Organophosphorus derivatives for electronic devices

D. Joly, Pierre-Antoine Bouit, M. Hissler

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D. Joly,[a] P.-A. Bouit,[a] M. Hissler[a*]

This review presents the main class of organophosphorus compounds (triaryl phosphines, phosphazenes, phospholes, phosphetes and diphosphacyclobutanes) which have been used in electronic devices (organic light-emitting diode (OLED), organic photovoltaic cell (OPV cell), dye-sensitized solar cell (DSSC), organic field-effect transistors (OFET), electrochromic cells).

Introduction

Since the pioneering work of Shirakawa, Heeger and McDiarmid in the 1970's,[1] the interest for organic π-conjugated systems has grown tremendously.[2] Indeed organic materials offer the possibility to process light-weight, flexible electronic devices. However, they have to satisfy a large number of technical requirements in order to be stable and efficient in the device.[3] For example, materials have to give pin-hole free homogenous layer by vacuum sublimation or wet processing, to be stable under electric fields, to undergo balanced charge carrier injection from or to both electrodes, to be thermally stable… In order to satisfy all the technical requirements and obtain efficient materials with high absorption, conductivity or photoluminescence quantum yield, chemists have synthesized and studied a large amount of chemical structures which, for some of them, have been successfully used in devices.[4] HOMO-LUMO gap is easily tuned by extension/modification of the π-conjugated system. Properties can be further modified by grafting lateral substituents on the backbone of conjugated systems. These side chains can, *via* supramolecular, steric or electronic effects, change the electronic properties but also the solubility or the solid-state packing.[5] The insertion of heteroelement into the backbone also appeared as an appealing way to tune the properties of the materials. Heterocycles like thiophene, pyrrole and all their derivatives are now widely used to modify chemical and physical properties of π-conjugated systems.[2] Interestingly, while the organophosphorus derivatives have been investigated for decades, their insertion into devices has been recently achieved.[6,7] Phosphorus has been named from the ancient greek *phos* ("light") and *phorus* ("bringing") due to the intense light emitted by white phosphorus (P_4). It is ironic to note that the element whose name is etymologically linked

to "phosphor" and "phosphorescence" was scarcely used in the emitting devices before the beginning of this century. The high reactivity and toxicity of many P-derivatives is the main reason. The ability of the chemists to stabilize and protect the P-atom allowed the introduction of organophosphorus derivatives in opto-electronic devices.

The present article does not aim to review all the different kinds of organophosphorus based materials,[7] but only those who have been inserted into electronic devices (organic light-emitting diode (OLED), organic photovoltaic cell (OPV cell), dye-sensitized solar cell (DSSC), organic field-effect transistors (OFET), electrochromic cells). Indeed, despite the interesting work on some organophosphorus π-conjugated materials like phosphalkenes[8] or diphosphenes[9] none of these derivatives have ever been used in electronic device, probably because of poor stability of the C=P and P=P bond. Actually five types of organophosphorus material have made the cut: triaryl phosphines, phosphazenes, phospholes, phosphetes and diphosphacyclobutanes (Fig. 1). This review will mainly focus on two types of opto-electronic devices: the OLEDs where the use of P-containing material is now widely developed, and the solar cells (either OPV or DSSCs).[10] The case of OFET and electrochemical cells will also be addressed but they are more particular, as only specific examples were found in the literature.

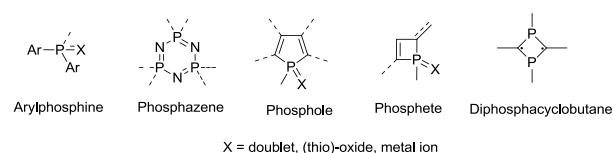**Fig. 1**: Organophosphorus building blocks used in organic electronic.

2. Phosphines

Helped by their extensive use as ligand toward transition metal in catalysis, the aryl phosphine building block is the most studied group of organophosphorus material. It has been shown that the lone pair of P is slightly involved in the delocalization within the conjugated system.[11] This is due to

the tetrahedral shape of the phosphorus and its high inversion barrier (30-35 kcal.mol^{-1}). Furthermore the doublet tends to quench the luminescence and these compounds rarely exhibit high fluorescence quantum yield. That is why only few examples were found of σ^3-λ^3 phosphine used as emitters.[12] Above all, σ^3-λ^3 phosphines are sensitive to oxidation, which clearly alter their stability in a device. This problem is overcome by oxidizing the phosphines to its σ^4-λ^5 phosphines oxide analog. Even though the oxidation breaks the delocalization, their chemical stability and electronic affinity make them valuable compounds for the development of electrons transport layer (ETL) and host materials in optoelectronic. This field has been reviewed in 2012 by Jeon *et al*..[13] That is why only compounds leading to outstanding performances (External Quantum efficiency (EQE) > 20%) and some of latest compounds published will be described here.

2.1. As charge transport layer

The role of a charge transport layer is to insure electron or hole injection and transport from the electrodes to the active layer of the device. The first study of a phosphine as charge transport layer goes back to 2001.[6] The authors showed that π-extended arylphosphines used as hole transport layer (HTL) have a better performance in OLED than its nitrogen analogs. However, their oxidized version (phosphine oxides) are mainly used for their electron transport ability as the high polarity of the P=O group makes it electron withdrawing. In this case, the LUMO of the ETL has to be low enough to insure electron injection from the electrode. In addition, phosphine oxides are stable toward oxidation. For example, a simple triphenylphosphine oxide, Ph$_3$PO, was used in a OLED by Ha *et al*. in 2008.[14] The results show that Ph$_3$PO has great electron transport ability but also that the driving voltage for luminance output is reduced by using a Ph$_3$PO layer over a Alq$_3$ layer. Pyridine based phosphine oxides were also investigated.[15] This family of derivatives exhibit electron transport properties and hole blocking ability due to deep HOMO levels. The association of the P=O moiety to a pyrene (**1**, Fig. 2) able to π-stack, gives to the phosphine oxide prepared by Oyamada *et al*. its electron transport ability.[16] Furthermore it was shown that the co-deposition of this phosphine oxide with cesium creates a charge transfer complex and enhances conductivity in the device (ITO/α-NPB/Alq$_3$/**1**:Cs/Al) by improving electron injection at the interface with aluminum. Many spirobifluorenes based phosphine oxide analogs were developed as ETL for OLEDs. For example, **2** or **4** (Fig. 2) were used in OLED as universal ETL as they were able to reduce the driving voltage whatever the host was for the adjacent emissive layer (EML).[17] The relatively high LUMO levels (-2.4 eV) of this phosphine oxide makes it suitable for electron injection in any host material. Many of these spirobifluorenes were used as ETL in OLED but also as host matrix for triplet emitters in these device (see **2.2**).[18,19,20]

A spirobenzofluorene based phosphine oxide **5** (Fig. 2) has been used as ETL in a OPV cell (ITO/PEDOT:PSS/P3HT:PCBM/**5**/Al) in order to improve performances (Fig. 2).[21] The use of this interlayer protects the active polymer from Al diffusion into the active layer leading to higher performances, and especially better V$_{oc}$. The coordination ability of the phosphine oxide onto the Al surface leads to band bending which also explains the V$_{oc}$ improvement. Performance improvement was also observed when the LiF layer was replaced by **2** (Fig. 2).[22]

The structure of another universal ETL was recently published, based on arylsilyl and phosphine oxide groups (**3**) (Fig. 2). [23] In these compounds, the Si atom breaks the conjugation. The compound thus possesses relatively high LUMO levels (-2.52 eV) for electron injection in most host, deep HOMO levels (-6.79 eV) for hole blocking and high triplet energy level (E_T) (-3.36 eV) for triplet blocking. High EQE was achieved using **3** (Fig. 2) as ETL in blue phosphorescent OLED (PHOLED).
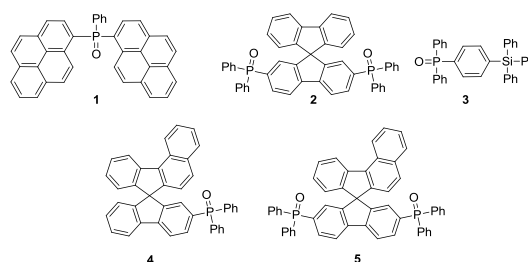

Fig. 2: Electron transport material for OLED and OPV cell.

2.2. As matrix for phosphorescent complexes

Designing efficient hosts for triplet emitters in OLEDs imply several requirements: in addition to the chemical and physical stability, the compound as to carry both holes and electrons (balanced charge transport) and to have suitable triplet energy level in order to transfer energy to the triplet emitter (usually an iridium complex, see supporting information).[24] Following the work developed by Padmapurna *et al*. on ETL for OLEDs,[6] phosphine oxides mainly gained interest as host matrix for triplet emitters. The P=O moiety is used as electron-withdrawing group to ensure the electron transport in association with an electron rich group that will transport the holes (usually an amine). Furthermore, the tetrahedral shape and the lack of conjugation through the P=O group do not affect the triplet energy of the molecule which remains high. This allows energy transfer from the host to the phosphorescent dopant. Since the first report of arylphosphine oxide as host for a blue triplet emitter in 2006 by Burrows *et al*.,[25] many derivatives were studied.

Highly efficient phosphine oxide based hosts include generally in their structure carbazole units, π-extended units (like spirobifluorene) and/or a silyl group. Due to its good hole transporting ability, the carbazole unit has been associated with a phosphine oxide, to prepare a host matrix with balanced charged transport. Substitution of carbazole by phosphine oxide units at position 2 and 7 (**6**) (Fig. 3) lowers the gap compared to a 3,6 substitution but even though it lowers driving voltage,[26] allowing high performances with light blue triplet emitters. It also lowers E_T, resulting in lower efficiency for deep blue triplet emitters. N,N'-Dicarbazolyl-3,5-benzene (mCP) modification by phosphine oxide overcomes poor electron transport and thermal stability of mCP while

maintaining high E_T. [27,28] Deep blue PHOLED using FCNIr were achieved with high efficiency with these two hosts. Actually **8** (Fig. 3) is one of the most efficient deep blue host for both vacuum and solution process PHOLED. [29] Han *et al.* studied several different hosts for red, green and blue triplet emitters based on the "carbazole-phosphine oxide" approach by tuning the π-linker. [30] They were able to modulate both transport properties and the T_1/S_1 energy level in order to efficiently transfer energy from the singlet state to triplet state of the emitter. The triphenylphosphine oxide substituted by two carbazole units (**7**, Fig. 3) possesses destabilized HOMO and LUMO compared to those of other hosts based also on carbazole but they retain high E_T and bipolar charge transport. **7** was found to be an efficient host for the three primary colors triplet emitters, especially for light blue FIrpic. Polymeric host based on carbazole scaffold were also studied and Shao *et al.* synthesized a triphenylphosphine oxide polymer with carbazole side chain, **P1** (Fig. 3). [31] This polymer showed balanced charge transport and high Tg. Efficiency close to 1% were achieved using single layer structure. This result was further improved to 10.8 % when a hole blocking layer was inserted in the device. 1,2,4-triazole was also associated with phosphine oxide and carbazole. In order to maintain high T_1 level, the carbazole was coupled in the *meta* position of the triazole core in **11** (Fig. 3). [32] Sky blue emitting Ir(dbi)$_3$ complex was picked as guest and high power and current efficiency of 43.0 lm.W^{-1} and 41.6 cd.A^{-1} were obtained with a multilayer configuration. Instead of carbazole, triarylamine was also associated with phosphine oxide through a non-conjugated cyclohexyl spacer, **12** (Fig. 3). [33] This design allows getting both bipolar transport and high T_1 level and was therefore used as host for blue phosphorescent complex FIr6. In combination with phosphine oxide based ETL, efficiency over 20% was achieved.

Phosphine oxide substituted by spirobifluorene showed only electron transport ability and therefore exhibit significant roll-off (i.e. decrease of efficiency with increasing current density). High performances could however be achieved with some of these derivatives. [2,7] Phosphine oxide substituted spirobifluorene (**2**, Fig. 2) was used as host for FIrpic and EQE of 20.3% was achieved and 19 % was obtained without LiF injecting layer. [34] In order to efficiently transfer energy from a dopant to a red triplet emitter, the E^T of the host should be lower than those used with blue emitters. The spirobifluorene core of **2** was thus modified to **5** (Fig. 2) resulting in a E^T of 2.32 eV against 2.83 eV for **2**. [35] Device with Ir(pq)$_2$acac as emitter and **5** as host displayed maximum EQE of 20 %. In 2015, Poriel *et al*. combined the diphenylphosphinospirobifluorene structure to the carbazole moiety to benefit the balanced charge transport given by both fragments (**9**, Fig. 3). [36] This platform allowed the authors to prepare one of the most efficient single layer green PhOLED to date (EQE = 13.2% with Ir(ppy)$_3$ as emitter).

Silyl group has also attracted attention due to the bulkiness and the non-conjugating properties of the phenylsilyl derivatives. Linked to carbazole and phosphine oxide, the tetraphenylsilyl derivatives host (**10**, Fig. 3) showed balanced

charged transport and high E^T for energy transfer to deep blue phosphorescent dopant and EQE of 22% was achieved. [37]

In 2013, Tao *et al.* proposed a new approach to develop ambipolar host involving N-P=O pattern where carbazole or arylamine are bonded to the phosphine oxide (**13**, Fig. 3). [38] The later possesses resonance structures which allow better delocalization. This established the possibility for regulating electrical processes and therefore improving charge transport and charge injection. This ability was illustrated in device using FIrpic as emitter. EQE as a high as 16.5 % was obtained using **13** as host for relatively low driving voltage showing the ability of the N-P=O pattern.

In a recent paper, Lin *et al.* studied the phototostability of several carbazole based host with different electron deficient units. [39] It turned out that the weak C-P bond in the phosphine based host leads to high instability of the device. Such evidence of instability has not been shown for other type of P-based host, if so it could become a major drawback to the development of device using these derivatives that chemists would have to tackle.
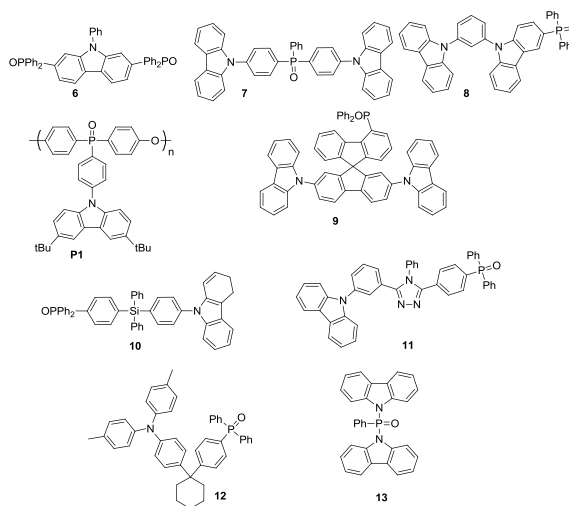

Fig. 3: Phosphine oxide based host structure for OLEDs

2.3 As emitting materials

The phosphine oxide pattern was also inserted into the backbone of oligomers. This allows developing deep blue emitters due to the disruption of the conjugation. Solution processability was maintained and the pyramidal geometry prevents solid-state aggregation. This geometric parameter is an intrinsic advantage of P-derivatives for all applications linked with solid-state emission (see also **4.2**).

Liu *et al.* synthesized different linear oligomers made of a phosphine oxide central core, oligo-phenylene/fluorene chains and N-phenylnaphthalen-1-amine end cap (**P2**, Fig. 4). [40] These structures allowed authors to obtain balanced charge transport and deep blue emission. EQE up to 2.06% was achieved with **P2** and very low efficiency roll-off. The same group later developed two-dimensional oligo-fluorenes **P3** with a central phosphine oxide (Fig. 4). [41] Oligomers were inserted into device with the following structure

(ITO)/PEDOT:PSS / EML / TPBI /CsF /Al. EQE up to 3.41% was achieved with fluorine based oligomers **P3-3** (Fig. 4) with deep blue emission. It turns out that 2D oligomers works better than their 1D analogs. Following their work on polymeric host[31] Wang *et al.* grafted phosphorescent complex (FIrPic) as side chain of the polymer backbone of **P4**.[42] The later consists of a fluorinated and non-fluorinated phosphine oxide with carbazole units (**P4**, Fig. 4). EQE up to 9 % was achieved along with 19.0 cd.A^{-1} luminous efficiency. In a further work, Shao *et al.* introduced an additional yellow phosphorescent emitter on the side chains in order to obtain white OLED (Fig. 4).[43] This approach is possible since the polymer backbone possess a high triplet energy making energy transfer from the backbone to the blue triplet emitter effective. The performances obtained are among the best for single polymer white OLED. Another approach to obtain a white emission is to generate exciplex.[44] In Qiu's work, a novel electro-deficient compound based on an anthracene diphenylphosphine oxide **15** (Fig. 4) forms exciplex at the interface with NPB where excitons are recombining. This phenomenon was also observable in a blend of **15** and NPB. As a result, pure white emission (CIE: x, 0.33; y, 0.33) was obtained with a simple bilayer structure (ITO/NPB/**15**/Mg:Ag/Ag).[21] Kim *et al.* developed an exciplex with a high triplet energy level by mixing a phosphine oxide based ETL, **14** (Fig. 4), and mCP as HTL. The exciplexes are formed efficiently in the host and the energy transfer from the exciplex to the blue phosphorescent dopant (FIrpic) is very efficient, enabling the triplet harvest without energy loss. As a result, blue PhOLED with high performance have been fabricated. The EQE reaches 30.3% with a maximal power efficiency of 66 lm W^{-1}.[45]
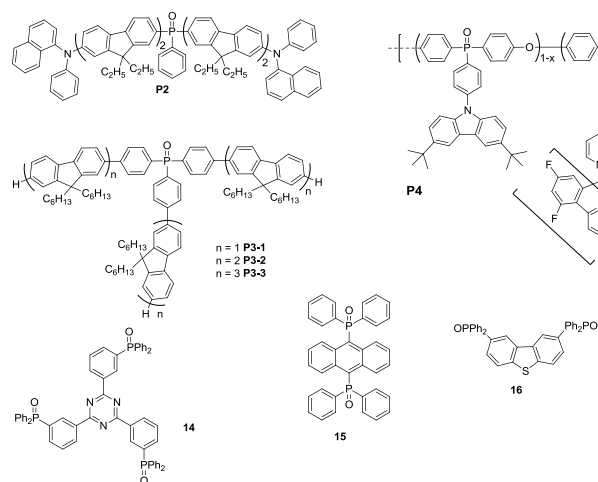

Fig. 4: Phosphine oxide based emitters for OLEDs

Finally one example of thermally activated delayed fluorescence (TADF) was reported by Adachi *et al.* in the exciplex state of a complex where **16** (Fig. 4) is used as electron accepting material.[46] EQE of 10% was obtained. Considering the several perspectives opened by this new phenomenon for fluorescent OLEDs, molecular design of novel

phosphine based TADF emitters is probably a future area of development for the phosphine based molecular materials.[47]

3. PHOSPHAZENES

Phosphazenes are organic compounds were P and N atoms are linked through a double bond. There is no evidence of conjugation in the phosphazene because these materials are ylides with highly polarized bond. Phosphazenes have been well studied in both linear and cyclic forms due to their various properties including excellent hydrolytic stability, flame retardant properties, thermal stability and liquid crystalline behavior among others. The phosphazenes have been inserted in DSSC and OLEDs. Cyclic phosphazenes are used as platform for the synthesis of star-shaped species for OLED applications taking advantage of their low Tg and high stability. Cyclic phosphazene cores possess some appealing advantage for organic electronics: they are easily functionalized and highly stable even under hard condition. The phosphazene core is "electronically" inert: the electronic and optical properties only come from the lateral π-conjugated system. The resulting compounds exhibit spherical shapes which lead to amorphous solid phase, an important property for OLED applications.

3.1. As electrolyte for DSSC

Polyphosphazene first caught the attention for lithium-ion battery applications[48] due to their ability to conduct efficiently lithium and their high thermal stability. They were then used as electrolyte for quasi-solid state or solid-state DSSC. In 2009, Xiang *et al*. reported an electrolyte based on two polymers: polyphosphazene with propionitrile and iodo-(ethylene oxide-co-propylene oxide) side chains (Fig 5), and oligo-organosiloxane grafting oligo-ethylene oxide and propylene oxide dimethylamine side chains.[49] The low Tg of both polymers enables deep penetration into the pores of the TiO$_2$ nanoparticles. The cross linking precursors on the side chains undergo a quaternization reaction upon thermal treatment making the electrolyte insoluble. Photoconversion efficiency with this electrolyte reached 2.66% upon doping with 20 wt% modified silica nanoparticles. In the early 2010s, the group of Allcock *et al*. studied the pores penetration[50] and the influence of iodide salt[51] of linear and cyclic phosphazene based non-volatile electrolytes. They showed that much alike other polymers, polyphosphazene face pore penetration issues that could partly be overcome with a heat-fluidization and solvent assistance. As a result, the use of smaller oligomers or cyclic phosphazene is preferable to facilitate infiltration. Performances obtained with this electrolyte remain low; their structure was probably not fully adapted to ionic transport in DSSC as they were initially designed for lithium-ion batteries. Nevertheless, molecular engineering of the side arm could lead to better results.

3.2. As emitters

Bolink *et al*. functionalized the phosphazene core with fluorescents (**17-20**, Fig. 5) or phosphorescents moieties (**21**, Fig. 5).[52] The compounds exhibited high T_d, high T_g without any T_m confirming the amorphous nature. They showed blue-green emission in solution and in film. Single layer OLEDs

(ITO/PEDOT:PSS/**17**(**18**-**20**)/Ba:Ag) led to low performances but showed that the fluorescent derivatives only had hole transport character due to the high numbers of triarylamine groups. In order to overcome such unbalanced charge transport, an ETL (TPBI) was used to give the following device configuration (ITO/PEDOT:PSS/**17**(**18**-**20**)/TPBI/Ba:Ag). Emission ranging from blue for compounds **17** and **18**, to green for larger compounds **19** and **20** was observed. Best performances were achieved with cyclic phosphazene (CP) **17**, reaching 11000 cd.m^{-2} at 12V and an EQE of 0.72% at 8V). In the case of phosphorescent derivative **21**, a matrix of PVK and PBD was employed to dilute the compound. The diode with the following structure ITO/PEDOT/PSS/PVK:PBD:**21**/TPBI/Ba/Si had an EQE of 7%. L. Bauge *et al* have developed several series of phosphorus-containing dendrimers decorated with fluorescent end groups (naphthalene, anthracene and pyrene). In thin films, the pyrene based dendrimers exhibit a very broad emission characteristic of excimers. OLED including an emitting layer based on a 4th generation dendrimer including 48 pyrenes units, **24-G4** (Fig. 5) in a PVK matrix has been fabricated. The electroluminescence spectrum presents the characteristic emission of the pyrene excimers but the emission of light is low (3.5 cd/m^2) and the threshold voltage is high (over 20V).[53]

3.3. As host matrix for triplet emitters

As in phosphine oxides, the absence of conjugation and the resultant high HOMO-LUMO gap added to high glass transition temperature make CP interesting hosts for phosphorescent derivatives. In that context, two different teams designed solution processed and vacuum processed CPs.[54,55] Soh *et al*. developed CP derivative **22** based on carbazole. No melting or crystallization points were observed showing that these materials are highly amorphous. The triplet energy band gaps of the two CPs were estimated at 3.0 eV which is higher than triplet level of the blue emitters (FIrpic) (2.62 eV). The following OLED structure was employed to evaluate the host abilities of the CPs: ITO/PEDOT:PSS/poly-TPD/**8**:emitter /BCP/BCP:Cs$_2$CO$_3$/Al. A green emitter (Ir(mppy)$_3$) and FIrpic were used in this case. Devices showed high luminance and power efficiency, twice better than reference device using PVK as host. Recently Schrögel *et al.* prepared a vacuum processable CP **23** host for deep blue triplet emitter. Thermal analysis showed that the CPs has high T_d and moderate T_g. Furthermore, morphologically stable amorphous films could be obtained from both solution and vacuum process. Single carrier device made from **23** showed that it has balanced charge transport properties. The triplet energy level of the CP was calculated at -3.2 eV and therefore **23** was used as host for deep blue triplet emitter (Ir(dbfmi)) in an OLED with the following structure ITO/MoO$_3$:NPD/DPBIC/DPBIC:Ir(dbfmi) /**23**:Ir(dbfmi)/DBFSi/TPBi/LiF/Al. The peak of power efficiency of 7.6 lm.W^{-1} is achieved at 5.5 V as the maximum luminance of 5000 cd.m^{-2} is reached at 13.5 V. These values are significantly lower than those obtain with other hosts[56] but this remains a proof of the flexibility of CPs which can be either processed by solution or vacuum.
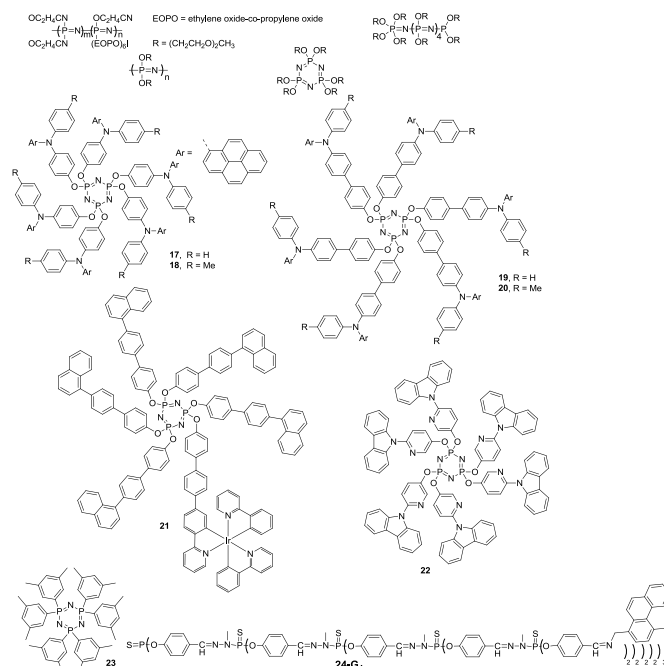

Fig. 5: Phosphazene derivatives used in electrolyte for DSCs, Fluorescent and phosphorescent CPs **3-7**, **13-G4** and CP host **9** and **10**.

4. PHOSPHOLES

Phospholes are a particular class of phosphines in which the P-atom is incorporated in an unsaturated 5-membered heterocycle. Unlike thiophene and pyrrole, 1-phenylphosphole is only slightly aromatic as the phosphorus lone pair does not participate in the intracyclic delocalization.[57] Actually its low aromaticity comes from the interaction between the exocyclic σ*(P-R) and the intracyclic dienic moiety. The lone pair of the phosphole is thus available for reactivity. In the case of σ^4-λ^5 phospholes oxide (P=O) or thio-oxide (P=S), the compounds become slightly antiaromatic.[58] These unusual electronic properties allowed to access compounds with rather low HOMO-LUMO gap. Furthermore, as already mentioned for phosphines, the pyramidal shape of the P-atom affords significant steric hindrance that prevents solid-state aggregation.

4.1. As charge transport layer

Benzophospholes (BP) **25**-**26** (Fig. 6) were developed by Tsuji *et al*. as ETL for OLEDs.[59] **25** and **26**, which only differs by the substituent at the P-atoms (O vs S), possess very similar physical and photophysical properties. They showed a highly stable amorphous phase due to the tetrahedral shape of the P-atom preventing formation of microcrystalline domains. They also have an average to good electron mobility, 5.10^{-6} cm^2.V^{-1}.s^{-1} for **25** and 2.10^{-3} cm^2.V^{-1}.s^{-1} for **26**. This difference is explained by the highly polar character of the P=O bond which trap electrons. They were therefore used as dopant in a Cs ETL which was incorporated in an OLED. The device including benzophosphole **26** showed slightly superior performances than the one based on **25** as the voltage at 1000 cd.m^{-2} was 5.0V and 5.9V and luminance efficiency was 1.8 lm.W^{-1} and 1.4 lm.W^{-1} respectively.

Similar properties were observed with benzophosphole **27** (Fig. 6) which were used as cathode buffer layer along with **25** and **26** in an OPV cell (ITO/PEDOT:PSS/BP/PB:SIMEF/**27**/Al).[60] The high glass transition observed for these compounds allows thermal annealing process without altering the layer. This process improves the power conversion efficiency (PCE) of the solar cell from 2.9 to 4.6%. Authors claim that coordination complexes are formed at the interface with Aluminum, like for phosphine oxide, resulting in lower resistance between the two layers. Inspired by this work, Matano *et al.* developed diarylaceneoxophospholes **28**-**31** (Fig. 6) exhibiting relatively high T*g* and modest mobilities.[61] Nevertheless their use in OPV cells as buffer layer (ITO/PEDOT:PSS/P3HT:IC$_{70}$BA/**28**-**31**/Al) gave better performances than with BCP, a common organic n-type material. Authors report that the nature of the 2,5-substituents of the phosphole ring impacts the performances due to different packing motifs and/or different contact resistance. In this case, oxophosphole worked significantly better than their thiooxo-counterparts.
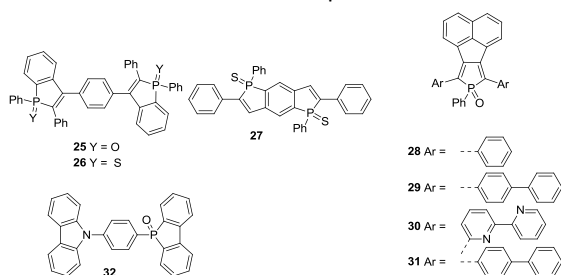

Fig. 6: Electron transport material for OLED and OPV.

One example of dibenzophosphole based host for triplet emitters was published in 2012 (**32,** Fig. 7).[62] The author prepared an OLED with a Os(II) based emitter presenting an EQE of 14% which is 3% higher than the reference device containing a CBP host. This effect was attributed to the better charge carrier mobility (both for holes and electron) of **32** compared to BCP.

4.2. As emitters in OLED

The insertion of phosphole derivatives as emitters in OLED goes back to 2003 by Fave *et al*. with 2,5-dithienylphosphole derivatives **33**-**34** (Fig. 7).[63] Derivatization can be performed on the reactive P-center to obtain either thiooxophospholes or Au(I) complexes. Several other phosphole-based conjugated systems were prepared and inserted in fluorescent OLEDs.[64] Along these studies, the only σ^3-λ^3 phosphole suitable for vacuum sublimation was **35** (Fig. 7) as these species are usually not thermally stable enough to stand this process. Green emission at 510 nm was obtained with EQE of 0.08% in single layer OLED (0.29% in a multilayer configuration). Thiooxophosphole derivatives **33**, **36**, **37** (Fig. 7) showed low performances in single layer OLED but they can be improved by using HTL (α-NPB) and ETL (Alq$_3$). Quantum efficiency can be increased by four to ten times depending on the structure of π-conjugated systems. For example, maximum EQE of emitters **33** goes from 0.16% to 0.80%. Interestingly, gold

complexes **34** or **38** (Fig. 7) have very low performances in single layer diodes. Furthermore, electroluminescence differ completely from photoluminescence in solution, unlike σ^3-λ^3 phosphole and thiooxophosphole. This phenomenon was later rationalized by Joly *et al*. on fluorenylphosphole **39**-**43** (Fig. 7).[65] They unambiguously showed that the lower energy emission was actually coming from fast decomposition of the gold complexes upon electric field. Some low molecular weight dibenzophospholes were inserted in OLED by vacuum sublimation without success as the devices characteristics show instability with increasing driving current.[65] On the contrary, polymers based on fluorene and benzophosphole **P5** / benzooxophosphole **P6**, Fig. 7) were used as EML in single layer device (ITO/PEDOT:PSS/EML/Al).[66] **P5** showed blue electroluminescence with brightness up to 1423 cd.m^{-2} whereas **P6** exhibited a white emission but with lower brightness (142 cd.m^{-2}).

So far, the best EQE recorded for an OLED with EML only based on phosphole derivative has been 1.8% with 2,5-difluorenylthiooxophosphole **41** (Fig. 7). In 2012, Kondo *et al.* reached 4.0% EQE which is close to the theoretical limit of fluorescent OLEDs, using dithienophosphole dopant **45** as emitter in a TBADN host.[67] A new type of phosphole based-emitter was developed by Chen *et al.* using benzofuran fused phosphole **46**. EQE in multilayer device was only 0.45%, limited by the poor transport properties of the phosphole and probable electromers formation as the electroluminescence was red shifted by 40 nm compared to neat film photoluminescence.

Phosphole emitters also appeared as original material in the context of white light emission, which remain a challenge for both academic and industrial purposes. To this end, orange emitting phospholes were chosen as dopant for blue emitting matrixes in order to achieve white light through energy transfer. Preliminary work was done by Fadhel *et al.* with 2,5-dithienylphosphole **33**, **34** and **47** (Fig. 7).[68] The amount of **33** required to dope DPVBi to achieve a white emission was too low and therefore tricky to control. The authors thus used the HTL, α-NPB, as matrix. A moderate increase of dopant amount allowed preparing an OLED with a satisfactory white emission (CIE: x, 0.28; y, 0.34). Same approach was used with dopant **47**. The red-shifted emission of **47** compared to **33**, allowed to prepare a purer white OLED using a doping rate of 0.2% in α-NPB. **43** and **44** (Fig. 7) were also used as dopant for DPVBi.[69] The optimum doping rate of **43** was found to be 0.3% (CIE: x, 0.27; y, 0.33) and EQE reached 2.1 %. The necessary amount of dopant **44** to achieve a white emission was surprisingly higher than for all other phosphole derivatives. Furthermore, it was found that this dopant was highly quench resistant as the EQE remains stable even at very doping rate. This was due to a combination of favorable factors such as structural and physical properties. A dopant based on 2,2'-bisphopshole **48** was later developed by Chen *et al.*.[70] In this family of compounds, the control of the distortion angle between the two phosphole units allowed fine-tuning of the optical/electronic properties and close to perfect CIE coordinate was achieved (CIE: x, 0.34; y, 0.34) by doping a

DPVBi matrix. Even if the working parameter of this device remain low, the proof of concept of using the torsion angle of biphosphole to adjust the HOMO-LUMO gap open very interesting perspective for every opto-electronic applications. Finally, we recently developed a new family of P-containing PAHs (compounds **49-50,** Fig 7).[71] These compounds were the first reported polyaromatic compounds featuring a P atom in their scaffold. They show high luminescence in the orange-red region in diluted solutions and this fluorescence remains high in solid matrix. WOLED devices were prepared using NPB as blue matrix. With a doping rate of 0.8%, white emission was achieved (CIE: x, 0.32; y, 0.37) with EQE of 1.2%.[72] In this case again, efficiencies remain low but optimization on this new family of P-derivative may lead to interesting improvement in the field of emitting materials.
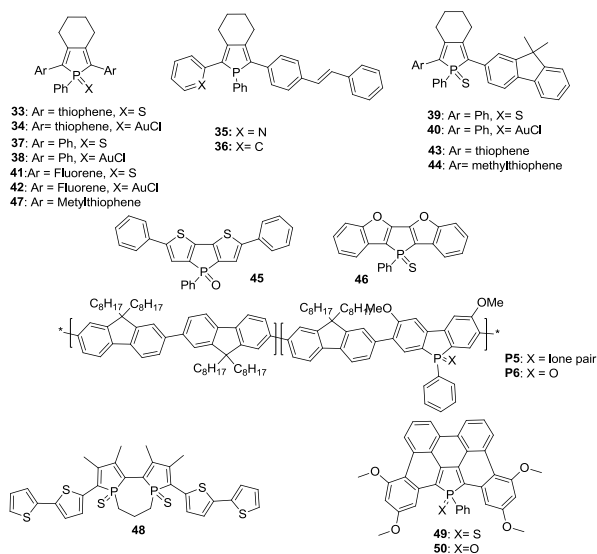

Fig. 7: Phosphole derivatives as emitters in OLED and WOLED

4.3. As dyes in Dye-sensitized Solar Cell (DSSC)

In 2010 Kira *et al.* developed a sensitizer for DSSC based on 1-hydroxy-1-oxydithienophosphole derivatives **51-52** (Fig. 8), used as both acceptor moiety and anchoring group.[73] The IPCE of the DSSC with TiO_2/**51** and TiO_2/**52** were estimated at 66 % and 43 %, respectively. Maximal efficiency was measured for **52** with PCE of 1.8%. Even if the efficiencies remain low, the originality of this work is the use of hydroxyoxophosphole moiety as binding motif toward TiO_2, as most of the studies use carboxylic acid or phosphinic acid which are not detailed in this review.[74]

More recently, the same team developed a new series of push-pull dyes featuring a triarylamine donor and a carboxylic acid-substituted thioxophosphole as acceptor (**53-54**, Fig. 8).[75] In this case, the anchoring group is not located at the P-atom. The sterically hindered P(V) center appear as an appealing system to prevent dyes aggregation. After optimization, PCE up to 5.6% have been obtained with better results for compound **54**. These performances were attributed to a better charge collection. These two examples show that the

phosphole backbone can be used as π-conjugated linker and as anchoring group for the development of new dyes for DSSCs.
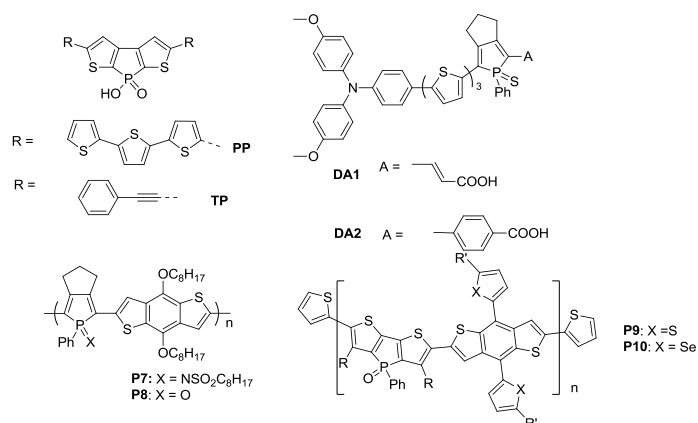

Fig. 8: dithienophosphole based dyes for DSSC and phosphole polymers Organic Solar cells.

4.4 As donors in organic photovoltaics

In 2014 was published the first example of phosphole-based polymer for organic photovoltaics. **P7** and **P8** (Fig. 8) were based on benzodithiophene and either imidophosphole or oxophosphole. Modification at the P atom does not modify the optical properties. Both polymers were used as donors in blend with $PC_{71}BM$ acceptor and significantly better photovoltaic performances were achieved with the oxophosphole derivatives (**P8**: J_{sc}=2.6 mA.cm^{-2}, V_{oc}= 0.63 V, FF= 0.40, η= 0.65 %; **P7**: J_{sc}= 0.45 mA.cm^{-2}, V_{oc}= 0.45V, FF= 0.35, η= 0.07%). These results show that P-substituents have a clear impact on the charge-generation efficiency and/or charge-carrier pathways in the blend. These pioneering results were recently overcome by the use of **P9-10** (Fig. 8).[76] In this case, the P-containing repeated unit is a dithienophosphole oxide that acts as electron deficient unit in donor-acceptor low-band gap polymer. Bulk heterojunction devices prepared by mixing the **P9-10** donors with $PC_{71}BM$ acceptor allowed the authors to reach a PCE of 7.1% in the case of solar cells processed with 1,8-octanedithiol as additive (**P9**: J_{sc}=13.2 mA.cm^{-2}, V_{oc}= 0.87V, FF= 0.53, η=6.10 %; **P10**: J_{sc}=14.8 mA.cm^{-2}, V_{oc}= 0.85V, FF=0.56, η= 7.08%). The authors attribute this efficiency to the high polarizability of the oxophosphole moiety. This efficiency is close to the best efficiency reached for all organic devices and paves the way for highly efficient P-containing polymers for photovoltaic applications.

4.5 Electrochemical cell

In 2012 Baumgartner *et al.* designed discotic dendritic phospholes that form luminescent gels and liquid crystalline phases.[77] In particular, they showed on compound **55** (Fig. 9) that oxidation allows tuning the colour and the photoluminescence of a simple electrochromic cell (ITO/**55**+NBu_4ClO_4/ITO). This was the first example of electrochromism on P-heterocycles. This concept was recently applied to derivative **56-57** (Fig. 9). This phosphole-viologen analogs display very low reduction potential and the electrochromic behaviour could be demonstrated with a switch from the colourless dication of **56** to its blue mono-cationic form.[78]

This concept was further applied to multicolour electrochromic devices using the 3 stable redox states of **57**.[79] These devices are not OLED as there is no electroluminescence, but these studies show that the amphoteric redox properties of phosphole allow tuning their absorption/emission upon electrical stimuli.
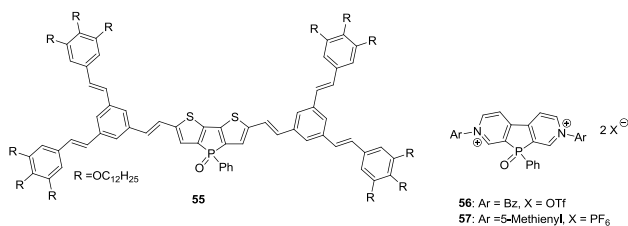

Fig. 9 : Phosphole derivatives used in electrochromic devices

5. 4-membered ring P-heterocycles

5.1 1,3-Diphosphacyclobutane-2,4-diyls

Ito *et al.* recently reported the synthesis of air-stable P-heterocyclic biradicals, namely 1,3-diphosphacyclobutane-2,4-diyls (Fig. 1 and 10).[80] These compounds were first prepared by Niecke *et al.*[81] but its only when Ito *et al.* modified the substituent at the P atom that air stable compound could be prepared. In particular, the use of amino-substituted triazine allowed them to prepare **58** as an air-stable derivative with low oxidation potential. FET device (Si/Si0$_2$ wafer with interdigitated Au bottom electrodes) using drop-casted **58** were prepared. The device exhibited p-semi-conducting properties with low mobility (2.3 10^{-8}cm^2.V^{-1}.s^{-1}) and an on/off ratio of 7. The lack of intra-molecular interactions in the solid-state is a possible reason for this low activity. These characteristics are rather low compared to benchmark organic semi-conductors. However, this first example of P-containing OFET-active compound clearly shows that these derivatives can be interesting for this application. Considering the electron affinity of phosphine/phosphole oxide, the preparation of OFET with n-type characteristics is clearly a perspective for all these compounds.[82]

5.2 Phosphete

Recently, 1,2-dihydrophosphete derivatives (Fig. 1 and 10) were also introduced as new π-conjugated systems for optoelectronic applications. This unsaturated four-membered P-heterocycle appeared as an appealing skeleton to develop novel P-based emitters. Like in phosphine and phospholes, the pyramidal shape of the P affords steric hindrance that prevents solid-state aggregation. A whole family of fluorophores based on this skeleton (**59-61**, Fig. 10) was prepared by Chen *et al.*[83] Multilayers OLEDs (ITO/CuPc/α-NPB/EML/DPVBi/BCP/Alq$_3$/LiF). All compounds displayed blue electroluminescence characteristic of the P-fluorophores. Efficiencies were higher when the compounds were doped in a matrix (CPB or DPVBi). This was attributed to moderate charge carrier mobility in the EML. In particular, devices prepared with **59** in a DPVBi matrix exhibited blue electroluminescence, good performances and current independent CIE coordinates.

This preliminary study paves the way for the development of efficient devices based on this new P-scaffold.
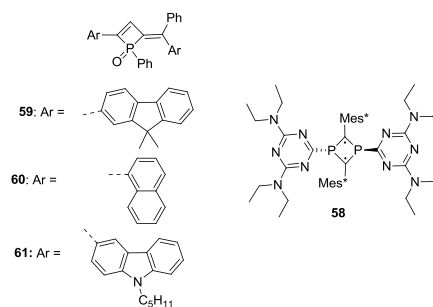

Fig. 10: Diphosphacyclobutane diradical **DPCB** used in FET device and phosphetes derivatives **Phos1-3** for OLEDs

Conclusions

This review presents the main class of P-containing π-conjugated compounds used in electronic devices (mainly OLEDs). By far, the most widely studied class of organophosphorus derivatives in optoelectronics are the triarylphosphines used as ETL or hosts for triplet emitters in OLEDs. Their thermal stability, the high electron affinity of the oxophosphine moiety associated with the easy modification of the aryl substituents made the use of the triarylphosphines very popular. The second class of compounds which is also widely used are the phospholes. They were mainly studied as emitters in OLEDs (including WOLEDs). The incorporation of the phosphole fragment in the π-system allows obtaining solid-state emission due to the pyramidal shape of P that prevents aggregation. Furthermore, the intrinsic low-band gap of phosphole allows obtaining compound with red-shifted absorption/emission compared to the phosphines. In addition to these two classes of P-derivatives, phosphazenes and phosphete derivatives have also been used in OLEDs.

In the case of the solar cells, the (thieno)phospholes appear as the most adapted P-backbone as it allows good light absorption due to its low HOMO-LUMO gap together with a good electron affinity and planarity that will favor charge transport in the solid-state. However, the examples of their use remain limited. Nevertheless, there are no theoretical limitations for the developments of these compounds for photovoltaic applications, including by replacing fullerenes as acceptor considering the excellent electron affinity of all phosphine oxide derivatives.

Finally, only one example of organophosphorus derivative for OFET application has been described to the best of our knowledge. Surprisingly, it is a p-type OFET based on an unusual diradical backbone structure, while the oxidized organophosphorus derivatives are widely used for their electron affinity. Here again, no technical limitation is responsible for the absence of P-derivatives. The recent development of highly planar P-derivatives and phosphahelicenes should give rise to new solid state organization and new physical properties interesting for the preparation of n-type OFETS or 3D-OLEDs, respectively.[71,84,85]

However, based on the variety of different P-scaffold described in the literature,[7,86] new efficient P-derivatives for opto-electronic applications are still to be discovered.

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