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2,5-Di(2-pyridyl)phospholes: model compounds for the engineering of π-conjugated donor–acceptor co-oligomers with a chemically tunable HOMO–LUMO gap

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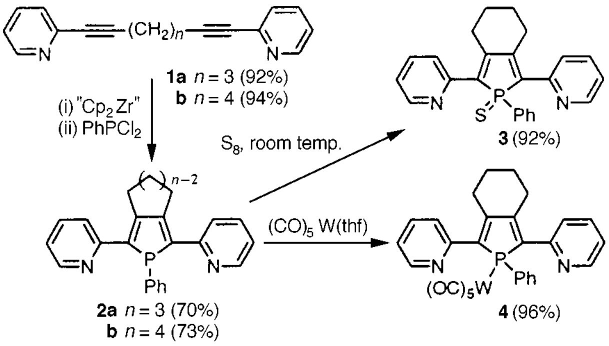
2,5-Di(2-pyridyl)phospholes possess an extended π-conjugated system with a charge transfer structure; high yielding chemical modifications involving the phosphorus atom allow fine tuning of the HOMO–LUMO gap.

The control of both the structure and HOMO–LUMO gap of linear π-conjugated oligomers is the focus of considerable interest. These compounds have been investigated in order to simulate the electronic and electrochemical properties of the corresponding polymers and they are now emerging as efficient molecular wires in electronics applications.[1] Group 15 and 16 heterocyclopentadienes have been widely used as building blocks for the design of well-defined linear π-conjugated oligomers.[1] However, there are only a few instances of phospholes having been used for such a purpose,[2] although they display particular properties which make them attractive synthons. Firstly, the aromaticity of phospholes is generally much lower than that of furan, pyrrole or thiophene.[3] This is a consequence of the inherent pyramidal geometry of the tricoordinate phosphorus atom which disrupts efficient orbital interaction within the five-membered ring. This property should have an impact on the molecular engineering of the HOMO–LUMO separation of linear π-conjugated systems since π-electron delocalization along the chain is favoured when the backbone features heterocycles of low resonance energy.[1a,3c] Secondly, and in contrast to thiophene or pyrrole, phospholes possess a heteroatom which retains a versatile reactivity.[3a,b] This may offer the possibility of tuning the HOMO–LUMO gap *via* chemical modifications. Recently, Mathey *et al.* prepared various α-oligophospholes (n = 2–4) and oligomers containing α-thienyl- or α-furyl-α-phospholyl links.[2a–e] X-Ray diffraction studies performed on these derivatives showed that they deviate notably from planarity. This rotational disorder prevents extended π-conjugation because the orbital overlap varies approximately with the cosine of the twist angle. A recent strategy to effect a coplanar arrangement in linear π-conjugated polymers involved constructing alternating [A-B] derivatives where the A and B units are electron-deficient and electron-rich, respectively.[4] These derivatives are considered to have a charge-transfer structure with double bond character between the A-B units. As the parent phosphole can be considered as a very electron-rich heterocyclopentadiene,[3c] we decided to investigate the preparation of derivatives based on alternating pyridine and phosphole rings with a well defined 2,5-linkage. Herein, we describe an efficient synthesis of the simplest model, namely a 2,5-di(2-pyridyl)phosphole, and we show the possibility of tuning its HOMO–LUMO gap through chemical modifications.

The target phospholes were prepared according to Fagan's method[5] which involves the reaction of zirconacyclopentadienes with dihalogenophosphines. In order to obtain the desired 2,5-substitution pattern, diynes **1a**,**b** possessing a flexible spacer were employed (Scheme 1).[6] A Sonogashira coupling of hexa-1,7-diyne with 2-bromopyridine allowed an efficient and large-scale preparation of derivatives **1a** (92%) and **1b** (94%). These compounds reacted at −78 °C with 'zirconocene'[6] *via* a regioselective ring-closing diyne coupling to give the corresponding zirconacyclopentadienes which were characterised by NMR spectroscopy. Isolation of the zirconium-containing metallacycles was not necessary; addition of 1.1 equiv. of $PhPCl_2$ to the reaction mixture at −78 °C afforded the desired phospholes **2a**,**b** in a 'one-pot' procedure. They were isolated as air-stable yellow powders after purification by chromatography (alumina) in 70 and 73% yield, respectively. Phospholes **2a**,**b** have been characterised by high resolution mass spectrometry and elemental analyses and they exhibit the expected NMR spectroscopic data. In the ^{13}C NMR spectrum, the endocyclic P–C_α carbon atoms of **2a** give a singlet, which is not unusual for phospholes,[2e,3a,b] while the other endocyclic carbon and the C_{ipso} atoms of the aromatic rings of compounds **2a**,**b** all appear as doublets with classical J_{PC} coupling constants.



Scheme 1

The crystal structure of derivative **2b** (Fig. 1) reveals that, as expected, the phosphorus atom is strongly pyramidalized [Σ(CPC angles) = 299.3°] and that the endocyclic P–C bond lengths [1.801(4) and 1.804(4) Å] approach that of a P–C single bond (1.84 Å). These data compare well with those observed for a 2,5-dialkynylphosphole[2c] [Σ(CPC angles) = 292.4°; P–C,

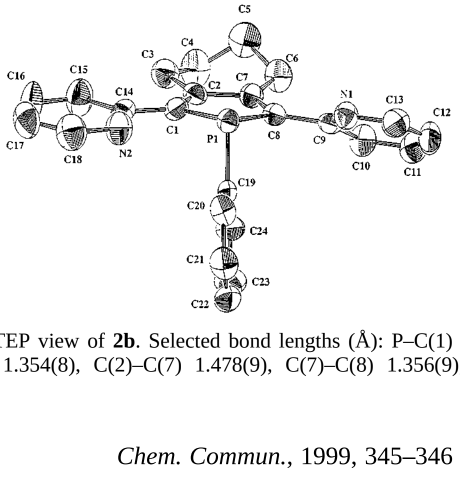


Fig. 1 ORTEP view of **2b**. Selected bond lengths (Å): P–C(1) 1.806(6), C(1)–C(2) 1.354(8), C(2)–C(7) 1.478(9), C(7)–C(8) 1.356(9), C(8)–P 1.806(6).

1.815–1.821 Å] and 1,2,5-triphenylphosphole[7] [P–C, 1.822 Å], two compounds for which it is proposed that ring delocalization is almost switched off, with the endocyclic subunit being conjugated with the C_2 and C_5 substituents.[3a,b] Of particular importance, the two bond lengths between the pyridyl rings and the slightly puckered phosphole ring [1.464(5) and 1.467(5) Å] have values that lie between those associated with single and double bonds, and the dihedral angles (25.6 and 7.0°) are relatively small, allowing an extended π-conjugation. These structural data clearly show that in 1-phenyl-2,5-di(2-pyridyl)phospholes the dienic moiety of the phosphole ring is conjugated with the two pyridine rings and not with the phosphorus atom.

The UV–VIS data for compounds **2a**,**b** and of the related 2,5-diphenylphosphole **2c** are given in Table 1. Derivative **2c** was isolated in only 10% yield according to the strategy presented in Scheme 1 starting from 1,8-diphenylocta-1,7-diyne.[6b] Interestingly, the λ_{max} observed for 2,5-pyridylphospholes **2a**,**b** are comparable, and notably longer to that of the 2,5-diphenylphosphole **2c** ($\Delta\lambda_{max} > 36$ nm). This observation, which is in line with the conclusion drawn from the solid state structure, highlights the importance of the alternating electron-deficient/electron-rich ring structure of derivatives **2a**,**b** which favours the delocalization of the π-system.

The next question was whether chemical transformation involving the phosphorus atom, which is not involved in the π-delocalized system, would significantly modify the HOMO–LUMO gap? Treatment of phosphole **2b** with elemental sulfur and W(CO)$_5$(thf) afforded derivatives **3** and **4**, respectively, in near quantitative yields. The molecular formulae of **3** and **4** were established by multinuclear NMR spectroscopy, high resolution mass spectrometry and elemental analyses. These chemical transformations resulted in a blue shift of λ_{max} relative to phosphole **2b** (Table 1), the effect being more pronounced for the sulfide **3** ($\Delta\lambda_{max} = 26$ nm) than for the complex **4** ($\Delta\lambda_{max} = 17$ nm). In order to evaluate the relative contribution of geometric effects (degree of planarity) on values of λ_{max} in this series, derivative **4** was subjected to an X-ray diffraction study (Fig. 2). The structural data for complex **4**[†] are very similar to those observed for the free phosphole **2b**, suggesting that the coordination of the metal did not result in a dramatic steric perturbation. As observed for the free ligand, the three heteroatoms are pointing in the same direction. Note that the sum of the CPC angles is 298.7° (**2b**, 299.3°) and that the two endocyclic P–C bonds [1.818(4) and 1.824(4) Å] are slightly longer than those of **2b** [1.801(4) and 1.804(4) Å]. The twist angles between the pyridyl and the phosphole rings (11.3 and 0.0°) are smaller than those observed for the non-coordinated phosphole **2b** (25.6 and 7.0°). Since the pyridine–phosphole–pyridine moiety of **2b** is more planar when coordinated, the origin of the blue shift observed on going from **2b** to **4** is likely to be due to electronic factors. It seems reasonable to propose that both oxidation with sulfur and the coordination of the phosphorus atom decreases the electron-density of the phosphole ring, leading to a decrease in the degree of charge transfer in the π-linear conjugated pyridine–phosphole–pyridine system. As expected, this effect is more pronounced for sulfide **3** than for complex **4**.

Table 1 UV–VIS data in THF for compounds **2a**–**c**, **3** and **4**

Compound	λ_{max}/nm	log ε
2a	390	3.96
2b	395	4.02
2c	354	4.20
3	364	3.28
4	373	4.01

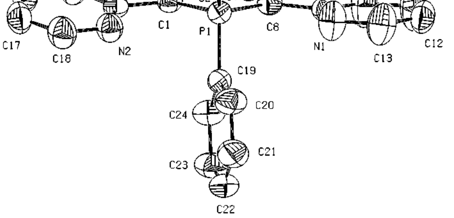


Fig. 2 ORTEP view of **4**. CO ligands have been omitted for clarity. Selected bond lengths (Å): P–C(1) 1.820(5), C(1)–C(2) 1.356(5), C(2)–C(7) 1.466(8), C(7)–C(8) 1.352(5), C(8)–P 1.819(4).

Derivatives **2a**,**b** and **4** are air-stable in the solid state and also in THF solution for days. Preliminary stability tests by thermogravimetric analysis and differential scanning calorimetry under nitrogen show that derivative **2a** (mp 186 °C) and **2b** (mp 192 °C) are stable up to 201 and 211 °C, respectively, whereas complex **4** (mp > 204 °C) decomposes at 204 °C.

The synthesis of alternating pyridine–phosphole co-oligomers with a well-defined 2,5-linkage is under active investigation.

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Notes and references

[†] *Crystal data* for **2b** and **4**: Samples were studied on a CAD4 NONIUS diffractometer with graphite monochromatized Mo-Kα ($\lambda = 0.71073$ Å) at 293(1) K. The whole structures were refined with SHELXL97. ORTEP views with 50% probability were realized with PLATON98.

Crystal data for **2b**: $C_{24}H_{21}N_2P$, $M = 368.42$; crystal size 0.32 × 0.22 × 0.18 mm, monoclinic, space group $P2_1/n$, $a = 8.619(2)$, $b = 14.127(2)$, $c = 16.116(4)$ Å, $\beta = 104.53(6)°$, $U = 1899.5(7)$ Å^{-3}, $Z = 4$, $D_c = 1.288$ g cm^{-3}, $\mu = 1.55$ cm^{-1}, $F(000) = 776$, 4398 reflections measured, 4128 were independent [1643 with $I > 2\sigma(I)$], 245 variables refined, $R_1 = 0.0654$ ($wR_2 = 0.1221$).

Crystal data for **4**: $C_{29}H_{21}N_2O_5PW$, $M = 692.33$; crystal size 0.40 × 0.22 × 0.12 mm, triclinic, space group $P\bar{1}$; $a = 9.943(2)$, $b = 11.122(9)$, $c = 13.590(5)$ Å, $\alpha = 78.34(3)$, $\beta = 72.90(2)$, $\gamma = 66.90(3)°$, $U = 1315(1)$ Å^{-3}, $Z = 2$, $D_c = 1.749$ g cm^{-3}, $\mu = 44.96$ cm^{-1}, $F(000) = 676$, 5715 reflections measured, 5377 were independent [4764 with $I > 2\sigma(I)$], 343 variables refined, $R_1 = 0.0278$ ($wR_2 = 0.0686$).

CCDC 182/1131. Crystallographic data is available in CIF format from the RSC Web site, see: http://www.rsc.org/suppdata/cc/1999/345/

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