**: **a**, X = H; **b**, X = NO$_2$; **c**, X = NMe$_2$. For yields, see the Supporting Information.

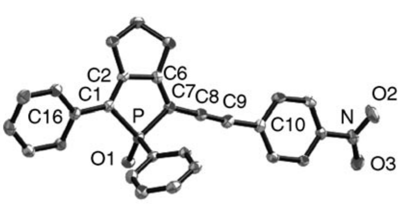


Figure 1. Top view of **11 b**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: C1–C2 1.348(2), C1–C16 1.467(2), C2–C6 1.469(2), C6–C7 1.353(2), C7–C8 1.411(2), C8–C9 1.199(2), C9–C10 1.430(2).

Et$_3$N, and a catalytic amount of [PdCl$_2$(PPh$_3$)$_2$]/CuI (15–20 mol %) initiated phenylation at the terminal acetylenic carbon atom. After 4 h at room temperature, **7** had been consumed completely, and the 2-(phenylethynyl)phosphole **9 a** was isolated in 49 % yield. Similarly, the 2-(arylethynyl) phospholes **9 b**,**c** containing a nitro (NO$_2$) or dimethylamino (NMe$_2$) group were prepared in 55 and 47 % yield, respectively, from the corresponding *para*-substituted iodoarenes. When **6 b** was used in place of **5 b**, the 2,5-bis(arylethynyl) phospholes **10 a**–**c** were produced in 35–41 % yield according to a similar procedure. The cross-coupling method starting from **5 b** and **6 b** is a highly promising approach to the functionalization of α-ethynylphospholes with π-conjugated functional groups that are otherwise difficult to introduce. The σ^3-P center of **9 a**–**c** and **10 a**–**c** was oxygenated with *m*-chloroperbenzoic acid (*m*CPBA) to give the corresponding *P*-oxides **11 a**–**c** and **12 a**–**c** in 72–93 % yield. Compounds **5**, **6**, and **9**–**12** are air- and moisture-stable; their structures were assigned by NMR spectroscopy, IR spectroscopy, and MS, as well as by elemental analysis.

The structure of **11 b** was determined unambiguously by X-ray crystallography (Figure 1).[9] The phosphorus center adopts a distorted tetrahedral geometry with C-P-X bond angles of 93.92(7)–117.81(7)° (X = C, O). The phosphole and nitrophenyl rings are almost coplanar with a dihedral angle of 3.2°. The length of the carbon–carbon triple bond in **11 b** (1.199(2) Å) is close to the lengths of the carbon–carbon triple bonds in 3,4-dimethyl-1-phenyl-2,5-bis(phenylethynyl)phosphole (1.199(3) and 1.201(3) Å), which was described by Mathey and co-workers.[5] The C7–C8 bond length (1.411(2) Å) is slightly shorter than the C9–C10 bond length (1.430(2) Å), which indicates an effective conjugation between the phosphole ring and the acetylene unit. In the packing structure, two acetylene-linked π systems are stacked in parallel with an average π–π distance of 3.58 Å (see Figure S1 in the Supporting Information).

To reveal the optical properties of the acetylene-bridged phosphole–arene π systems, we measured UV/Vis absorption and fluorescence spectra of **9**–**12** in THF (Table 1; see Figure S2 in the Supporting Information). The absorption maxima (λ_{ab}) due to the π–π* transition of the extended π-conjugated system of 2,5-bis(arylethynyl) phospholes **10 a**–**c** are red-shifted relative to those of the corresponding 2-(arylethynyl) phospholes **9 a**–**c**, whereas the fluorescence maxima (λ_{em}) of **10 a**–**c** are blue-shifted or slightly red-shifted relative to those of **9 a**–**c**. As a consequence, the Stokes shifts of **10 a**–**c** are smaller than those of **9 a**–**c**, which reflects the difference in the symmetry of these two π systems.[10] P-oxidation of the NMe$_2$ derivatives (from **9 c**, **10 c** to **11 c**, **12 c**) shifts both the λ_{ab} and λ_{em} values to longer wavelengths ($\Delta\lambda_{ab} = 35$–45 nm; $\Delta\lambda_{em} = 77$–86 nm), whereas P-oxidation of the NO$_2$ derivatives (from **9 b**, **10 b** to **11 b**, **12 b**) has little impact on their λ_{ab} and λ_{em} values. It seems that P-oxidation enhances the π-conjugative push–pull interaction for the NMe$_2$ derivatives (see below).

To gain more insight into substituent effects on the optical properties of these compounds, we also measured the

Table 1: Optical[a] and electrochemical[b] data for **9**–**14**.

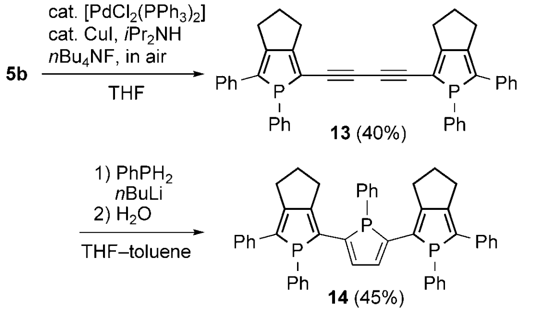
Compd	λ_{ab}[c] (log ε)	λ_{em}[c] (Φ_f[d])	Δλ[e]	E_{ox}, E_{red}[f]
9 a	385 (4.33)	462 (0.13)	4.33	+0.60, −2.37
9 b	416 (4.43)	543 (0.07)	5.62	+0.78, −2.00 (−1.46)
9 c	411 (4.40)	515 (0.13)	4.91	+0.24, −2.46 (+0.50)
10 a	398 (4.48)	449 (0.13)	2.85	+0.68, −2.19
10 b	429 (4.62)	499 (0.09)	3.27	+0.93, −1.72 (−1.43)
10 c	441 (4.53)	518 (0.10)	3.37	+0.15, −2.42 (+0.45)
11 a	402 (4.22)	523 (0.02)	5.76	+1.09, −1.89
11 b	417 (4.40)	536 (< 0.01)	5.33	+1.26, −1.76 (−1.42)
11 c	446 (4.29)	592 (0.01)	5.53	+1.18, −1.95 (+0.36)
12 a	418 (4.32)	502 (0.05)	4.00	+1.00, −1.66
12 b	435 (4.52)	503 (0.07)	3.11	+1.37, −1.46 (−1.32)
12 c	486 (4.35)	604 (0.01)	4.02	+1.20, −1.86 (+0.30)
13	436 (4.56)	501 (0.08)	2.98	+0.56, −2.07
14	502 (4.39)	634 (< 0.01)	4.15	+0.16, −2.10

[a] UV/Vis absorption and fluorescence measurements were made in THF. [b] Redox potentials were determined by DPV in CH$_2$Cl$_2$ with 0.1 M nBu$_4$N$^+$PF$_6^-$ (Ag/AgNO$_3$). [c] Absorption and emission maxima are given in nm. [d] Fluorescence quantum yield relative to quinine sulfate. [e] Stokes shift (in 10^3 cm^{-1}). [f] Oxidation (E_{ox}) and reduction (E_{red}) potentials are given in V versus the Fc/Fc$^+$ couple. Values in parentheses are the potentials of the oxidation (+) and reduction (−) processes occurring at the *para* substituents.

solvatochromic effects of nine solvents with different polarity on the λ_{ab} and λ_{em} values of **9b**,**c** and **11b**,**c** (see Table S1 and Figure S3 in the Supporting Information). In all cases, the solvent effects on the λ_{em} values were considerably larger than those on the λ_{ab} values, which indicates that the excited states of **9b**,**c** and **11b**,**c** are more polarizable than their ground states. Kamlet–Taft analysis[11] of the λ_{em} values gave a linear solvation-energy relationship (LSER) with the solvatochromic parameter (π^*). The slope (s, as an absolute value) of the LSER of **11b** ($s = 0.9\times10^3\ \mathrm{cm}^{-1}$) is significantly smaller than that of **9b** ($s = 6.2\times10^3\ \mathrm{cm}^{-1}$), which indicates that the push–pull interaction between the σ^3-P phosphole unit and the electron-withdrawing NO_2 group in **9b** is indispensable for the excited state to have a high charge-transfer (CT) character. On the other hand, the solvent effect on the λ_{em} value of **11c** ($s = 3.3\times10^3\ \mathrm{cm}^{-1}$) is larger than that observed for **9c** ($s = 2.9\times10^3\ \mathrm{cm}^{-1}$), which implies that P-oxidation results in the enhancement of CT between the phosphole unit and the electron-donating NMe_2 group in the excited state. These results based on a simple chemical modification at the P center show clearly that the phosphole ring alters the polarizability of the acetylene-linked π system dramatically.

To investigate substituent effects on the electrochemical properties of these compounds, the redox potentials of **9**–**12** were measured by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). As shown in Table 1, P-oxidation leads to a positive shift in the redox potential. In the nonsubstituted series, the σ^3-P derivatives (**9a** and **10a**) showed irreversible oxidation processes at $E_{ox} = +0.60$ and $+0.68$ V (versus Fc/Fc^+), and the *P*-oxide derivatives (**11a** and **12a**) displayed reversible reduction processes at $E_{red} = -1.66$ and -1.89 V. The introduction of NO_2 and NMe_2 groups led to positive ($\Delta E = 0.13$–0.47 V) and negative ($\Delta E = 0.06$–0.47 V) shifts in the redox potential, respectively, which implies that the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the phosphole–acetylene–arene π-conjugated systems are sensitive to the *para* substituent on the aryl group. Furthermore, the NO_2 derivatives (**9b**–**12b**) underwent additional reduction steps at $E_{red} = -1.32$ to -1.46 V, and the NMe_2 derivatives (**9c**–**12c**) underwent additional oxidation steps at $E_{ox} = +0.30$ to $+0.50$ V. These processes are attributable to redox reactions occurring at the NO_2 and NMe_2 functional groups.[12]

In sharp contrast to oligothiophenes, oligophospholes have apparently received little attention in materials chemistry.[3] Having developed a convenient method for the generation of the 2-ethynylphosphole **7**, we also examined a concise synthesis of a terphosphole from **5b** (Scheme 3). The palladium/copper-promoted oxidative coupling of **7**, generated in situ from **5b** and nBu_4NF, gave the 1,4-bis(2-phospholyl)-1,3-diyne **13** in 40% yield. The treatment of **13** with $PhPH_2$ in the presence of *n*BuLi in THF–toluene, followed by quenching with water, afforded the desired phenyl-capped terphosphole **14** as an air- and moisture-stable dark-red solid in 45% yield.[13] To our knowledge, **14** is the first example of a directly α,α′-linked terphosphole.



Scheme 3. Synthesis of terphosphole **14**.

Two sets of peaks were observed in the $^{31}P\{^1H\}$ NMR spectrum of **14** at room temperature; they coalesced at 90 °C (in $Cl_2CDCDCl_2$) to one set of peaks. These results indicate the presence of two diastereomers in solution. The recrystallization of **14** from CH_2Cl_2–hexane afforded single crystals of the major isomer, **14A**. The three phosphole rings in **14A** are arranged with a head-to-tail geometry and are almost coplanar (Figure 2). The dihedral angles between the phosphole rings of **14A** are 16.8 and 18.2°, and thus considerably smaller than those observed for the head-to-head quarterphosphole **15** described by Mathey and co-workers (25.1–49.7°).[14] Presumably, the 3,4-unsubstituted central phosphole unit in **14A** reduces the steric congestion between two adjacent phosphole rings as compared to the inner 3,4-dimethylphosphole units in **15**. Each phosphorus center adopts a trigonal-pyramidal geometry with C-P-C bond angles of 90.90(17)–104.15(18)°, and the phenyl rings attached to P atoms are oriented in the same direction. In the crystalline state, a dichloromethane molecule is sandwiched

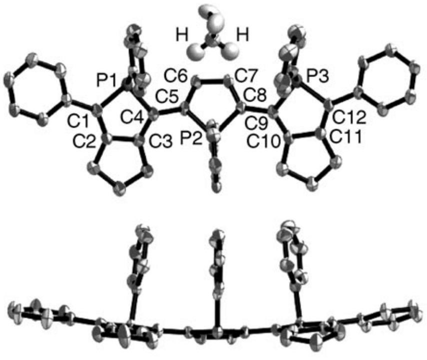
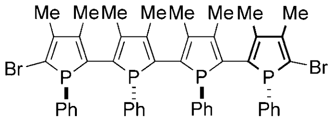
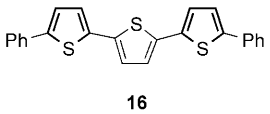


Figure 2. Top and side views of **14A**. Hydrogen atoms are omitted for clarity, except in CH_2Cl_2 (top). Selected bond lengths [Å]: C1–C2 1.345(5), C2–C3 1.466(5), C3–C4 1.366(5), C4–C5 1.453(5), C5–C6 1.356(5), C6–C7 1.454(5), C7–C8 1.364(5), C8–C9 1.452(5), C9–C10 1.357(5), C10–C11 1.467(5), C11–C12 1.357(5).



15



16

between the two parallel *P*-phenyl rings through dual CH–π interactions. The spectral and structural features observed for **14** suggest that π conjugation can occur effectively over the three phosphole rings.

The absorption and emission maxima of the phenyl-capped terphosphole **14** in THF appear at $\lambda_{ab} = 502$ nm and $\lambda_{em} = 634$ nm, respectively (see Figure S5 in the Supporting Information). These values are significantly red-shifted relative to the λ_{ab} and λ_{em} values of the phenyl-capped terthiophene **16** ($\lambda_{ab} = 404$ nm; $\lambda_{em} = 470/500$ nm) described by Hotta and co-workers[15] and 2,5-diphenylphosphole ($\lambda_{ab} = 354$ nm; $\lambda_{em} = 466$ nm), which was described by Réau and co-workers.[4b] The experimentally determined HOMO–LUMO gap of **14** (2.21 eV) is much smaller than that of **16** (2.85 eV),[16] in good accordance with a theoretical prediction for terheterole models.[17] Thus, α,α′-linked oligophospholes are promising candidates for heterole-based π-conjugated materials with narrow HOMO–LUMO gaps.

In summary, we have applied a titanium(II)-mediated cyclization protocol to the preparation of two kinds of silyl-capped α-ethynylphospholes. These precursors were successfully converted into α-(arylethynyl) phospholes and a terphosphole through the in situ generation of α-ethynylphosphole intermediates without terminal substituents. The ready introduction of π-conjugative functionalities, such as NO_2 and NMe_2 groups, through palladium/copper-catalyzed cross-coupling reactions enabled us to investigate substituent effects on the optical and electrochemical properties of the acetylene-bridged phosphole–arene π systems. A planar, phenyl-capped terphosphole was found to have a narrow HOMO–LUMO gap of 2.21 eV. The present results demonstrate the potential utility of α-ethynylphospholes as precursors for new phosphorus-based π-conjugated systems.

Received: January 29, 2009

Keywords: acetylenes · charge transfer · cross-coupling · homocoupling · phospholes

---

[1] a) K. Sonogashira, *J. Organomet. Chem.* **2002**, *653*, 46–49; b) R. R. Tykwinski, *Angew. Chem.* **2003**, *115*, 1604–1606; *Angew. Chem. Int. Ed.* **2003**, *42*, 1566–1568; c) E. Negishi, L. Anastasia, *Chem. Rev.* **2003**, *103*, 1979–2018; d) R. Chinchilla, C. Nájera, *Chem. Rev.* **2007**, *107*, 874–922.

[2] a) U. H. F. Bunz, *Chem. Rev.* **2000**, *100*, 1605–1644; b) J. M. Tour, *Acc. Chem. Res.* **2000**, *33*, 791–804.

[3] For reviews, see: a) F. Mathey, *Angew. Chem.* **2003**, *115*, 1616–1643; *Angew. Chem. Int. Ed.* **2003**, *42*, 1578–1604; b) M. Hissler, P. W. Dyer, R. Réau, *Coord. Chem. Rev.* **2003**, *244*, 1–44; c) L. D. Quin, *Curr. Org. Chem.* **2006**, *10*, 43–78; d) T. Baumgartner, R. Réau, *Chem. Rev.* **2006**, *106*, 4681–4727 (Correction: T. Baumgartner, R. Réau, *Chem. Rev.* **2007**, *107*, 303); e) M. Hissler, C. Lescop, R. Réau, *Pure Appl. Chem.* **2007**, *79*, 201–212; f) M. G. Hobbs, T. Baumgartner, *Eur. J. Inorg. Chem.* **2007**, 3611–3628; g) C. Lescop, M. Hissler in *Tomorrow's Chemistry Today* (Ed.: B. Pignataro), Wiley-VCH, Weinheim, **2008**, pp. 295–319; h) Y. Matano, H. Imahori, *Org. Biomol. Chem.* **2009**, *7*, 1258–1271.

[4] For example, see: a) S. S. H. Mao, T. D. Tilley, *Macromolecules* **1997**, *30*, 5566–5569; b) C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulászi, R. Réau, *Chem. Eur. J.* **2001**, *7*, 4222–4236; c) Y. Morisaki, Y. Aiki, Y. Chujo, *Macromolecules* **2003**, *36*, 2594–2597; d) I. Tomita, M. Ueda, *Macromol. Symp.* **2004**, *209*, 217–230; e) T. Baumgartner, W. Bergmans, T. Kárpáti, T. Neumann, M. Nieger, L. Nyulázi, *Chem. Eur. J.* **2005**, *11*, 4687–4699; f) T. Sanji, K. Shiraishi, M. Tanaka, *Org. Lett.* **2007**, *9*, 3611–3614; g) N. H. T. Huy, B. Donnadieu, F. Mathey, A. Muller, K. Colby, C. J. Bardeen, *Organometallics* **2008**, *27*, 5521–5524; h) H. Tsuji, K. Sato, L. Ilies, Y. Itoh, Y. Sato, E. Nakamura, *Org. Lett.* **2008**, *10*, 2263–2265; i) A. Fukazawa, H. Yamada, S. Yamaguchi, *Angew. Chem.* **2008**, *120*, 5664–5667; *Angew. Chem. Int. Ed.* **2008**, *47*, 5582–5585.

[5] S. Holand, F. Gandolfo, L. Ricard, F. Mathey, *Bull. Soc. Chim. Fr.* **1996**, *133*, 33–37.

[6] a) Y. Matano, T. Miyajima, T. Nakabuchi, Y. Matsutani, H. Imahori, *J. Org. Chem.* **2006**, *71*, 5792–5795; b) Y. Matano, T. Nakabuchi, T. Miyajima, H. Imahori, H. Nakano, *Org. Lett.* **2006**, *8*, 5713–5716; c) Y. Matano, T. Miyajima, H. Imahori, Y. Kimura, *J. Org. Chem.* **2007**, *72*, 6200–6205; d) T. Miyajima, Y. Matano, H. Imahori, *Eur. J. Org. Chem.* **2008**, 255–259; e) Y. Matano, T. Miyajima, T. Fukushima, H. Kaji, Y. Kimura, H. Imahori, *Chem. Eur. J.* **2008**, *14*, 8102–8115.

[7] F. Sato, H. Urabe, S. Okamoto, *Chem. Rev.* **2000**, *100*, 2835–2886.

[8] J. J. Langer, G. P. Moss, *Mol. Cryst. Liq. Cryst.* **1993**, *237*, 457–461.

[9] **11b**: monoclinic, $0.45 \times 0.15 \times 0.05$ mm^3, $P2_1/c$, $a = 15.072(6)$, $b = 7.859(3)$, $c = 17.645(6)$ Å, $\beta = 92.546(4)°$, $V = 2088.0(14)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.391$ g cm^{-3}, $\mu = 1.627$ cm^{-1}, collected: 15573, independent: 4724, parameters: 290, $R_w = 0.0826$, $R = 0.0426$ ($I > 2.00\sigma(I)$), GOF = 1.072. **14**: monoclinic, $0.20 \times 0.15 \times 0.08$ mm^3, $P2_1/n$, $a = 7.887(4)$, $b = 25.483(13)$, $c = 20.207(11)$ Å, $\beta = 94.141(8)°$, $V = 4051(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.301$ g cm^{-3}, $\mu = 3.14$ cm^{-1}, collected: 28319, independent: 9062, parameters: 488, $R_w = 0.1618$, $R = 0.0859$ ($I > 2.00\sigma(I)$), GOF = 1.060. CCDC 717638 (**11b**) and CCDC 717639 (**14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.)

[10] The λ_{ab} values observed for **10a–c** are red-shifted by 42–55 nm relative to those reported for 2,5-bis(arylethynyl) thiophenes with the same *para* substituents: J. S. Siddle et al., *New J. Chem.* **2007**, *31*, 841–851; see the Supporting Information.

[11] M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham, R. W. Taft, *J. Org. Chem.* **1983**, *48*, 2877–2887.

[12] a) J.-P. Gisselbrecht, N. N. P. Moonen, C. Boudon, M. B. Nielsen, F. Diederich, M. Gross, *Eur. J. Org. Chem.* **2004**, 2959–2972; b) B. Schäfer, E. Öberg, M. Kritikos, S. Ott, *Angew. Chem.* **2008**, *120*, 8352–8355; *Angew. Chem. Int. Ed.* **2008**, *47*, 8228–8231.

[13] For the synthesis of 2,5-diaryl phospholes from 1,3-diynes and $PhPH_2$, see: a) G. Märkl, R. Potthast, *Angew. Chem.* **1967**, *79*, 58; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 86; b) E. H. Braye, I. Caplier, R. Saussez, *Tetrahedron* **1971**, *27*, 5523–5537; c) M. Ogasawara, A. Ito, K. Yoshida, T. Hayashi, *Organometallics* **2006**, *25*, 2715–2718.

[14] E. Deschamps, L. Ricard, F. Mathey, *Angew. Chem.* **1994**, *106*, 1214–1217; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1158–1161.

[15] S. A. Lee, S. Hotta, F. Nakanishi, *J. Phys. Chem. A* **2000**, *104*, 1827–1833.

[16] $\Delta E_{HOMO-LUMO}$ [eV] $= 1240\{(1/\lambda_{ab} + 1/\lambda_{em})/2\}$ [nm^{-1}].

[17] D. Delaere, M. T. Nguyen, L. G. Vanquickenborne, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1522–1530: The HOMO–LUMO gaps of unsubstituted terphosphole and terthiophene were calculated to be 2.7 and 3.3 eV, respectively, at the B3LYP/SV(P) level.