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The Rise of Organophosphorus Derivatives in π-Conjugated Materials Chemistry

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Abstract This chapter concerns the synthesis and properties of π-conjugated oligomers and polymers containing phosphorus moieties, an area of increasing interest since the early 1990s. Emphasis is placed on the versatility engendered by the incorporation of phosphorus, especially with regard to tuning the photophysical and electronic characteristics of the new materials. This review also describes the first applications of these P-based materials in optoelectronics (nonlinear optics, organic light emitting diodes, *etc.*).

Keywords π-Conjugated systems · Phosphorus · Phosphaalkenes · Phospholes · Optoelectronics

Abbreviations

Alq$_3$	Aluminium tris(2-hydroxyquinolate)
β	Quadratic hyperpolarisability
DCJTB	4-(Dicyanomethylene)-2-tert-butyl-6 (1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran
DR1	Disperse red 1
Eg	HOMO-LUMO gap
EL	Electroluminescence
ITO	Indium-tin-oxide
NLO	Nonlinear optic
α-NPD	*N*′-Diphenyl-*N*, *N*′-bis(α-naphthyl)-1,1′-biphenyl-4,4′-diamine
OLED	Organic light emitting diode
PDI	Polydispersity index
PPV	*para*-Phenylene-vinylene
T_g	Glass transition temperature

1
Introduction

In the last decade, π-conjugated oligomers and polymers based on a backbone of sp^2-bonded carbon atoms have attracted huge interest owing to their potential application in electronic devices (e.g. light-emitting diodes, thin film transistors, photovoltaïc cells, laser dyes, NLO materials, etc.) [1]. These conjugated organic materials combine the advantages of being lightweight with ease of processing and offer the potential to have their optical and electronic properties tuned by exploiting the enormous versatility and scope of organic chemistry. Significantly, oligomers are not only model compounds used for elucidating the properties of the corresponding polymers, but can also themselves be used as advanced materials for devices (e.g. OLEDs, field effect transistors, etc.) [1].

The simplest organic π-conjugated polymer, polyacetylene (**A**) (Fig. 1) can exhibit conductivities in the metallic regime upon doping [2]. Following this seminal discovery in the 1970s, there has been intense research into the preparation of new linear-conjugated frameworks of increased robustness and enhanced performance. Aromatic building blocks have been widely used due both to their high stability and ease of substitution, allowing chemical engineering on the molecular scale. A prominent class of organic material of this type are

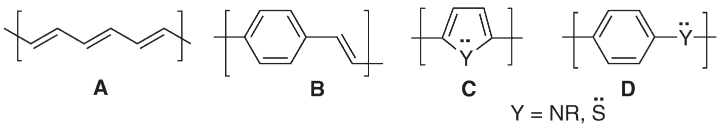


Fig. 1 Structure of classical organic π-conjugated systems

the poly(*p*-phenylenevinylene)s (**B**) (PPVs), which are probably nowadays the most studied π-conjugated systems [1]. The discovery in 1990 that PPVs are electroluminescent was a milestone in the field of molecular materials, with modified PPVs now being used commercially for the manufacture of OLEDs [3].

A related, but equally fruitful strategy for the preparation of new opto-electronic materials, involves the incorporation of heteroatoms into the backbone of conjugated polymers, with two general approaches being possible. The first involves the use of aromatic heterocyclopentadiene subunits, such as pyrrole or thiophene. Oligomers and polymers (**C**) (Fig. 1) are two important classes of conjugated systems offering a combination of novel electronic properties, excellent stabilities and structural diversity. Thiophene-based derivatives (**C**) are among the most widely investigated π-conjugated systems and have been used in numerous applications (e.g. electrical conductors, sensors, NLO materials, etc.) [1].

The second strategy is to replace the vinylene bridges of PPV (**B**) by a heteroatom possessing a lone pair that can participate in the π-conjugation [4]. Representative examples of this class of derivative (**D**) (Fig. 1) are the polyanilines and poly(*p*-phenylenesulfide) [1a,b].

Clearly, the development of new advanced organic materials is directly related to the ability of chemists to design and create novel structures and, subsequently, to establish structure–property relationships, with a view to further honing the desired attributes of the materials. It is now well recognised that the optical and electronic properties of macromolecules (**A**)–(**D**) vary significantly with both the magnitude of their HOMO-LUMO gaps and the electron density associated with their carbon backbones [1e–h, 5]. The most commonly used approach for tuning these two parameters consists of introducing pendent substituents with specific electronic and/or steric properties. However, derivatives (**C**) and (**D**) offer another unique tuning mode, which arises due to the presence of heteroatomic moieties in the main polymer backbone. This opens up the possibility of incorporating heteroatoms with different properties (such as electronegativity, polarisability, size of atoms and orbitals, energies of s and p valence orbitals, hybridisation, etc.), which allows materials engineering to be undertaken at the molecular level. Nitrogen and sulphur have been used extensively for such purposes. In marked contrast, phosphorus has received little attention until very recently. This is rather surprising, since organophosphorus derivatives offer a variety of structures and exhibit a versatile reactivity [6, 7].

This account will summarise results in the development of π-conjugated materials incorporating phosphorus moieties with emphasis on the conceptual design and specific properties that result directly from the presence of the P-atom. Polyphosphazenes, which are the most familiar synthetic polymers incorporating phosphorus [8], will not be included in this review since they do not display the type of π-conjugation as sought in systems (**A**)–(**D**).

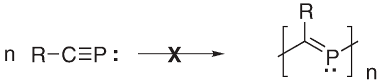
2

Macromolecules Containing Phosphaalkene Moieties

The properties and reactivity of low-coordinate carbon and phosphorus species are very similar in many regards [6]. The P=C unit is almost apolar, and its conjugative properties are comparable to those of the C=C bond [6, 9]. Thus, using this diagonal analogy, the simplest π-conjugated system incorporating phosphorus that can be envisaged would be poly(phosphaalkyne) (**F**) (Fig. 2), the P-containing analogue of polyacetylene. Indeed, it has been established that phosphaalkynes (**E**) that lack sterically demanding R substituants (e.g. those bearing merely R=H, Ph) can undergo thermally induced polymerisation reactions [6, 7]. However, the resulting macromolecules feature mainly saturated trivalent P-fragments with only some phosphaalkene moieties [10]. In contrast, thermolysis of the more hindered *t*-BuC≡P affords a mixture of tetraphosphacubane and other cage compounds [6, 11a]. Alternatively, in the presence of metal complexes, several types of oligomer can be formed including 1,3,5-triphosphabenzene, tricyclic derivatives or cage compounds [6, 11b,c].

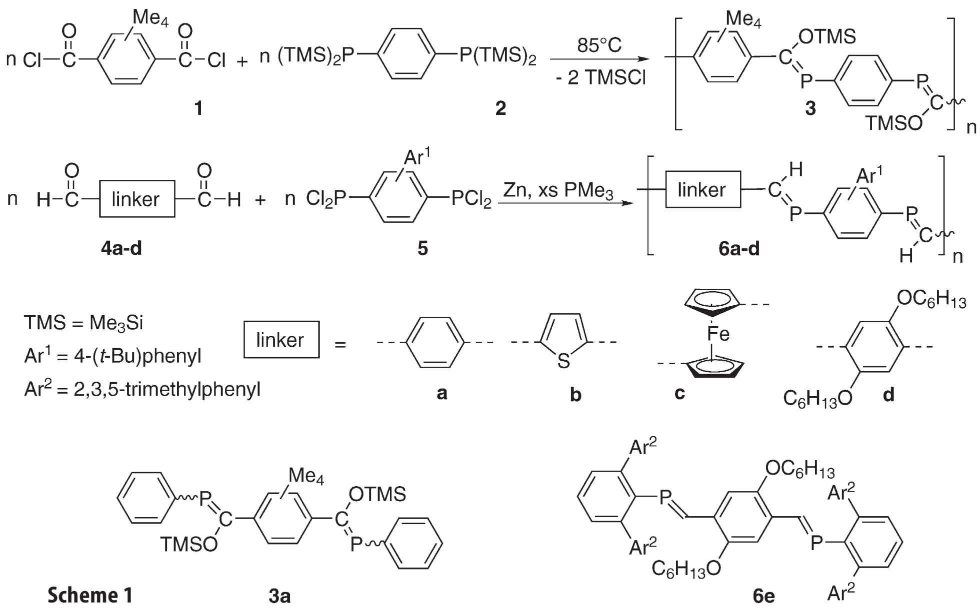
Kinetically stabilised 1,3-diphosphabutadienes are known [7, 12], but the formation of oligomers or polymers (**F**) (Fig. 2) is probably hampered by the quite low thermodynamic stability of the P=C π-bond (43 kcal mol^{-1} versus 65 kcal mol^{-1} for ethylene). Hence, by once again invoking the carbon-phosphorus analogy [6], incorporation of an aromatic aryl group into the backbone of the polymers appeared as a clear strategy for increasing the stability of these π-conjugated systems. Indeed, the first π-conjugated macromolecule containing phosphaalkene moieties was the PPV-analogue (**3**) (Scheme 1) [13]. This compound was prepared by thermolysis of bifunctional derivatives (**1**) and (**2**), a process involving thermodynamically favourable [1,3]-silatropic rearrangements of an intermediate acylphosphine to phosphaalkene moieties [7]. According to NMR measurements, macromolecule (**3**) is a mixture of *Z* and *E* isomers, with the degree of polymerisation varying from 5 to 21. Remarkably, thermogravimetric analysis revealed that this polymer is stable up to 190 °C under an atmosphere of dry helium [13].

The family of P=C-containing polymers was considerably broadened following the introduction of a highly efficient synthetic strategy based on intermediate "di-phosphaWittig" reagents [14]. Polymers (**6a–d**) featuring different linkers were readily obtained from aryl-substituted derivative (**5**) (Scheme 1) [15]. The soluble macromolecule (**6d**) contains an average of 12 phosphaalkene moieties per chain (n=6) in an *E*-configuration. Remarkably, although (**6d**) decomposes slowly in solution, it is stable under air for a week in the solid state [15].



E **F**

Fig. 2 Structure of poly(phosphaalkene)



Scheme 1

Derivatives (**3**) and (**6d**) (Scheme 1) exhibit broad absorption bands with values of $\lambda_{\max}$ of 328–338 nm and 445 nm, respectively. In both cases, these bands extend into the visible region with high optical end absorption, λ_{onset} ca. 400 nm for (**3**) and ca. 540 nm for (**6d**), revealing rather low optical HOMO-LUMO separations. These low energy transitions are not observed for model diphosphaalkenes (**3a**) and (**6e**) (Scheme 1) featuring the same substitution pattern [13, 15]. Together, these data are clearly in favour of extended π-conjugation involving the phosphaalkene moieties in oligomers (**3**) and (**6d**). Notably, (**6d**) showed fluorescence with broad emission centred around 530 nm [15]. However, the fluorescence intensity is weak compared to that of the corresponding all-carbon analogues.

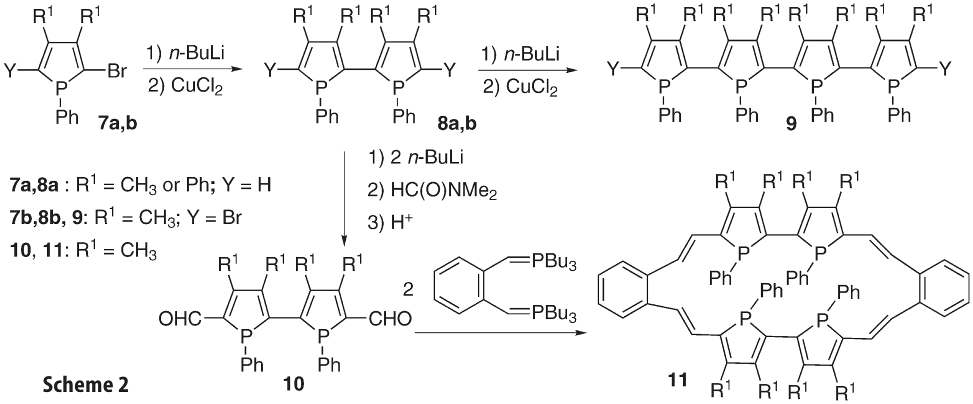
These preliminary results show that oligomers incorporating phosphaalkene moieties are readily available by different routes and suggest that the P=C units exhibit efficient conjugative ability. Although structure/property relationships have still to be established, it is clear that macromolecules of increased stability, higher degree of polymerisation and controlled chain length are exciting targets.

3
Macromolecules Containing Phosphole Rings

The extraordinary impact of thiophene and pyrrole derivatives for the engineering of π-conjugated materials, naturally led to the consideration of phospholes as potential building blocks. However, phosphole exhibits electronic properties that are markedly different from those of the highly aromatic thiophene and pyrrole rings [16]. The tricoordinate phosphorus atom of phosphole possesses a pyramidal geometry, with a lone pair having pronounced s-character. These geometric and electronic features prevent an efficient endocyclic conjugation of the electron-sextet. In fact, delocalisation within the phosphole ring arises from a hyperconjugation involving the exocyclic P-R σ-bond and the π-system of the dienic moiety [17]. The consequence, which was confirmed by experimental and theoretical studies [16], is that phosphole exhibits low aromatic character. This property, which sets phosphole apart from thiophene and pyrrole, may be of great interest for the tailoring of π-conjugated materials since conjugation is enhanced for macromolecules built from monomer units exhibiting low resonance energies [1h, 5a]. This phenomena is nicely illustrated by theoretical work that showed that the energy gaps *E*g of oligo(phosphole)s are significantly lower than those of the corresponding oligo(pyrrole)s (ΔEg=0.9–1.6 eV) or oligo(thiophene)s (ΔEg=0.5–0.8 eV) [5a, 18a].

3.1
Oligo(phosphole)s and Derivatives

Phospholes can readily be prepared on a large scale and are known with a vast range of substituants [6, 16b,c]. However, the synthesis of oligo(phosphole)s analogous to (**C**) (Fig. 1) is a real synthetic challenge since the low aromatic character of phosphole prevents the functionalisation of the P-Cα,α′ carbon atoms via electrophilic substitution and inhibits their preparation using electropolymerisation. As a consequence, no poly(phosphole)s have yet been reported, although bi- and tetra-phospholes have been prepared by stepwise routes (Scheme 2).



Scheme 2

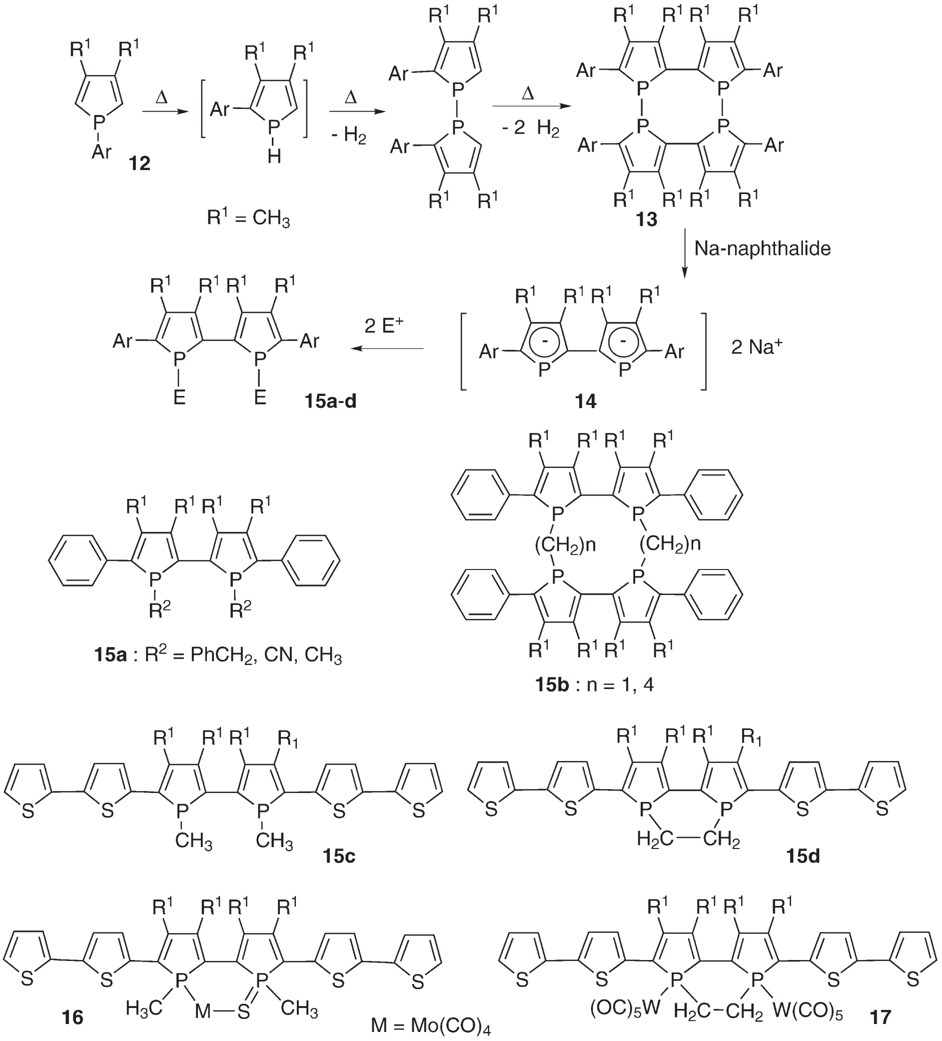
The discovery that the oxidative coupling of 2-lithiophosphole, obtained from (**7a**), led to biphosphole (**8a**) (Scheme 2) was a breakthrough [19], opening the way to oligo(phosphole)s. This very efficient methodology has been applied to the preparation of the quater(phosphole) (**9**), the longest oligo(phosphole) known to date, using bromo-capped biphosphole (**8b**) (Scheme 2) [20]. Di- and tetra-(phosphole)s are generally obtained as mixtures of diastereoisomers, due to the presence of stereogenic P-centres.

X-ray diffraction studies of (**8a**) (R^1=CH_3) and (**9**) revealed that these derivatives suffer from rotational disorder. The dihedral angle between the two phosphole rings in (**8a**) is about 46.6° [21], while in (**9**) the twist angle between the two inner rings is 25.1°, and that between the outer pair is 49.7° [20]. These distortions should preclude these oligo(phosphole)s from possessing extended π-conjugated systems. However, the twists are probably due to packing effects in the solid state since the colour of these compounds varies from pale yellow (**8a,b**) to deep orange (**9**), suggesting rather high λ_{max} values and, consequently, low optical HOMO-LUMO gaps. The red shift observed on going from (**8a,b**) to (**9**) hints that, in line with theoretical studies [5a, 18], the energy gap of oligo(phosphole)s seems to decrease with increasing chain length.

Bromo-capped biphosphole (**8b**) is also the precursor of cyclic derivatives, as illustrated by the synthesis of the fully unsaturated macrocycle (**11**), via a Wittig reaction involving the 5,5′-bis(carboxaldehyde) (**10**) (Scheme 2) [22]. An X-ray diffraction study revealed that macrocycle (**11**) is distorted, with an *all-trans*-disposition of the four P-phenyl substituants.

Other conjugated systems featuring biphosphole cores have also been prepared by an elegant and efficient method, which starts from the readily available 1-arylphospholes (**12**) (Scheme 3) [23]. Thermolysis of (**12**) yields the cyclic tetramer (**13**) via a series of concerted [1,5]-sigmatropic shifts of Ar, H and P, together with two dehydrogenation steps (Scheme 3). The reductive cleavage of the P-P bonds of (**13**) gives the 2,2′-biphospholide dianions (**14**), which act as bidentate nucleophiles towards a wide variety of electrophiles, allowing for the preparation of oligomers (**15a-d**) [23, 24]. Note that 2,2′-biphospholes lacking from substituent at the 5,5′-postions are also accessible via the dehydrohalogenation of the corresponding 1,1′-di(halogenophospholium) salts.

The versatility of this latter synthetic approach is underlined by the diversity of substituents that can be included on the P-ring (e.g. phenyl, dithienyl) and the secondary structures possible (namely linear or cyclic). Furthermore, the reactivity of the P-atom of the phosphole ring is retained in these compounds (**15a–d**), affording ready access to derivatives including those bearing transition metal fragments (**16**) and (**17**) [24]. Complexes (**16**) and (**17**) were obtained as single diastereoisomers and were studied by X-ray diffraction [24]. In both compounds, the bithienyl moieties are almost coplanar, the angles between the phosphole and the thiophene rings being rather small (15.2°–24.3°), while the phosphole-phosphole interplane twist angles are somewhat larger: 66.26±0.14° for (**16**) and 55.6±0.3° for (**17**). The lengths of the C–C links between the rings (1.42–1.47 Å) are in the range expected for Csp^2–Csp^2 single bonds. These data suggest a certain degree of delocalisation of the π-system over the six heterole rings, in spite of the rather large twist angles. This assumption is supported by an electrochemical study performed on the bis(thioxophosphole)



Scheme 3

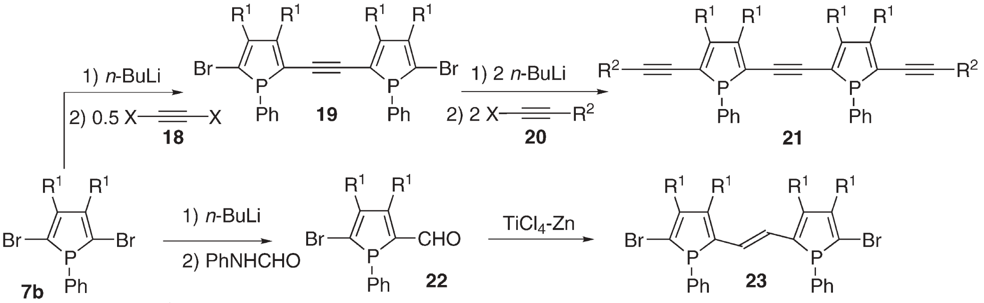
derivatives of (**15a**) and (**15c**), which revealed that the anion-radicals and dianions exhibit relatively good stabilities and that the nature of the 2,5-biphosphole substituents (phenyl versus bithienyl) has a profound influence on the electrochemical behaviour of these species [23c].

In conclusion, a variety of linear or cyclic oligo(phospholes)s and their derivatives are accessible via a set of efficient synthetic strategies. The potential of these compounds as advanced π-conjugated systems is broadened by the presence of reactive trivalent P-centres, which allow a range of additional chemical modifications to be achieved. However, elucidation of structure–property relationships for these derivatives is still needed.

3.2
Co-Oligomers and Derivatives

3.2.1
Phospholes Linked by All-Carbon Bridges

Macromolecules in which aromatic building blocks are linked by ethenyl or ethynyl bridges (e.g. PPV, oligo(thienylenevinylene)s [1h, 25], poly(*para*-phenyleneethynylene)s [26], etc.) are versatile molecular wires that have found numerous applications in the field of OLEDs, NLOs, sensors, polarisers for liquid crystal displays, etc. Surprisingly though, very few derivatives incorporating phosphole rings linked by a double or a triple bond have been reported to date. Initially, access to oligo(phospholyleneethynylene)s was hampered since 2,5-dibromophosphole (**7b**) (Scheme 4) and its iodo-bromo analogue were found not to undergo Stille-type couplings with 1-stannyl-alkynes [27]. Again, a route to the target co-oligomers was made possible using 2-lithiophospholes. Treating the intermediate 2-lithio-5-bromophosphole with (*tert*-butylsulfonylacetylene **18**) (Scheme 4) gave rise to derivative (**19**) that can be converted into (**21**) using the same synthetic strategy employing trimethylsilyl-protected alkyne (**20**) (Scheme 4). The modest yields of these reaction sequences (typically around 30%) precludes using this approach to prepare polymers starting from (**18**) and (**19**).



$R^1 = CH_3$ (**7b, 19**, **21**, **22**, **23**) or Ph (**7b**, **22**, **23**)

18 : X = $t\text{-}BuSO_2$; **20** : $R^2 = SiMe_3$, X = $p\text{-}CH_3C_6H_4SO_2$

Scheme 4

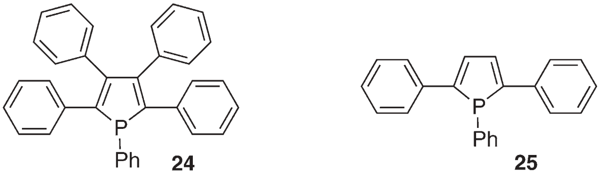
Only the simplest oligo(phospholylenevinylidene), i.e. two phosphole rings linked by an ethenyl bridge, is known to date. The aldehyde (**22**) (Scheme 4), readily obtained from the corresponding 2-lithiophospholes, undergo McMurry coupling to afford the *E*-derivatives (**23**) in high yields [19b]. The efficiency of this synthetic route from (**7b**) to (**23**) underlines the robustness of the phosphole ring!

Notably, derivatives (**19**), (**21**) and (**23**) are all orange in colour, suggestive of the presence of an extended π-conjugated system [19b, 27]. This is supported by an X-ray diffraction study of 2,5-di-(phenylethynyl)phosphole, which revealed that the C–C linkages between the P-ring and the C≡C moieties are rather short, 1.423(3)–1.416(3) Å [27].

Thus, compounds (**19**), (**21**) and (**23**) are potential building blocks for the preparation of longer oligomers or polymers since they possess reactive termini. However, further progress towards longer oligomers or polymers is currently hampered by the low efficiency of coupling reactions involving phosphole rings.

3.2.2
Alternating Phosphole–Heterole Structures

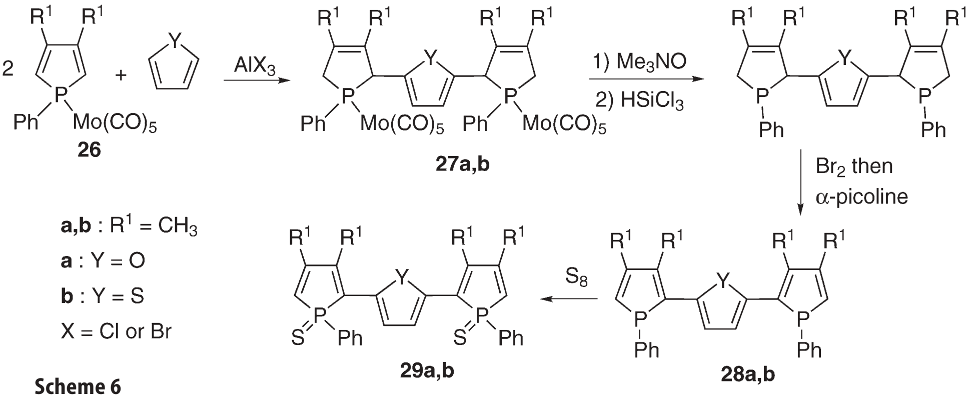
Amazingly, the 2,5-diphenylphospholes (**24**) and (**25**) (Scheme 5), which were the first phospholes to be prepared in the early sixties [28], exhibit extended π-conjugated systems. Both derivatives show absorption in the visible region, λ_{max} 358 nm for (**24**) and 374 nm for (**25**), and Stoke's shifts varying from 100 nm for (**24**) to 120 nm for (**25**) [29]. Furthermore, X-ray analysis of compound (**25**) revealed that the three rings are almost coplanar [30]. However, this important structural observation was not considered at that time. Consequently, the interest in the use of phospholes as building blocks for the construction of π-conjugated systems only dates from the 1990s.



Scheme 5

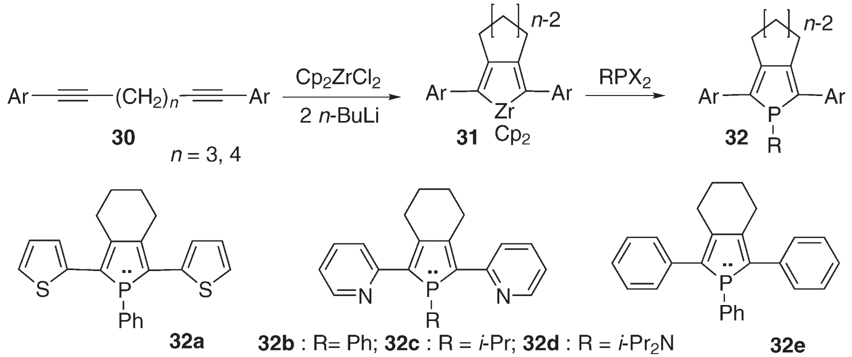
In 1991, Mathey et al. prepared a series of 2,5-(diphosphole)-thiophene and -furan oligomers (**28a,b**), and the corresponding thiooxo-derivatives (**29a,b**) (Scheme 6) [31]. The key step in their synthesis is an electrophilic substitution performed on the protected phosphole (**26**). Adducts (**27a,b**) [31] were then transformed into the σ^3,λ^3-phospholes (**28a,b**) through a classical deprotection–bromination–dehydrohalogenation sequence [32]. No UV-vis or electrochemical data are reported for these co-oligomers, however, the colour of the crystalline derivatives (**28a**) (orange) and (**28b**) (bright yellow), suggest relatively high values of λ_{max}. Note that an X-ray diffraction study of (**28b**) showed that one phosphole ring is coplanar with the central furan unit, while the second P-heterocycle is twisted (dihedral angle, 40.1±0.1°). The two inter-ring C–C bond distances, 1.452(4) and 1.461(6) Å, lie between those observed for C–C single and double bonds, a feature that is in favour of a certain degree of delocalisation [31].

The first systematic evaluation of the optical and electrochemical properties of phosphole-based co-oligomers, and subsequent optimisation of their struc-



Scheme 6

ture for optoelectronic applications, was undertaken with 2,5-di(heteroaryl)-phospholes (**32**) (Scheme 7). These compounds are not accessible by electrophilic substitution on protected phosphole (**26**) (Scheme 6), since this reaction gives rise to 2,4-dithienylphospholene [31]. However, they are readily prepared via a general organometallic route known as the Fagan–Nugent method [33].



Scheme 7

The key to obtaining the desired 2,5-substitution pattern is to perform the metal-mediated oxidative coupling of diynes (**30**) possessing a $(CH_2)_3$ or a $(CH_2)_4$ spacer (Scheme 7) [34,35,36,37]. The zirconacyclopentadienes (**31**) are extremely air- and moisture-sensitive derivatives that react with dihalogenophosphines to give the corresponding phospholes (**32a–e**) in medium to good yields (Scheme 7). This route is highly flexible since it not only allows electron-deficient and electron-rich rings to be introduced in the 2,5-positions, but also permits the nature of the P-substituent to be varied. This is a crucial point in order to be able to fully elucidate the structure/property relationships for these new types of phosphole-based co-oligomers.

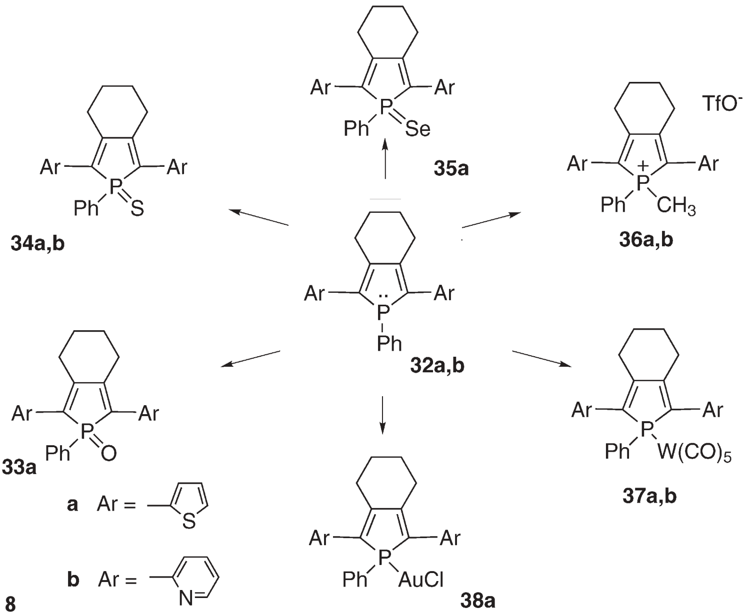
At the outset, it is interesting to note that the stability of derivatives (**32**) is directly related to the nature of the P-substituent. 1-Phenylphospholes are easily purified, air-stable solids, while the 1-alkyl- (**32c**) and 1-amino-phospholes (**32d**) (Scheme 7) are extremely air- and moisture-sensitive compounds. According to X-ray diffraction studies, the three heterocycles of σ^3,λ^3-phospholes (**32a**) [35] and (**32b**) [34] are almost coplanar, with the phosphorus atoms being strongly pyramidalised. For both compounds, the lengths of the C–C linkages between the rings are in the range expected for Csp^2–Csp^2 single bonds. These solid state data suggest a delocalisation of the π-system over the three heterocycles.

In solution, phospholes (**32a–e**) present broad absorptions in the visible region attributed to π-π* transitions [36]. The values of λ_{max} and the optical end absorption λ_{onset}, depend dramatically upon the nature of the 2,5-substituents of the phosphole ring [34, 35, 36]. An important red-shift was recorded on replacing the phenyl groups of (**32e**) either by 2-pyridyl (λ_{max}=36 nm) or 2-thienyl rings (λ_{max}=58 nm) [36]. These data suggest that the HOMO-LUMO gap gradually decreases in the series (**32e**)/(**32b**)/(**32a**), a feature that was confirmed by high-level theoretical calculations. The origin of these bathochromic shifts was initially interpreted in terms of intramolecular charge transfer that favours the delocalisation of the π-system [36]. The observation that the highest value of λ_{max}, i.e. the lowest HOMO-LUMO gap, was recorded for 2,5-dithienylphosphole (**32a**) was attributed to the fact that phospholes possess low-lying LUMO levels (high electron affinity), favouring charge-transfer from the electron-rich thienyl substituents. A recent study proposed that the more pronounced π-conjugation in (**32a**) was due to a better interaction between the HOMO of phosphole with the HOMO of thiophene, compared to that with pyridine [18e].

The optical data and theoretical studies show that the lowest HOMO-LUMO gap is achieved for (**32a**), structurally based on an alternating arrangement of thiophene and phosphole rings. The value of λ_{max} recorded for (**32a**) (412 nm) is considerably more red-shifted than those of related 2,5-dithienyl-substituted pyrrole (322 nm), furan (366 nm) or thiophene (355 nm), and very close to that of the 2,5-dithienyl-derivative based on a non-aromatic silole unit (420 nm) [38]. These results clearly establish that phospholes are excellent building blocks for the construction of π-conjugated co-oligomers exhibiting low HOMO-LUMO gaps.

Not only the absorption behaviour, but also all the physical properties of derivatives (**32**) are related to the nature of the 2,5-substitution pattern. For example, a blue-green emission is observed for di(2-pyridyl)phosphole (**32b**) whereas the emission of di(2-thienyl)phosphole (**32a**) is red-shifted ($\Delta\lambda_{em}$= 35 nm) [36]. Likewise, cyclic voltammetry (CV) revealed that derivative (**32a**), featuring electron-rich thienyl substituents, is more easily oxidised than compound (**32b**), which possesses electron-deficient pyridyl substituents [36].

In contrast to other heterocyclopentadienes (e.g. siloles and pyrroles), phospholes possess a reactive heteroatom. This feature allows direct access to a range



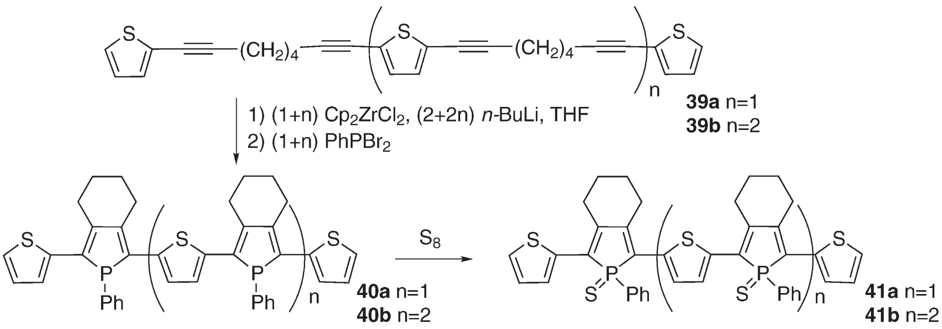
Scheme 8

of new π-conjugated systems (**33**)–(**38**) from single P-containing chromophores (**32a**,**b**), without the need for additional multi-step syntheses (Scheme 8). Significantly, these chemical modifications of the nucleophilic P-centres have a profound impact on the properties of the phosphole oligomers as a whole. Exploitation of this unique way of tailoring π-conjugated systems has led to the optimisation of the properties of thiophene-phosphole co-oligomers, which have subsequently been used as materials for OLEDs. Upon sublimation, phosphole (**32a**) decomposed while the more thermally stable thioxo-derivative (**34a**) formed homogeneous thin films on an indium-tin-oxide semi-transparent anode (ITO), allowing a simple layer OLED to be prepared [39]. This device exhibited yellow emission for a relatively low turn-on voltage of 2 V. The comparatively low maximum brightness (3613 cd m^{-2}) and electroluminescence (EL) quantum yields (0.16%) can be increased by nearly one order of magnitude using a more advanced device, in which the organic layer consisting of (**34a**) was sandwiched between hole- and electron-transporting layers (α-NPD and Alq_3, respectively). Upon doping the layer with the red-emitting dopant (DCJTB), the EL efficiency is further enhanced up to 1.83% with a maximum brightness of ca. 37,000 cd m^{-2} [39]. These results constitute the first examples of OLEDs based on π-organophosphorus materials.

In an extension to this work, the ligand behaviour of (**32a**) can be utilised in an innovative approach whereby metal complexes are investigated as materials for OLEDs. The Au(I) complex (**38a**) is thermally stable enough to give homogeneous thin films upon sublimation in high vacuum. The corresponding single layer device exhibited an EL emission covering the 480–800 nm domain

[39]; the low energy emissions are very probably due to aurophilic interactions in the solid state [40]. This work nicely illustrates the contribution of P-chemistry to the tuning of the optical properties of phosphole-based materials.

The evolution of optical and electrochemical properties with increasing chain length is one of the central principles used in the understanding of the characteristics of novel π-conjugated systems [1e,h, 41]. Considering the interest in thiophene-phosphole (Th-Phos) derivatives as smart materials, the synthesis of yet longer, but still well-defined oligomers, has been investigated [42]. The Fagan–Nugent method allows for the preparation of oligomers (**40a,b**) (Scheme 9), in moderate yields, from the corresponding bis- and tris-diynes (**39a,b**). Compounds (**40a,b**), as well as their thiooxo-derivatives (**41a,b**), are obtained as air stable powders. They exist as a mixture of diastereoisomers due to the presence of stereogenic P-centres.

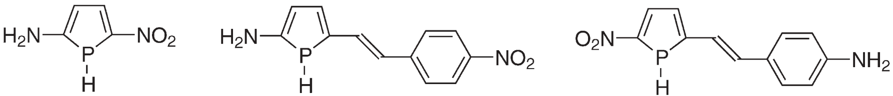


Scheme 9

The UV-vis spectra of Th-(Phos-Th)$_2$ (**40a**) revealed a λ_{max} (490 nm) considerably higher than that recorded for quinquethiophenes (ca. 418 nm) [43]. Thus, as observed for the model molecule (**32a**), replacing a thiophene subunit by a phosphole ring induces an important decrease in the optical HOMO-LUMO gap. It is also noteworthy that oxidation of the P-atoms of (**40a**) induces a bathochromic shift in the value of λ_{max} [42]. A similar trend has been observed with the shorter oligomers (**32a**), hence it seems a general feature that oligo(α,α′-thiophene-phosphole)s incorporating σ^4-P rings have smaller HOMO-LUMO gaps relative to those based on σ^3-P rings. The absorption maxima (λ_{max}), as well as the longest wavelength absorption (λ_{onset}) regularly shift to lower energy as the extent of the π-conjugated path increases [42]. Chain extension also leads to a decrease in their oxidation potentials and an increase of their reduction potentials. These data clearly showed a lowering of the HOMO-LUMO gap upon increasing the chain length of the α,α′-(thiophene-phosphole) oligomers. It is thus likely that the saturation of the effective conjugation has not been reached with oligomer (**41b**) containing seven rings. This result, along with the good stability and solubility of Th-(Phos-Th)$_{2,3}$, should encourage the search for new pathways to longer oligomers with alternating thiophene and phosphole subunits.

3.2.3
Miscellaneous Structures

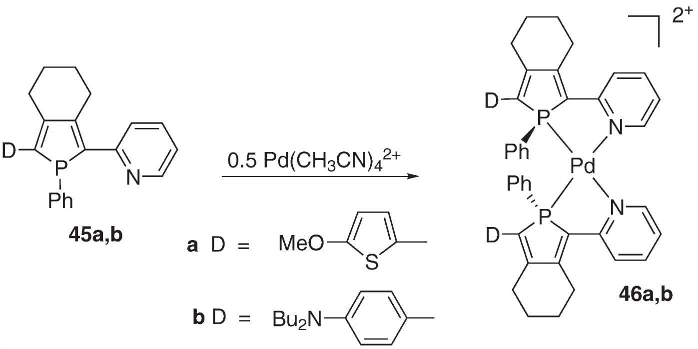
The fact that phospholes can act as ligands toward transition metals has considerably expanded the potential of phosphole-based derivatives for further development as OLEDs. The situation is very similar in the field of NLO materials. The archetypical NLO-phores can be represented as *D*-(π-bridge)-*A*, where *D* and *A* are donor and acceptor groups, respectively [44]. Theoretical studies have suggested that phospholes can act as efficient (π-bridges) for the engineering of NLO-phores [16f, 5b]. The NLO response of donor/acceptor-substituted phosphole (**42**) (Scheme 10) (β_x=6.17×10^{-30} e.s.u.) was computed to be significantly greater than that of related derivatives featuring a pyrrole (β_x=5.59×10^{-30} e.s.u.), a thiophene (β_x=5.49×10^{-30} e.s.u.) or a cyclopentadiene (β_x=6.04×10^{-30} e.s.u.) central ring [5b]. This trend was attributed to the low aromatic character of phosphole compared to that of either the pyrrole or thiophene rings. However, the electronic density (i.e. the excess/deficiency of electrons) associated with the π-bridge has also been shown to play a crucial role. According to theoretical calculations, chromophores (**43**) and (**44**) (Scheme 10) having stilbene-like bridges in which one phenyl is replaced by a phosphole ring, also exhibit good NLO responses [5b]. As expected from the quite high electronic density found on the α-P carbon atoms [5b], the highest NLO activity is observed for derivative (**44**) having a donor NH_2 substituent on the phosphole ring.



42 **43** **44**

Scheme 10

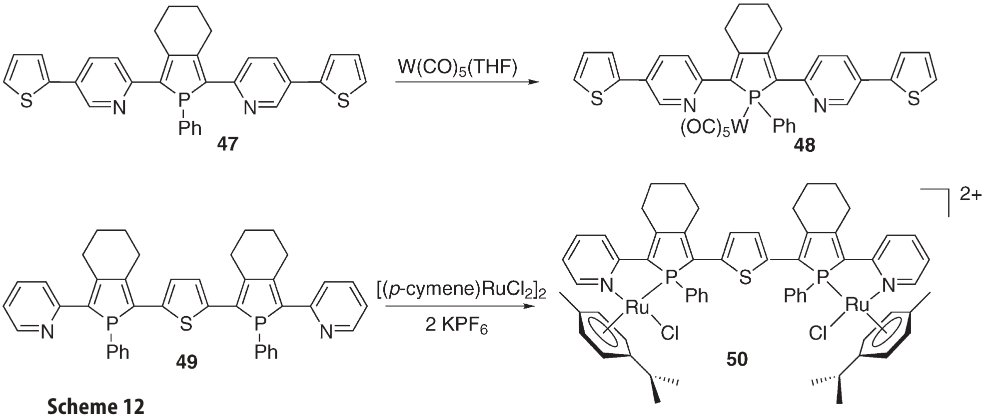
Phospholes (**45a**) and (**45b**) (Scheme 11), which bear an electron-deficient pyridine group and a classical electron-donor group at the 2- and 5-positions, respectively, exhibit moderate NLO activities ($\beta_{1.9\,\mu m}$, ca. 30×10^{-30} e.s.u.) compared to classical chromophores such as DR1 (β_0, 50×10^{-30} e.s.u.) [45]. These low values are consistent with the weak acceptor character of the pyridine group. However, the potential of dipoles (**45a**) and (**45b**) in NLO is considerably increased by their P,N-chelate behaviour towards d^8 metal centres such as Pd(II) [37, 46]. 2-(2-Pyridyl)phospholes (**45a,b**) react with $[Pd(CH_3CN)_4][BF_4]_2$ to afford the corresponding complexes (**46a,b**) (Scheme 11). In accordance with the *trans-influence* [47], heteroditopic P,N-dipoles (**45a,b**) undergo a stereoselective coordination leading to a close parallel alignment of the dipoles on the square-planar d^8 palladium template. Thus, the *trans-influence* can overcome the natural anti-parallel alignment tendency of dipolar chromophores at the molecular level. Furthermore, complexes (**46a,b**) exhibit high NLO activities ($\beta_{1.9\,\mu m}$, ca. 170–180×10^{-30} e.s.u), which are much higher than the sum of the



Scheme 11

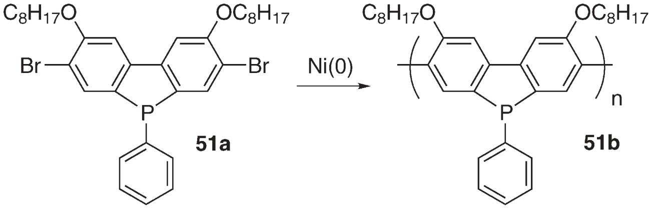
contributions of the two sub-chromophores (**45a,b**) [45]. The augmentation of the NLO activity upon coordination is probably due to the onset of ligand-to-metal-to-ligand charge transfer that contributes coherently to the second harmonic generation.

Other types of π-conjugated systems incorporating pyridylphosphole moieties have been prepared with a view to establishing structure–property relationships (derivative (**47**), Scheme 12) or to study the photophysical properties of dinuclear transition metal complexes containing bridging π-conjugated ligands (derivative (**49**), Scheme 12). As expected, derivative (**47**) exhibits a value of λ_{max} that has been red-shifted compared to the simple di(2-pyridyl)-phosphole (**32b**) ($\Delta\lambda_{max}$=37 nm). An X-ray diffraction study of the corresponding complex (**48**) showed that the five heterocycles are almost coplanar with twist angles ranging from 1.8(16)° to 18.3(17)° [35]. Dinuclear transition metal complexes (**50**), containing bridging π-conjugated ligands based on two terminal 2-pyridylphosphole moieties bridged by a thiophene ring, are readily obtained from (**49**) (Scheme 12) [48]. Coordination of chromophore (**49**) to ruthenium centres has been shown to have only a marginal influence on the π-π* transition of the extended conjugated system [48].



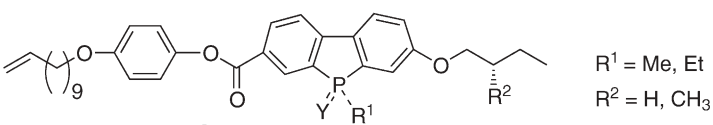
Scheme 12

Dibenzophosphole was the first phosphole to be prepared [49], and the related fused dithienophosphole derivative (**54**) (Scheme 15) is also known [50]. It is important to note that these benzo-annulated derivatives do not exhibit the typical electronic properties and reactivity pattern of phospholes, since the dienic system is engaged in the delocalised benzene or thiophene sextet [6b, 16]. Dibenzophospholes have only very recently been used as building blocks for the preparation of π-conjugated systems (**51b**) (Scheme 13) relevant to OLED applications [51]. This polymer (**51b**), prepared by Ni-catalysed coupling of derivative (**51a**) (Scheme 13), is obtained with a high polydispersity (M_n= 5×10^2, M_w=6.2×10^3). Interestingly, this macromolecule is photoluminescent in the solid state with a λ_{em} of 516 nm [51].



Scheme 13

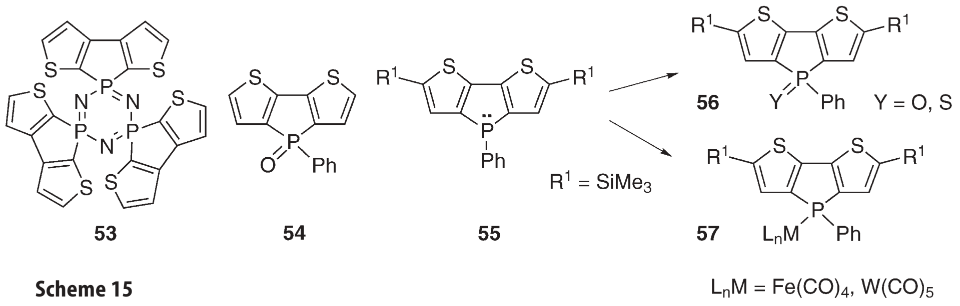
P-chiral dibenzophosphole oxide (**52a**) (Scheme 14) shows liquid crystalline behaviour [52], a property that is of interest in the area of electro-optical displays [53]. Chiral resolution of (**52a**) was achieved by column chromatographic separation of the diastereoisomers obtained following coordination of the σ^3-benzophosphole (**52b**) to chiral cyclometallated palladium(II) complexes [52]. Notably, the presence of a stereogenic P-centre is sufficient to generate a chiral cholesteric phase.



52a: Y = O
52b: Y = lone pair

Scheme 14

Two types of symmetric fused dithienophospholes exist, which differ according to the position of the S atoms as illustrated by compounds (**53**) [54] and (**54**) [50] (Scheme 15). The σ^3,λ^3-dithieno[3,2-*b*:2′,3′-*d*]phosphole (**55**) has recently been considered as a potential subunit for the construction of π-conjugated materials [55] (Scheme 15). Exploitation of the reactivity of the nucleophilic P-atom of (**55**) allows access to derivatives (**56**) and complexes (**57**) (Scheme 15). The absorption and emission behaviour of these species varies with the nature of the P-moieties. Upon oxidation of the P-centre of (**55**), bathochromic shifts of λ_{max} and λ_{em} were observed: λ_{max} 344 nm for (**55**) and ca. 373 nm for (**56**), and λ_{em} 422 nm for (**55**) and ca. 460 nm for (**56**) [55]. These results nicely illustrate

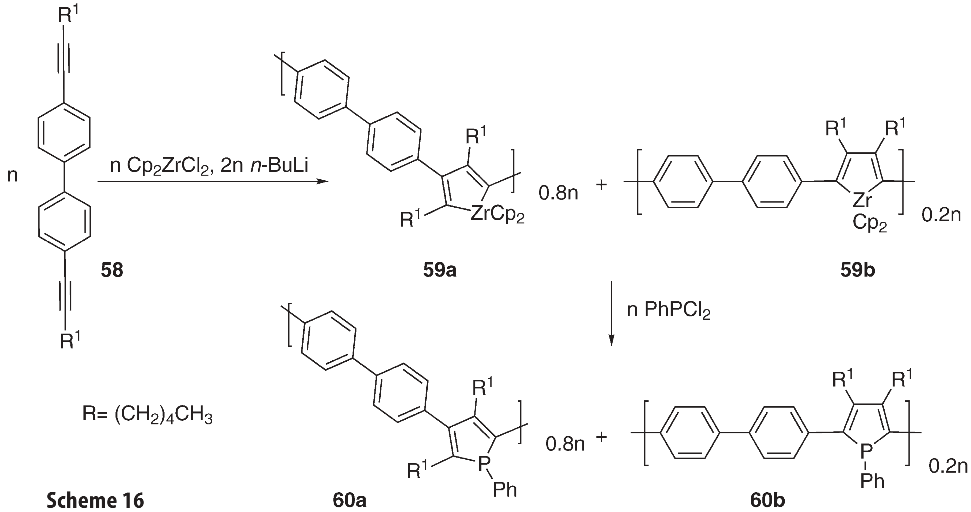


Scheme 15

how the tuning of the optical properties of these chromophores can be achieved via modifications at phosphorus.

3.3
Copolymers

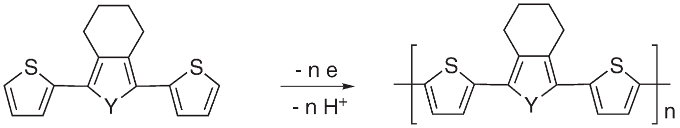
Although, to date, no homo-polymers based on phosphole are known, three types of copolymer incorporating phosphole rings have been prepared. The first type, (**60a,b**) (Scheme 16), has been described by Don Tilley and co-workers [56]. These macromolecules were obtained as an 80/20 isomeric mixture of 2,4- and 2,5-connected phospholes by zirconocene-coupling of rigid diynes (**58**), affording intermediate complexes (**59a,b**) (Scheme 16) [56]. The biphenylphospholyl polymers were isolated as air stable, soluble powders exhibiting rather high molecular weights (M_w=16,000, M_n=6200) according to GPC analysis. Although multinuclear NMR spectroscopy and elemental analysis support the proposed structures, the presence of a small number of diene units cannot be ruled out [56]. The polymer mixture (**60a,b**) exhibits an absorption maxima



Scheme 16

in its UV-vis spectrum at 308 nm with a λ_{onset} of 400 nm. These values are consistent with a relatively high band gap, probably due to a preponderance of cross-conjugated segments [56]. Polymers (**60a,b**) exhibit interesting photoluminescence properties with emissions in the bluish-green region associated with large Stokes shifts of 162 nm.

A second type of phosphole-containing π-conjugated copolymer was obtained by electropolymerisation of thienyl-capped monomers [35, 36], which involves the generation and coupling of radical cations [57]. The major coupling process should induce α,α′-linkages, but the formation of some 2,4-linkages that disrupt the conjugation can also take place. Insoluble and electro-active materials (**61**) (Scheme 17) were obtained on the working Pt electrode with 2,5-(dithienyl)phosphole monomers featuring σ^3,λ^3-, σ^4,λ^4- and σ^4,λ^5-P moieties (Scheme 17) [35, 36]. Polymers (**61**) were amenable to p- and n-doping processes with good reversibility. Absorption spectra of the de-doped polymers showed that the values of λ_{onset} were considerably red-shifted compared with those observed for the corresponding monomers (**32a**)–(**36a**) (Scheme 17, Table 1) [36]. These data suggest that the electro-active materials formed on the electrode possess rather long conjugation pathways. A remarkable feature is that the electrochemical (doping range) and optical properties (λ_{max}, λ_{onset}) of these materials obtained by electropolymerisation depend on the nature of the phosphorus moiety (Scheme 17, Table 1), exactly as was observed for the P-containing monomers (**32a**)–(**36a**).



32a-36a

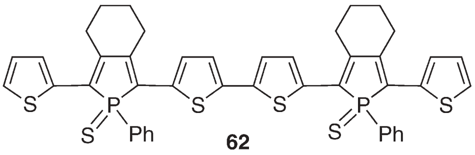
61

Scheme 17

Table 1

	Y	λ_{max}	λ_{onset}		λ_{max}	λ_{onset}
32a	PPh	434	500	poly(**32a**)	463–567	724
33a	P(O)Ph	432	496	poly(**33a**)	568	780
34a	P(S)Ph	423	503	poly(**34a**)	529	754
36a	P^+MePh	442	528	poly(**36a**)	627	905

It is difficult to establish the degree of polymerisation of materials (**61**) due to their insolubility, which prevents GPC analysis and standard spectroscopic studies. The important bathochromic shift of the λ_{onset} observed in the series: (**34a**) (496 nm)/(**62**) (600 nm) (Scheme 18)/poly(**34a**) (754 nm), suggests that (**61**) are oligomers. Note that electropolymerisation of monomers (**40a**) and

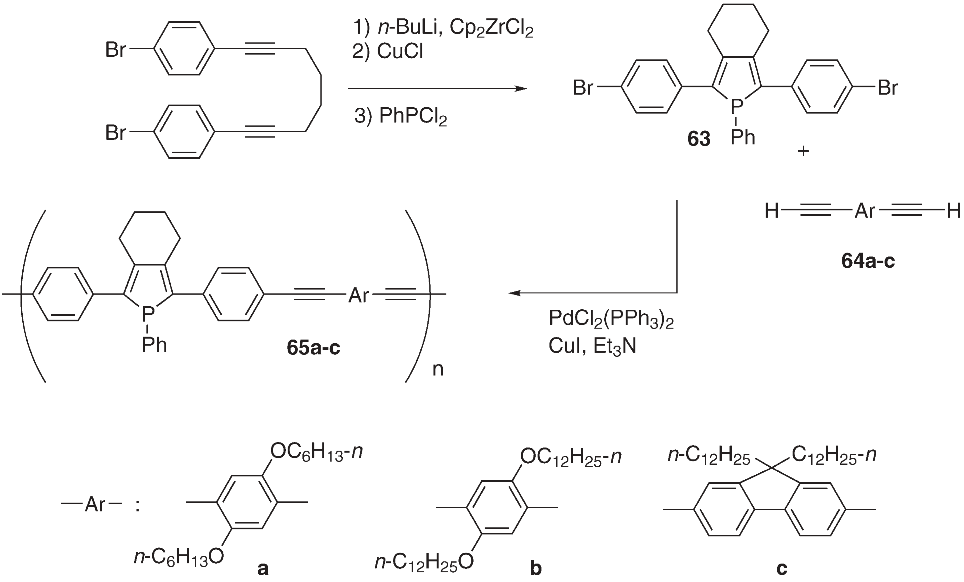


Scheme 18

(**41a**) (Scheme 9) also leads to electro-active materials presenting almost reversible p-doping behaviour [42].

The first well-defined π-conjugated polymer having a phosphole ring in a repeating unit was obtained by Chujo et al., using the Heck-Sonogashira coupling of (**63**) with the co-monomers (**64a–c**) (Scheme 19) [58]. Note that the preparation of 2,5-(diaryl)-phosphole of type (**63**) according to the Cu-modified Fagan–Nugent method (Scheme 19) was recently patented [59]. Macromolecules featuring free σ^3,λ^3-P centres (**65a–c**) are isolated in moderate to low yields as soluble powders. They are air-stable in the solid state and their degree of polymerisation ranges from 15, for (**65a**), to 7 for (**65c**). The UV-vis absorptions of (**65a–c**) are red-shifted in comparison to that of 2,5-diphenylphosphole (**32e**) (Scheme 7), indicating an effective extension of the π-conjugation. The emission properties of these macromolecules can be tuned by varying the nature of the co-monomer, green and blue emission are observed with polymers (**65a,b**) and (**65c**), respectively [58].

Polymers incorporating phosphole subunits are still very rare. However, the pioneering work described in this section shows that such macromolecules are



Scheme 19

accessible via diverse synthetic routes, and that they exhibit quite good stability as well as valuable optical and electrochemical properties.

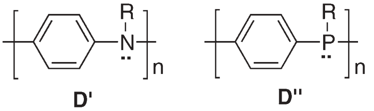
4
Macromolecules Containing Phosphine Moieties

Over the last decade, poly(*p*-phenylenevinylene)s and related materials have found a place amongst the most industrially significant materials for the preparation of OLED-type devices [1, 60]. Since replacing carbon moieties by heteroelements as constituents of the primary polymer backbone has proved an excellent means of tuning the materials' opto-electronic properties, it is unsurprising that phosphorus-containing analogues of PPV and related macromolecules have been prepared and investigated.

4.1
Poly(*p*-Phenylenephosphine)s

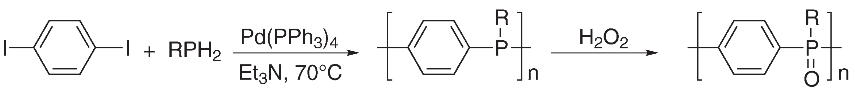
Redox active polyanilines (**D′**) (Fig. 3), in which the heteroatom participates in π-conjugation by virtue of its lone pair, are amongst the oldest and best known photochromic materials, often prepared by galvostatic polymerisation of aqueous HCl solutions of anilines [61]. More recently, polymer (**D′**) has been prepared via metal-mediated C–N bond formation from aryl-halides or -triflates with amines, affording N-substituted polyanilines [62] and oligoanilines [63]. Despite the prevalence of such polymers containing nitrogen, the corresponding poly(*para*-phenylenephosphine)s (**D″**) that possess main chain σ^3,λ^3-phosphorus centres have appeared only recently.

By analogy with modern routes for the preparation of well-defined polyanilines (**D′**), palladium-catalysed cross coupling of 1,4-diiodobenzene and primary aryl- and alkyl-phosphines affords the comparatively short chain polymers (**66a–c**) (M_n=1000–4000) (Scheme 20), that can be oxidised either by atmospheric



D' **D''**

Fig. 3 Structure of polyanilines and poly(*para*-phenylenephosphine)s



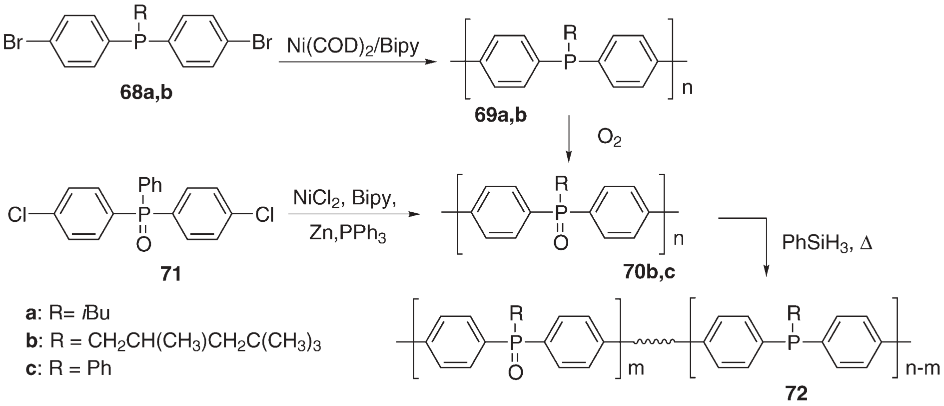
66a-c **67a-c**

Scheme 20

a : R = $CH_2CH(CH_3)_2$ (n = 10)
b : R = Ph (n = 7)
c : R = $CH_2CH(CH_3)CH_2C(CH_3)_3$ (n = 14)

oxygen or by H_2O_2 to afford derivatives (**67a–c**) [64]. Soluble materials (**66a–c**) are formed with narrow polydispersities (PDI=1.3–1.5) and are amenable to characterisation by GPC and multinuclear NMR spectroscopy. The UV-vis spectra of polymers (**66a–c**) show absorption values attributed to π-π^* transitions with $\lambda_{\max}$ ranging between 276 and 291 nm [64]. These rather low values are probably due to the fact that the P-atoms of these polymers retain a tetrahedral geometry that prevents efficient conjugation of the phosphorus lone pair with the aryl groups. However, the bathochromic shift observed on going from triphenylphosphine ($\lambda_{\max}$=263 nm) to 1,4-diphenylphosphinobenzene ($\lambda_{\max}$=275 nm) and then to (**66b**) ($\lambda_{\max}$=291 nm) is supportive of the presence of some extended π-delocalisation for the latter. Contrastingly, the oxidised materials (**67a–c**) exhibit a number of new absorption bands and all display a shift in λ_{onset} from 520 (unoxidised) to 800 nm (oxidised).

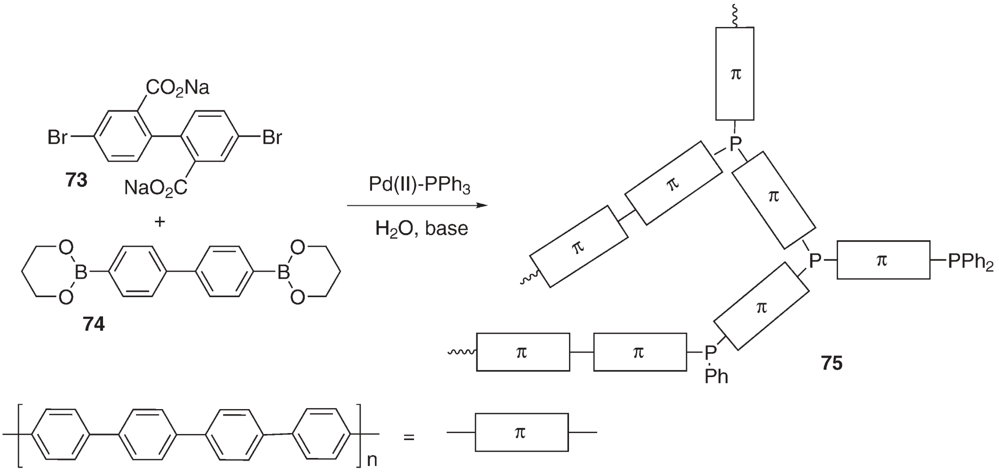
Since metal-catalysed C–C bond-forming reactions are extremely well-established and reliable, an alternative route to polymers (**D″**) has been investigated starting with the bis(*p*-bromophenyl)phosphines (**68a,b**) (Scheme 21) [65]. Disappointingly, though, this approach was also found to be inappropriate for the formation of high molecular weight polymers. A dark red insoluble solid was isolated from the Ni-catalysed coupling reaction of (**68a**), which was believed to be (**69a**). However, homo-coupling of phosphine (**68b**) afforded a low molecular weight (M_n=1000), pale yellow material (**69b**), which could be oxidised to afford (**70b**). The colour of (**69b**) is indicative of limited π-conjugation.



Scheme 21

Although of limited success, this Ni-catalysed coupling strategy builds on a previous report of the successful, direct synthesis of poly(4,4′-diphenylphenylphosphine oxide) (**70c**) from bis(*p*-chlorophenyl)-phenylphosphine oxide (**71**) (Scheme 21) [66]. The white soluble material (**70c**) ($\lambda_{\max}$~280 nm) was found to have a single phosphorus environment by ^{31}P NMR spectroscopy, a comparatively high molecular weight (M_n=15,300) together with a low molecular weight distribution (PDI=1.6), and to exhibit a high T_g (365 °C) with considerable thermal stability (<5% weight loss at 550 °C). Reduction of (**70c**) was achieved by reaction with phenylsilane, to give a poorly soluble, intensely brown-red-coloured material (**72**). Surprisingly, however, despite the intense coloration, only a small red-shift was observed relative to (**71**) ($\Delta\lambda_{max}$~20 nm), which has been attributed to a possible partial re-oxidation at phosphorus.

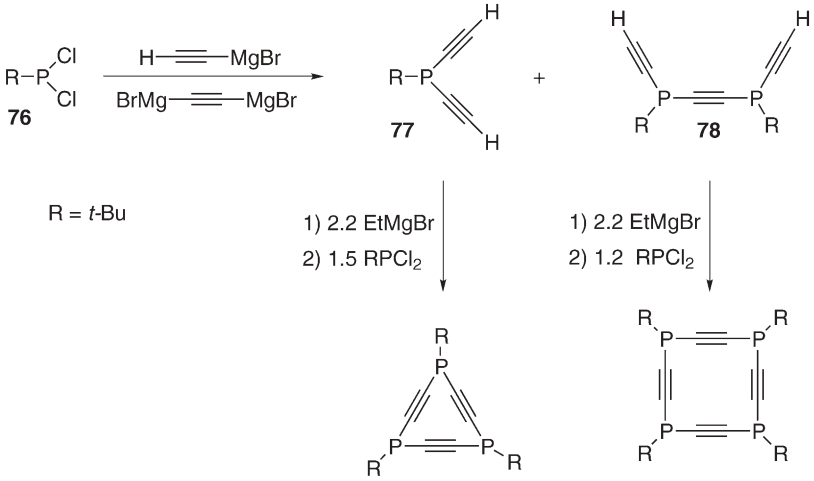
An example of branched (*p*-phenylene)s (**75**) incorporating phosphorus moieties (Scheme 22) was obtained adventitiously during attempts to synthesise soluble linear (*p*-phenylenes) using Pd-catalysed Suzuki couplings [67a]. Thus, reaction of derivatives (**73**) and (**74**) in the presence of a palladium-tri-(*o*-tolyl)phosphine catalyst system, led to the formation of linear poly(*p*-phenylene)s of high molecular weight [67a]. In contrast, on replacing tri(*o*-tolyl)-phosphine by triphenylphosphine, aryl-aryl interchange took place with the $ArPd(PPh_3)_2I$ complexes [67b] leading to the formation of branched polymer (**75**) (Scheme 22). It should be noted that although the concentration of the phosphine 'defects' is very low, they have a significant impact on the properties (e.g. molecular weight, viscosity, etc.) of the polymers. A related exchange between phenyl groups of triphenylphosphine and iodophthalocyanines in the coordination sphere of Pd(II), leading to mono-, bis- and tris-(phthalocyanine)aryl phosphonium salts, has recently been reported [68].



Scheme 22

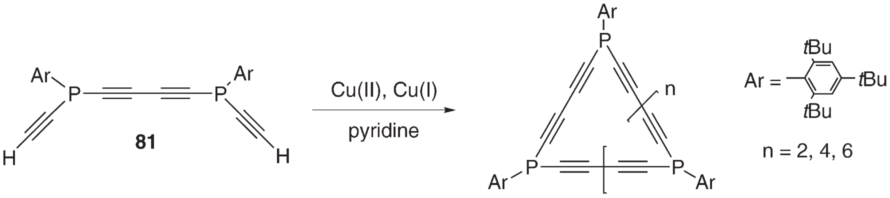
4.2
Phosphine-Ethynyl Co-Oligomers

Replacement of the *para*-substituted phenyl unit of alternating phosphine-arylene polymers by an ethynyl group, gives rise to a new family of π-conjugated materials. Indeed, compounds (**77**) and (**78**) were prepared in 53% and 3% isolated yields, respectively, through reaction of dihalophosphine (**76**) with an excess of ethynylmagnesium bromide (Scheme 23) [69]. These derivatives were subsequently transformed into triphospha[3]pericyclyne (**79**) and tetraphospha[4]pericyclyne (**80**) via a double deprotonation, followed by addition of 1.5 equivalents of dihalophosphine (**76**). Notably, derivatives (**79**) and (**80**) exhibit strong absorption bands in their UV-vis spectra that extend out to nearly 300 nm, showing that these heterocycles display cyclic electronic interactions [69].



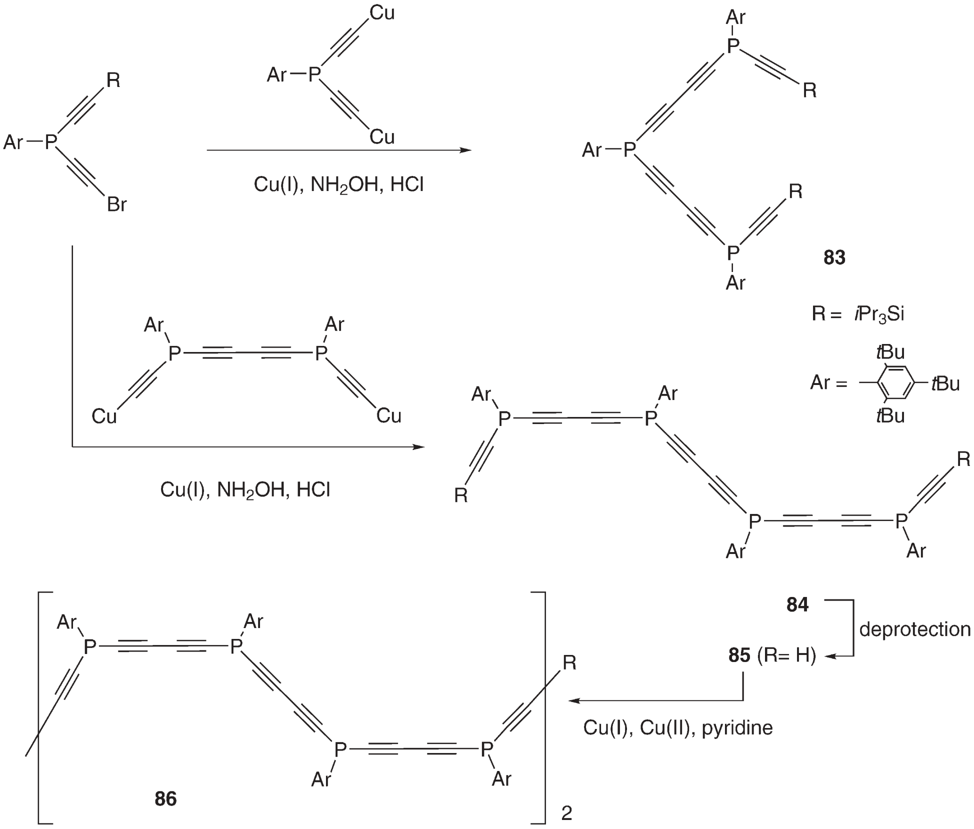
Scheme 23

In a related strategy, ethynylphosphines (**81**) have been prepared with a view to synthesising polyphosphacyclopolyyne materials such as (**82**) (Scheme 24) [70]. Interaction between the phosphorus lone pairs and the organic π-systems is supported by the fact that the phosphorus atoms of mono- and di-silyl-capped analogues of bis(arylphosphine) derivative (**81**) exhibit an unusually low inversion barrier (65 kJ mol^{-1} versus 130–140 kJ mol^{-1} for classical alkyl- or aryl-phosphines). Indeed, the rings (**82**) exhibit values of $\lambda_{\max}$ at ca. 300 nm, consistent with this assumption.



Scheme 24

In a further extension to this approach, longer chain oligomers (**83**)–(**86**) have been prepared via two different methodologies, either a Cadiot–Chodkiewicz coupling involving bis(copper) salts, or an Eglinton coupling of terminal alkyne moieties (Scheme 25) [70]. Each of the oligomers (**83**)–(**85**) presents a number of bands in their UV-vis spectra in the range $\lambda_{\max}$=308–210 nm, consistent with a degree of extended π-conjugation. Notably, however, the insolubility of the higher molecular weight, yellow-coloured oligomer (**86**) precluded UV-vis analysis.



Scheme 25

It is noteworthy that photoluminescent poly(vinylene-arsine)s have also been prepared by radical copolymerisation of phenylacetylene and an arsenic atomic biradical equivalent [71].

4.3
Phosphine-Ferrocene Co-Oligomers

Ferrocene has been extensively used as a building block to prepare organometallic polymers and heteroatom-bridged poly(metallocenes)(**G′**)–(**G‴**)(Fig. 4).

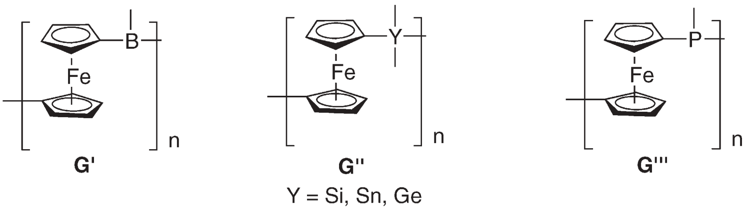
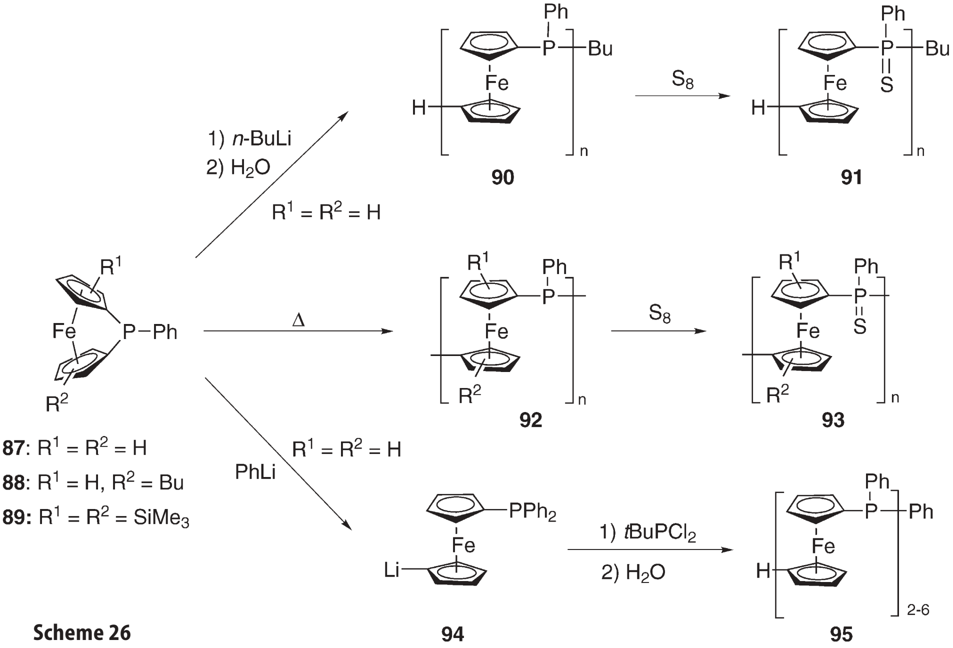


Fig. 4 Heteroatom-bridged poly(metallocenes)

These derivatives have been the focus of numerous investigations since the nature of the bridging atom has key implications for the properties of the polymers [72]. Although, not π-conjugated materials in the true sense, the phosphorus-containing materials (**G‴**) show a range of properties that offer significant promise for the future. In particular, the ring-opening polymerisation (ROP) of the strained [1]-ferrocenophane monomers (**87**)–(**89**) allows the various polymers (**90**)–(**95**) to be prepared with high molecular weights and narrow polydispersities (Scheme 26) [73]. In line with the living nature of this process, block copolymers with either poly(dimethylsiloxane) or poly(ferrocenylsilane) segments have also been isolated.

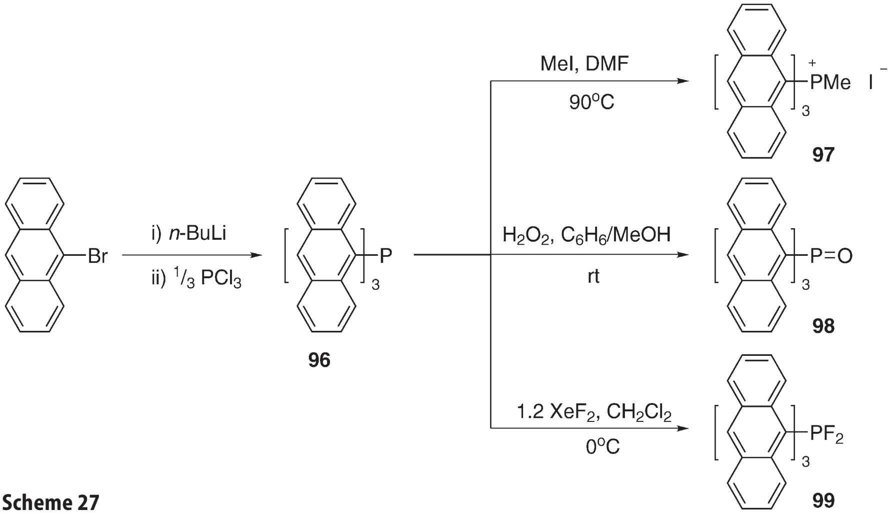


Scheme 26

5
Phosphorus Bearing Extended π-Conjugated Substituents

Conceptually and synthetically more straightforward molecules can be prepared through incorporation of chromophores onto simple phosphine moieties. The phosphorus fragment can be used either to influence or to organise the π-conjugated systems. This section will focus only on derivatives tailored in order to exhibit specific properties related to applications in NLO, opto-electronics or as sensors.

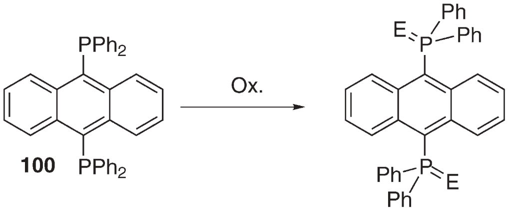
In a series of remarkable papers, K. Tamao and S. Yamaguchi have shown that the physical properties of triarylboranes and triarylsilanes can be modified using structural changes induced by increasing coordination numbers [74]. In the same way, the tuning of the photophysical properties of PAr_3 systems (**96–99**) (Scheme 27) according to the coordination number of the P-atom has been achieved [75].



Scheme 27

UV-vis spectroscopic analysis revealed that the σ^3,λ^3-phosphine (**96**) exhibits a broad absorption band at ~390 nm due to the π-π* transitions associated with the anthracene moieties, together with a band at 437 nm, probably due to extended π-conjugation through the P-lone pair [76]. The UV-vis spectra of derivatives (**97**)–(**99**) are blue-shifted ($\Delta\lambda_{\text{onset}}$, ca. 40–80 nm). This bathochromic shift can be ascribed to the inductive effects of the phosphorus moieties or to a through-space interaction between the anthracene substituents [75]. Moreover, it has been established that the fluorescence properties of these partially conjugated molecules are highly dependent upon the coordination number of the central P-atom. The σ^3,λ^3-phosphine (**96**) has almost no fluorescence as a result of quenching by the P-lone pair. The σ^4,λ^4- (**97**) and σ^4,λ^5- (**98**) derivatives show weak fluorescence with relatively large Stokes shifts, again presumably as a result of through-space interactions between the anthracene substituents. In sharp contrast, the penta-coordinate σ^5,λ^5-compound (**99**) shows an intense fluorescence with a small Stokes shift; the quantum yield is ~30–100 times greater than those of either (**97**) or (**98**), comparable to that of anthracene itself. This latter phenomenon is thought to result from the equatorial disposition of the three anthracenyl moieties, an arrangement evident from ^{31}P NMR spectroscopy.

More recently, the fluorescence properties of related 9,10-diphospha-anthracenes (**100–103**) (Scheme 28) have been investigated [77], since previous studies have shown that the analogous N- and Si-disubstituted species exhibit-photoluminescence [78], electroluminescence, and are potential materials for light-emitting electroluminescent devices [79]. Starting from the known phosphine 9,10-$(Ph_2P)_2C_{14}H_{18}$ (**100**) [80], the bis(chalcogenide) derivatives (**101**)–(**103**) have been isolated in high yields (Scheme 28).

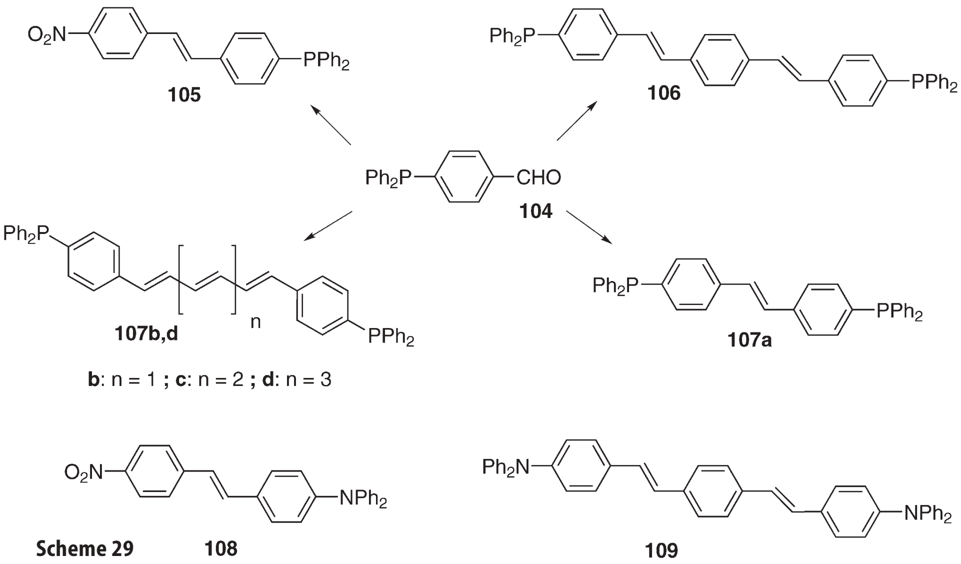


101: E = O, Ox. = $H_2O_2.(NH_2)_2C{=}O$
102: E = S, Ox. = S_8
103: E = Se, Ox. = Se

Scheme 28

In solution, only compound (**101**) exhibits a detectable emission (λ_{em}~ 450 nm). Contrastingly, in the solid state, derivative (**102**) shows very intense fluorescence at λ_{em}=508 nm, (**101**) displays a weak, broad emission at λ_{em}= 482 nm, while (**103**) shows no emission at all [77]. However, it was established that the presence of near stoechiometric quantities of toluene are necessary to observe fluorescence of (**102**) in the solid state. Indeed, the asymmetric unit of (**102**), established crystallographically, contains one toluene molecule that interacts via its *ortho*-hydrogen atoms with the central ring of the anthracene. The emission is thus due to this solid state T-shaped excimer. Hence, (**102**) can act as a potential toluene chemosensor [77]. It is noteworthy that this T-shaped orientation is not possible with derivatives (**101**) and (**103**), nicely illustrating the possible impact of P-chemistry for tuning the properties of π-conjugated systems in the solid state.

Diphenylphosphino groups have also been investigated as auxiliary donor groups for the tailoring of potential second- and third-order NLO-phores. Their syntheses used the versatile starting material *p*-diphenylphosphanyl-benzaldehyde (**104**) (Scheme 29) and a set of classical synthetic transformations (e.g. Wittig reactions, McMurry couplings) [81]. Dipole (**105**) exhibited a blue-shifted value of λ_{max}, relative to that of its N-analogue (**108**). This property may be of interest in terms of a trade-off between transparency and NLO activity,



Scheme 29

which are important parameters for the engineering of valuable second order NLO-phores [44]. Again, these results highlight the ease of tuning of the opto-electronic properties of heteroatom-containing polymers.

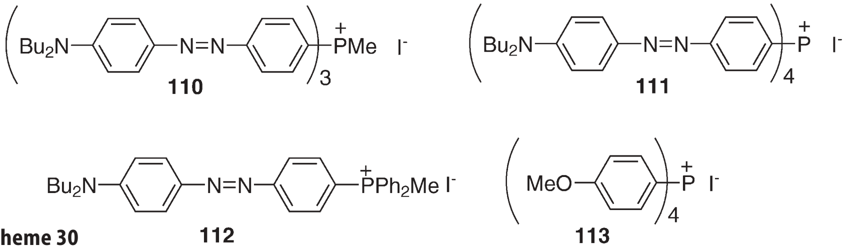
Two series of centrosymmetric diphenylphosphino-capped chromophores (**106**) and (**107a–d**) (Scheme 29) have been synthesised with a view to preparing materials with potential third order NLO properties [81]. Comparison of the UV-vis data of compounds (**106**) and (**109**) confirms that replacing N by P induces a blue-shift in the value of λ_{max} [81]. The systematic increase in the number of conjugated C–C double bonds in the series of polyenes (**107a–d**) (Scheme 29) led to a pronounced red-shift in the values of λ_{max}: 341 nm for (**107b**) and 418 nm for (**107d**), as expected. Notably, these UV-vis data are significantly blue-shifted from the values obtained for the analogous series of bis(diphenylaminodiphenyl)polyenes, which span the range λ_{max} 389 (n=1) to 449 nm (n=3) [81].

The opto-electronic properties of branched structures have been an area of some interest for a number of years, especially as NLO and light-emitting materials [82]. In particular, the use of π-conjugated dendrimers (mono-disperse macromolecules [83]) has flourished for a number of reasons:

1. The possibility of their bearing multichromophores (arranged either symmetrically or asymmetrically about the core)
2. Their ability to achieve a high chromophore density (for example, it is possible to introduce three conjugated chains about a single N-atom core in contrast to the two more normally possible with a linear macromolecule) [84]
3. The prospect of investigating the ternary structure of these materials as a consequence of their potentially 3D nature [85]

Indeed, conjugated dendrimers built from an N-containing core exhibit impressive energy transfer efficiencies as well as very strong electronic interactions of the participating chromophore building blocks, a result of planarisation at nitrogen facilitating good orbital overlap between the different chromophores [86].

More recently, efforts have been made to prepare P-containing dendritic core branched structures bearing π-conjugated substituents. The 3-D chromophores (**110**) and (**111**) with a C_3 and D_2 (approximate T) symmetry (Scheme 30), respectively, have been prepared according to classical routes [87]. The UV-vis data suggest that the subchromophores in (**110**) and (**111**) are almost electronically independent. Derivative (**110**) has a small dipole moment, and can be viewed as an almost purely octupolar system, like (**111**). Compared to their tin analogues, the phosphorus derivatives (**110**) and (**111**) have higher β values due to the more efficient phosphonium acceptor [87]. Furthermore, the NLO activity of octupolar compound (**111**) is almost three times larger than that of the dipolar subchromophore (**112**) with almost no cost in terms of transparency. The related octupolar phosphonium salt (**113**) (Scheme 30) was investigated with the aim of obtaining NLO-active crystals that remain transparent across all, or nearly all, the visible region [88]. Structural analysis of (**113**) revealed a weakly distorted ionic structure of the NaCl-type. The tetrahedral phosphonium ion retains an almost pure octahedral symmetry in the solid state. The crystal is transparent throughout the visible region and exhibits a moderate NLO activity [88]. These two examples nicely illustrate the potential of phosphorus derivatives for the engineering of octupolar derivatives.

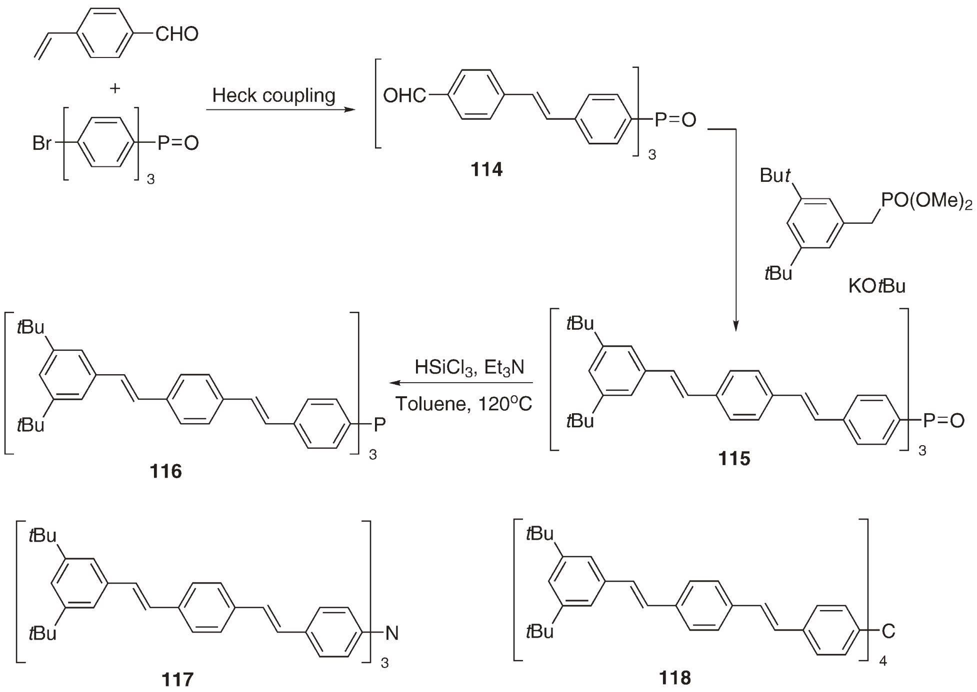


110 **111** **112** **113**

Scheme 30

More recently, P-cored derivative (**116**) was prepared from a straightforward combination of a Heck coupling, to afford an intermediate functionalised stilbene phosphine oxide (**114**), a Horner–Wittig reaction yielding the phosphine oxide (**115**), and finally trichlorosilane reduction (Scheme 31) [89]. Using similar strategies, both the valence isoelectronic N- (**117**) and C- (**118**) cored dendrimers have been prepared (Scheme 31).

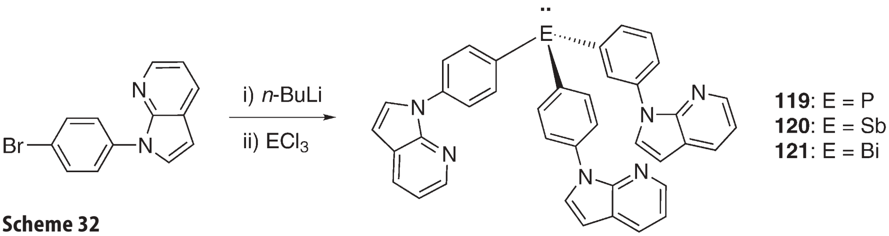
The geometry of the central core P-atom of (**116**) was found to be pyramidal, as might be expected for a (p-substituted triphenyl)-σ^3,λ^3-phosphine, while that for the N-based systems was trigonal planar (in agreement with the pla-



Scheme 31

nar structure of NPh_3 [90]). An examination of the UV-vis spectra of derivatives (**116**)–(**118**) revealed that the value of λ_{max} for the P-containing species (376 nm) is red-shifted relative to that for the C-cored species (λ_{max}=325 nm), but blue-shifted with respect to the N-based analogues (**117**) (λ_{max}=430 nm). This effect has been rationalised in terms of mesomeric effects. For the planar-cored compound (**117**) an efficient overlap of the N-lone pair with the adjacent carbon p-orbital gives rise to efficient conjugation with the oligo-PPV chains, whereas for the larger pyramidal phosphorus (**116**), the P-lone pair to Cp-orbital overlap will be significantly less efficient. Further studies to examine the fluorescence behaviour of the three compounds (**116**)–(**118**), found that the geometry, structural arrangement of dipoles about the core, and extent of electronic delocalisation, all have a direct impact on this property [89]. This conclusion was confirmed by a study on related tris(4-styrylphenyl)phosphine derivatives [91].

A similar investigation has probed the photophysical behaviour of some related "dendrimer-like" σ^3,λ^3-pnictogens (**119**)–(**121**) bearing potentially conjugating side chains (Scheme 32) [92]. These molecules are related to 1,3,5-tris(*N*-7-azaindolyl)benzene and 4,4-bis(*N*-7-azaindolyl)benzene that have shown considerable promise as bright blue-emitting OLEDs [93]. Each of the three group 15-based compounds has been shown to adopt a similar pyramidal geometry, with a propeller-like, approximate C_3 symmetry, characterised in



Scheme 32

the solid state by X-ray crystallography; the C–E–C bond angles decrease down the series, as expected.

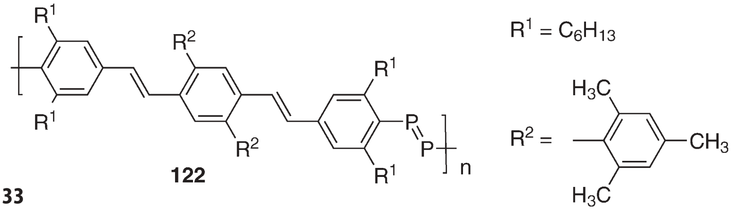
Luminescence studies revealed that compounds (**119**)–(**121**) displayed broad emission bands at 298 K, with λ_{max} ranging from 387 nm to 371 nm for the P to Bi derivatives, respectively [92]. On cooling to 77 K, compound (**119**) displays both a fluorescent band (λ_{max}=372 nm) and a phosphorescent band (λ_{max}=488 nm, lifetime 38(6) ms). For the heavier congeners only an enhanced phosphorescent band could be observed at 77 K (λ_{max}=483 nm (**120**), lifetime 3.44(4) ms; λ_{max}=478 nm (**121**), lifetime 0.577(8) ms), consistent with efficient interstate mixing of the singlet and triplet states. The attenuation in phosphorescent decay lifetimes down the series corresponds with the increasing heavy-atom effect. These luminescence data have been probed using ab initio calculations for compounds (**119**) and (**120**), which revealed that although both have HOMOs involving π-orbitals localised on the side chains, for (**105**) the HOMO is dominated by the P-lone pair. Significantly, however, the HOMO-LUMO gap is comparable for both compounds, suggesting that the observed luminescence is due to π-π* transitions with some lone pair contribution from the central atom, E. The low phosphorescent emission intensities and long decay lifetimes in the solid-state makes compounds (**119**)–(**120**) poor candidates for OLED emitter components. However, this investigation does, once again, highlight that incorporation of main group elements into conjugated systems can have a profound influence on photophysical properties.

6
Conclusions

The chemistry of π-conjugated systems incorporating P-moieties has really only come to the fore following the pioneering work started in 1990 on phosphole-based oligomers, and that on related phosphine-ethynyl co-oligomers. The last five years have seen an extraordinary expansion in this new area with the synthesis of novel derivatives exhibiting a plethora of different structures. However, the chemistry of π-conjugated systems incorporating P-units remains in its infancy. Structure–property relationships have still to be established in order to fully exploit the potential of P-moieties in the construction of conjugated frameworks. Furthermore, new methodologies are needed to prepare oligomers and polymers of defined structure and length. Nevertheless, it has already been clearly established that organophosphorus derivatives offer specific advantages in comparison with their widely used sulphur or nitrogen analogues. Three are particularly noteworthy: First, phospholes appear to be excellent building blocks for the tailoring of low band gap materials due to the low aromatic character of this P-ring. Second, the possibility of chemically modifying λ^3-P centres gives a unique way to tune the physical properties of P-containing π-conjugated systems. This facet is of particular importance for the tailoring of organophosphorus materials for applications in optoelectronics. Lastly, the coordination ability of λ^3-P centres toward transition metals offers manifold opportunities to build supramolecular architectures in which the π-systems can be organised in a defined manner.

The possibility of using organophosphorus π-conjugated systems as materials for applications in the field of nonlinear optics, organic light emitting diodes or conductive polymers has been demonstrated. However, considering the richness and diversity of phosphorus chemistry, their true potential has not yet been fully exploited. It is very likely that new developments will occur in this area in the near future, which exploits the specific properties of organophosphorus derivatives to the full.

Note Added in Proof This is nicely illustrated by the landmark publication of Protasiewicz et al. [94] who describe derivative (**122**), the first conjugated polymers featuring phosphorus–phosphorus multiple bonds (Scheme 33). The diphosphene-PPV (**122**) exhibits an extended π-conjugated system as shown by the optical HOMO-LUMO gap that is close to that of related PPV [94].



Scheme 33

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