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Synthesis and Properties of Bisphosphole-Bridged Ladder Oligophenylenes

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Abstract: Ladder-type oligophenylenes (LOPP) with bridging heteroatoms are interesting systems as they offer novel electronic and photophysical properties on account of the rigid structural features, more efficient electron delocalization on the coplanar aromatic framework, and strong intermolecular interactions. LOPPs incorporating multiple phosphorous centers combine the excellent electronic properties of phospholes and rigidified conjugated framework of LOPPs, thus positioning themselves as an attractive class of organic semiconductors. To date, there still lacks an effective synthetic methodology towards LOPPs with multiple phosphorous bridges. Herein, we describe the synthesis and properties of a new class of bisphosphole-bridged ladder oligo(p-phenylene)s and the related phosphoxides. The synthesis of phosp-

Keywords: free-radical phosphanylation • fluorescence • heteroacenes • organic semiconductors • phospholes holes was achieved by a four-fold freeradical phosphanylation reaction of a tetrabromo *p*-terphenylene or biphenyl-thiophene. Sequential trapping of four highly reactive aryl radicals occurred effectively to give the desired phosphorous-containing ladder compound. The oxides of the phospholes are shown to be strong fluorophores that can be used as potential *n*-type building blocks for organic semiconducting materials.

Introduction

Organic π -conjugated materials have attracted increasing attention owing to their great potential as semiconducting materials for smaller, more efficient electronic devices.^[1] Many efforts have been directed towards modification of the molecular structures of the materials to obtain desired electronic and optical properties. In particular, ladder-type π systems with fully fused polycyclic conjugated skeletons offer^[2] novel electronic and photophysical properties because of their rigid structural features, more efficient electron delocalization on the coplanar aromatic framework, and strong intermolecular π - π interactions. Incorporating heteroatoms to replace the bridging carbon atoms into the π -conjugated system has been an effective strategy in fine-tuning their electronic structures. Ladder oligo(p-phenylene)s (LOPPs) with bridging carbon atoms^[3] or heteroatoms such as nitrogen,^[4] sulfur,^[5] and silicon^[6] (Scheme 1) have been synthesized and applied in electronic devices. Conjugated molecules incorporating trivalent phosphorus centers,^[7] the simplest being phosphole,^[8] have received considerable attention recently. Due to the orbital pyrimidalization on the tricoordinate phosphorus center, the phosphole's lone pairs

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have weakened interactions with the conjugated system. This results in a low degree of electron delocalization relative to planar pyrrole analogs.^[7a,d] The anellated ring systems containing extended π systems, such as dithienophosphole,^[9] dibenzophosphole,^[10] (Scheme 1b) or arene-fused phospholes,^[11] are considered nonclassical phospholes because the aromatic character of the phosphole units is further reduced due to strong retention of π electrons of the parent aromatic units. On the other hand, the $\sigma^* - \pi^*$ interaction between the endocyclic π system of the butadiene moiety and the σ^* orbital of the exocyclic P-C bond results in a low-lying LUMO energy level.^[12] This hyperconjugation in phospholes, including those with phosphorus (V) centers (the oxides), makes them particularly attractive as *n*-type organic semiconductors. Compounds that combine the excellent electronic properties of phospholes and rigidified conjugated framework of LOPPs, especially those with multiple phosphorous centers (2a and 3a in Scheme 1c), represent an attractive class of π systems. However, an effective synthetic methodology towards such compounds has been very limited despite the remarkable synthetic progress for phospholebridged heteroaromatics.^[13] Herein, we report the synthesis of a bisphosphole-bridged LOPP and a related ladder biphenyl-thiophene using a free-radical phosphanylation reac-

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tion protocol. Oxidation of such LOPPs into their corresponding phosphoxides gives further opportunities for finetuning the electronic and photophysical properties.

Results and Discussion

We first attempted the synthesis of the bisphosphole LOPP **2a** using a standard lithiation and trapping method. Tetralithiation of tetrabromide $4a^{[6g]}$ followed by trapping with dichlorophenylphosphane only resulted in oligomeric side products. We then turned to the recently developed radical phosphanylation of reactive aryl radicals, which was a highly efficient approach for the synthesis of arylphosphanes and strained bis(phosphoryl)-bridged biphenyls.^[14] This reaction route, despite involving multiple radical phosphanylation of a tetrabromide in one step, worked effectively to give the desired product.

The tetrabromide **4a** was treated with readily prepared $(Me_3Sn)_2Ph$ at 125 °C using 1,1'-azobis(cyclohexane-1-carbonitrile) (V-40) as the free-radical initiator (Scheme 2).



Scheme 3. Synthesis of bisphosphole 2b and the oxide 3b.

peaks at -9.6 and -23.6 ppm, and these peaks correspond to the benzophosphole and thienophosphole moieties, respectively. In the spectrum of oxide **3b**, these peaks undergo a characteristic downfield shift and now resonate at 32.9 and 22.5 ppm, respectively.

The photophysical properties of the ladder bisphospholes and oxides were evaluated in CHCl₃ by UV/Vis and fluorescence spectroscopy and the corresponding data are summarized in Table 1, together with those of dibenzophosphole



with those of dibenzophosphole oxide $P2^{[10b]}$ (R=Ph) and bissilole-bridged terphenyl $1d^{[6g]}$ (R=Ph) for comparison. The absorption maxima at the longest wavelength for bisphospholes **2a** and **2b** are at 330 nm and 332 nm, respectively

Scheme 2. Synthesis of bisphosphole 2a and the oxide 3a. V-40 = 1,1'-azobis(cyclohexane-1-carbonitrile).

From the cooled reaction mixture an isomerically pure bisphosphole 2a in its trans geometry was isolated in 37% yield as a white solid, which showed only one single resonance in its ³¹P NMR spectrum (³¹P: $\delta = -9.4$ ppm). The chemical shift is significantly upfield as compared to those of the parent phospholes reported by Reau et al.^[8a] (³¹P: $\delta =$ 11–45 ppm), but very close to dibenzophosphole P2 (R = Ph, ³¹P: $\delta = -12.8 \text{ ppm}$,^[10a] consistent with its benzophosphole characteristics rather than those characteristics of a classic phosphole. Compound 2a is stable in the solid state while in solution, it slowly isomerizes to give a mixture of trans/cis isomers, as indicated by the appearance of a new peak at -9.6 ppm (see Figure S1 in Supporting Information) in the ³¹P NMR spectrum, and it reaches a ratio of 3:2 (trans/cis) in three weeks. Oxidation of trans-2a with H₂O₂ gave the corresponding oxide trans-3a, which showed a single resonance at 33.7 ppm in its ³¹P NMR spectrum.

The successful phosphanylation reaction on the *p*-terphenyl tetrabromide allows for the synthesis of new bisphosphole-bridged LOPPs. As an initial test, we applied this reaction protocol to the biphenyl-thiophene tetrabromide **4b**, which was synthesized from Suzuki coupling between iodide $5^{[6g]}$ and boronic acid **6** (Scheme 3). After being subjected to similar radical phosphanylation conditions, *trans*-**2b** was isolated in pure form by simple filtration from the reaction mixture, which was readily oxidized by H_2O_2 to give the oxide *trans*-**3b**. The ³¹P NMR spectrum of **2b** shows two

Table 1. Photophysical properties of the bisphospholes, dibenzophole **P2**, and bissilole $\mathbf{1d}$.^[a]

Compound	UV/Vis absorption		Fluorescence	
	$\lambda_{\mathrm{abs}} [\mathrm{nm}]^{\mathrm{[b]}}$	$\varepsilon [M^{-1} cm^{-1}]$	$\lambda_{em} [nm]^{[c]}$	$arPsi_{ m f}^{[d]}$
trans-2a	330	9719	409, 420	0.21
trans-2b	332	9400	420	0.05
trans- 3a	383	2780	420	0.81
trans-3b	381	4819	408, 423	0.11
P2 ^[e]	332	794	366	0.04
1 d ^[f]	328	40300	395	0.56

[a] In CHCl₃. [b] Only the absorption maxima at longest wavelength are listed. [c] Emission maxima upon excitation at 330 nm. [d] Absolute quantum yields were measured by a calibrated integrating sphere system with ± 3 % error. [e] See ref. [10b]. [f] See ref. [6g].

(Figure 1), and are similar to the silole-bridged LOPP 1d. In comparison, low-intensity absorption maxima at 383 and 381 nm are observed for the corresponding oxides 3a and 3b, respectively, which are attributed to intramolecular charge transfer from the conjugated π systems to the phosphole oxide groups. More pronounced peaks at around 330 nm are attributed to the π - π * HOMO-LUMO electronic transitions. In addition, both 3a and 3b absorb at higher wavelength than the monophosphole oxide P2 owing to extended π -electron delocalization in the ladder framework. Compounds 2a, 2b, 3a, and 3b are blue fluorescent, with the emission maxima all at around 420 nm (Figure 2). However, their quantum yields vary significantly. Both oxides



Figure 1. UV/Vis spectra of *trans*-2a,b and *trans*-3a,b. Solvent: CHCl₃.



Figure 2. Normalized fluorescence spectra of *trans*-2a,b and *trans*-3a,b. Solvent: CHCl₃.

have higher quantum yields than the corresponding trivalent phospholes, and **3a** exhibits the strongest fluorescence with a high quantum yield of 0.81.

Numerous efforts in growing crystals suitable for single crystal X-ray analysis failed. The optimal molecular geometries were then modeled by using density functional theory (DFT) at B3LYP/6-31G** level. A highly coplanar conjugated framework was observed for **2a**, **2b**, **3a**, and **3b**, as shown in Figure 3 for **3a** and Figure S3 in the Supporting In-

a) b) the second second

Figure 3. Ball-and-stick representation of the optimized geometry of 3a at B3LYP/6-31G** level. a) front view, and b) side view.

formation for **2a**, **2b**, and **3b**. The frontier orbitals and energies were also computed by using DFT and are shown in Figure 4. The π systems are well delocalized over the oligo-



Figure 4. Computed frontier orbitals and energy levels of *trans*-2a, b and *trans*-3a, b.

phenylene skeleton. The highest occupied molecular orbitals (HOMO) are antibonding combinations of the HOMOs of constituent phenylene or thiophene units, with no (for 2a and **2b**) or little contribution (for **3a** and **3b**) from the σ_{P-Ph} orbitals. On the other hand, the lowest unoccupied molecular orbitals (LUMO) are bonding combinations of the LUMOs of the oligophenylenes, with contributions from the σ_{P-Ph}^* orbitals. The LUMO energy levels of the oxides **3a** and 3b are more than 0.6 eV lower than the corresponding phospholes 2a and 2b, owing to the electron-withdrawing effect of the oxygen atoms. The HOMO energies of both oxides are also lower than the free phospholes, albeit to a lesser extent (ca. 0.3 eV). Overall the oxidation of the phosphorus centers into their pentavalent coordination geometry results in a decreased HOMO-LUMO gap, which correlates well with the bathochromic shift observed in their absorption spectra.

The electrochemical properties of phosphole oxides **3a** and **3b** were evaluated in CHCl₃ using the standard threeelectrode setup^[15] and the ferrocene/ferrocenium (F_c/F_c^+) redox couple as the internal standard. While the cyclic voltammogram (CV) of **3a** is irreversible, the CV of **3b** shows (Figure S3 in the Supporting Information) one quasi-reversible reduction peak at -1.40 V (vs Fc/Fc⁺). This reduction potential is significantly more negative than the $E_{\rm red}$ value of the monophosphole **P2** (-1.93 V vs SCE or -2.41 vs Fc/ Fc⁺),^[10b] thereby indicating that the incorporation of two phosphole bridges in the LOPPs is effective in enhancing the electron-accepting abilities. The low-lying LUMO energy of -3.4 eV, derived from the following equation: LUMO = $-(E_{\rm red}+4.8 \text{ eV})$,^[17] affirms good *n*-type characteristics of this type of LOPP.

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Conclusions

We have synthesized a new class of bisphosphole-bridged ladder oligophenylenes from a four-fold free-radical phosphanylation reaction. The effective synthesis allows access to other ladder heteroarene systems, as demonstrated in the synthesis of a thiophene isologue of bisphosphole-bridged LOPP. The electronic structures and photophysical properties of these bisphosphole LOPPs were characterized and modeled by DFT calculations. The oxides of the phospholes are shown to be strong fluorophores while having good electron-accepting characteristics, thereby rendering them as potential *n*-type building blocks for organic semiconducting materials. The synthetic protocol is to be extended to other isologues of bisphosphole-bridged LOPPs. The implementation of such materials into organic electronic devices is currently underway.

Experimental Section

General Methods

Thin-layer chromatography (TLC) was carried out using aluminum sheets, precoated with silica gel 60F (Merck 5554). The plates were inspected by UV light. ¹H NMR, ¹³C NMR, and ³¹P NMR spectra were recorded on a Bruker Avance500 II, using the deuterated solvent and tetramethylsilane (¹H NMR and ¹³C NMR) or 85% phosphoric acid as internal standards (³¹P NMR). All chemical shifts are quoted in ppm, and all coupling constants (J) are expressed in Hertz (Hz). High-resolution electrospray mass spectra (HR-ESI-MS) were measured on a VG ProSpec triple focusing mass spectrometer. Cyclic voltammetry was performed using a 273 A potentiostat (Princeton Applied Research), wherein glassy carbon, platinum, and Ag wire act as the working electrode, the counter electrode and the pseudo-reference electrode, respectively. Samples were prepared in a CHCl₃ solution with tetrabutylammonium hexafluorophosphate (0.1 M) as the electrolyte at a scan rate of 100 mV s^{-1} , using ferrocene/ferronium $(F_c/F_c{}^{\scriptscriptstyle +})$ redox couple as an internal standard. UV/Vis spectra were recorded using a Cary 500 UV/Vis-NIR spectrometer. Fluorescent spectra were recorded using Horiba NanoLog Spectrofluorometer system. All chemicals were purchased from Sigma-Aldrich unless otherwise noted. Compounds 4a,^[6g] 5,^[6g] and PhP(SnMe₃)₂^[14d] were synthesized according to literature procedures.

Computational Methods

All calculations were performed using Q-Chem 3.2.^[17] The free software Avogadro and Q-Chem User Interface (QUI) were used as the molecular builder and the script editor, respectively. The geometry and energy level of the HOMO and the LUMO of the molecules were carried out at the DFT level^[18,19] using B3LYP/6–31G** basis set. DFT/B3LYP/6–31G** has been found to be an accurate formalism for calculating the structural and electronic properties of many molecular systems.^[20] No symmetry constraints were imposed during the optimization process. The HOMO/ LUMO orbitals were plotted with an isovalue of 0.01.

Synthesis of 4b

A mixture of 2,2',5-tribromo-4-iodobiphenyl (5) (517 mg, 1.00 mmol), boronic acid 6 (248 mg, 1.20 mmol), $[Pd(PPh_3)_4]$ (58 mg, 50 µmol), and K₃PO₄ (424 mg, 2.00 mmol) in *N*,*N*-dimethylformamide (DMF) (15 mL) was stirred under N₂ for 18 h at 100 °C. After removal of the solvent by evaporation, the residue was diluted with water and extracted with CH₂Cl₂. The organic layers was combined and dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The mixture was purified by column chromatography (silica gel, hexanes 100%) to give **4b** (380 mg, 69% yield) as a white solid. M.p. 208–209°C. ¹H NMR (CDCl₃, 298 K, 500 MHz): δ =7.73 (dd, *J*=7.5 Hz, 1.0 Hz, 1 H), 7.63 (s, 1 H), 7.58 (s, 1 H), 7.44 (dt, *J*=7.5 Hz, 1.0 Hz, 1 H), 7.42 (d, *J*=3.0 Hz, 1 H), 7.39 (d, *J*=3.0 Hz, 1 H), 7.34–7.31 ppm (m, 2 H); ¹³C NMR (CDCl₃, 298 K, 125 MHz): δ =143.3, 140.4, 139.7, 137.5, 135.3, 134.6, 132.8, 130.9, 129.9, 127.3, 125.5, 123.6, 123.3, 122.8, 122.0, 112.0 ppm. MS (HR-ESI): [*M*-Br]⁺ calcd for C₁₆H₈Br₄S: 468.7897; found: 468.7899 (100 %).

Synthesis of trans-2 a and trans-3 a

A mixture of tetrabromo-p-terphenyl (4a) (150 mg, 276 µmol), V-40 (33 mg, 138 µmol), and (Me₃Sn)₂PPh (450 mg, 1.02 mmol) in trifluorotoluene (15 mL) was heated under nitrogen at 125 °C for 40 h. The mixture was cooled to RT and the resulting precipitate was collected by filtration and washed with trifluorotoluene. The precipitate was dried under high vacuum to afford trans-2a (45 mg, 37% yield) as an off-white solid. M.p. 319–320 °C. ¹H NMR (CDCl₃, 298 K, 500 MHz): $\delta = 8.28$ (d, J =6.0 Hz, 2H), 7.97 (d, J=7.5 Hz, 2H), 7.71 (dd, J=7.5 Hz, 5.0 Hz, 2H), 7.48 (dt, J = 7.5 Hz, 1.0 Hz, 2H), 7.39–7.27 ppm (m, 12H). ¹³C NMR (CDCl₃, 298 K, 125 MHz): $\delta = 143.8$, 143.2, 142.9, 133.0 (d), 130.4 (d), 129.5, 128.8 (m), 127.7 (m), 123.2 (d), 121.5 ppm. ³¹P NMR (CDCl₃, 298 K, 212 MHz): $\delta = -9.43$ ppm. HR-MS (MALDI-TOF): [M]⁺ calcd for C₃₀H₂₀P₂: 443.1040; found: 443.0432 (100%). When a CDCl₃ solution of 2a was left at RT in a degassed J-Young NMR tube for an extended period of time, a new phosphorus signal slowly emerged, thereby indicating the *trans/cis* isomerization (*trans-*2**a**: -9.46 ppm; *cis-*2**a**: -9.60 ppm). 2a (40 mg, 92 µmol) was dispersed in CH2Cl2 (8 mL), water (4 mL), and H₂O₂ (50% in water, 0.4 mL), and the mixture was stirred at RT for 1 h. The mixture was extracted with CH_2Cl_2 (3×20 mL), the organic phase was washed successively with a saturated aqueous Na₂S₂O₃ solution and NaCl solution and dried over MgSO4. The solvents were evaporated under reduced pressure to afford 3a (42 mg, 98%) as a white solid. The filtrate from the phosphanylation reaction was evaporated to dryness to give a yellow residue, to which CH2Cl2 (15 mL), water (9 mL), and H2O2 (50% in water, 0.9 mL) were added and the mixture was stirred at RT for 1 h. The mixture was extracted with CH2Cl2 (3×20 mL), the organic phase was washed successively with saturated aqueous Na2S2O3 solution and NaCl solution and dried over MgSO4. The solvents were evaporated under reduced pressure and the residue was subjected to column chromatography (silica gel, CH₂Cl₂/Me₂CO 10:1 to 1:1) and afforded 3a (15 mg, 12% yield) as a white solid. The combined yield for 3a over the two steps (phosphanylation and oxidation) is 48 %. ¹H NMR (CDCl₃, 298 K, 500 MHz): $\delta = 8.16$ (dd, J = 10.0 Hz, 2.5 Hz, 2 H), 7.81 (dd, J = 7.5 Hz, 2.5 Hz, 2H), 7.76–7.70 (m, 6H), 7.63 (t, J=7.5 Hz, 2H), 7.58 (t, J= 7.5 Hz, 2H), 7.50–7.43 ppm (m, 6H). ¹³C NMR (CDCl₃, 298 K, 125 MHz): $\delta = 133.9$, 133.5 (m), 132.7, 131.8 (m), 131.1 (d), 129.0 (d), 128.9 (m), 122.4, 121.8 ppm (d). ³¹P NMR (CDCl₃, 298 K, 212 MHz): $\delta =$ 33.70 ppm. MS (HR-ESI): $[M+1]^+$ calcd for $C_{30}H_{20}O_2P_2$: 475.0939; found: 475.0935 (100%).

Synthesis of trans-2 b and trans-3 b

A mixture of tetrabromide (**4b**) (300 mg, 0.544 mmol), V-40 (65 mg, 0.272 mmol), and (Me₃Sn)₂PPh (710 mg, 1.63 mmol) in trifluorotoluene (15 mL) was heated under nitrogen at 125 °C for 50 h. The mixture was cooled to RT and the resulting precipitate was collected by filtration and washed with trifluorotoluene. The precipitate was dried under high vacuum to afford **2b** (60 mg, 24% yield) as an off-white solid. M.p. > 400 °C (dec.). ¹H NMR (CDCl₃, 298 K, 500 MHz): δ = 8.17 (d, *J* = 6.0 Hz, 1H), 8.06 (d, *J* = 5.0 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.69 (dd, *J* = 7.5 Hz, 6.0 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.44 (dt, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.42–7.31 ppm (m, 12 H). The ¹³C NMR spectrum was not acquired due to limited solubility. ³¹P NMR (CDCl₃, 298 K, 212 MHz): δ = -9.57, -23.56 ppm. MS (HR-ESI): [*M*+1]⁺ calcd for C₂₈H₁₈P₂S: 449.0204; found: 449.0204 (100%).

3a (40 mg, 89 µmol) was dispersed in CH₂Cl₂ (8 mL), water (4 mL), and H₂O₂ (50% in water, 0.4 mL), and the mixture was stirred at RT for 1 h. The mixture was extracted with CHCl₃ (3×20 mL), the organic phase was washed successively with saturated aqueous Na₂S₂O₃ solution and NaCl solution and dried over MgSO₄. The solvents were evaporated under reduced pressure to give **3b** (44 mg, 92% yield) as a white solid.

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The filtrate from the phosphanylation reaction was evaporated to dryness to give a brown residue, to which CH₂Cl₂ (30 mL), water (10 mL), and H_2O_2 (50% in water, 1 mL) were added and the mixture was stirred at RT for 1 h. The mixture was extracted with CH2Cl2 (3×10 mL), the organic phase was washed successively with saturated aqueous $Na_2S_2O_3$ solution and NaCl solution and dried over MgSO4. The solvents were evaporated under reduced pressure and the residue was subjected to column chromatography (silica gel, CH2Cl2/Me2CO 10:1 to 1:1) to afford 3b (35 mg, 13 % yield) as a white solid. The combined yield for 3b over the two steps (phosphanylation and oxidation) is 35 %. ¹H NMR (CDCl₃, 298 K, 500 MHz): $\delta = 8.08$ (dd, J = 10.0 Hz, 2.5 Hz, 1 H), 7.99 (dd, J =10.0 Hz, 2.5 Hz, 1 H), 7.82 (dd, J = 5.0 Hz, 2.5 Hz, 1 H), 7.78 (dd, J =7.5 Hz, 2.5 Hz, 1H), 7.75-7.68 (m, 5H), 7.63-7.53 (m, 3H), 7.53 (t, J= 2.0 Hz, 1H), 7.49–7.42 ppm (m, 5H); ¹³C NMR (CDCl₃, 298 K, 125 MHz): δ=145.2, 145.0, 144.5, 143.7, 142.0 (dd)*, 140.8, 140.6, 139.3 (dd)*, 139.0, 138.2, 136.2, 125.3, 133.9 (d), 133.2, 132.7 (m)*, 132.5 (d)*, 132.3(d)*, 131.1 (dd)*, 130.7, 130.1 (m)*, 128.8 (m)*, 123.1 (t)*, 122.9 (t)*, 121.6 (d)*, 118.0 ppm (d)*. The star (*) symbols indicate multiplets due to C–P coupling. ³¹P NMR (CDCl₃, 298 K, 212 MHz): $\delta = 32.91$, 20.52 ppm. MS (HR-ESI): $[M+1]^+$ calcd for $C_{28}H_{18}O_2P_2S$: 481.0503; found: 481.0504 (100%).

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FULL PAPER



A new class of bisphosphole-bridged ladder oligo(*p*-phenylene)s have been synthesized by a four-fold free-radical phosphanylation reaction of a tetrabromo *p*-terphenylene or biphenylthiophene. The oxides of the phospholes are shown to be strong fluorophores that could be used as potential *n*-type building blocks for organic semiconducting materials.

Oligophenylenes

David Hanif	, Andrew Pun,	
Yi Liu*		

Synthesis and Properties of Bisphosphole-Bridged Ladder Oligophenylenes

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