Polyaromatic phosphetenes: versatile platforms for circularly polarized luminescence generation through chiral perturbation.

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ABSTRACT: We describe the synthesis of four new polyaromatic fluorophores fused to a phosphetene ring (4-membered P-ring). These compounds are fully characterized including X-ray diffraction. Due to the presence of the stereogenic P-atom, all compounds are found as racemic mixture, which could be separated by chiral separation. The impact of both the polyaromatic platform and the P-ring on the structure, the optical and redox properties are investigated both experimentally and theoretically. Although neither the P centre nor the 4-membered ring significantly takes part in HOMO or LUMO orbitals, both of these structural features have an important modulating role in distorting the symmetry of the orbitals, leading to chiroptical properties. In this case, the stereogenic P-atom is used as chiral perturbator to induce circularly polarized luminescence of the polyaromatic system.

Polycyclic Aromatic Hydrocarbons (PAHs) are π-conjugated systems consisting of fused aromatic rings that find many applications in the field of opto-electronics.[1] Their properties are mainly defined by their fusion patterns at the molecular level. For example, linearly fused systems display high charge carrier mobility and thus have been widely used as p-semiconductors in Organic Field-Effect Transistors (OFETs).[1] When the rings are angularly arranged, the compounds displays a helical π-framework which is configurationally stable depending on the number of ortho-fused rings and their substituents. Such compounds, called helicenes (for example [6]helicene **A**, Fig. 1) show excellent chiroptical properties due to the inherent chirality of the π-framework: e. g. optical rotation, circular dichroism and circularly polarized luminescence (CPL) with luminescence dissymmetry factor (g_{lum}) values up to 10^{-2} for substituted [6]helicenes.[2] As an example of applications, [6]helicenes were used to design circularly polarized organic light-emitting diodes (CP-OLEDs).[3] An elegant alternative strategy for designing CP-emitters is to prepare a chirally perturbated fluorophore.[4] In such a derivative, a chiral centre is located in the vicinity of an achiral emitter, inducing its chiroptical properties. BINOL substituted-BODIPY **B** (Fig. 1) is a representative example of this emerging class of CP-emitters that also found application in OLEDs.

In this work, we aimed to use the chiral perturbation of a stereogenic P-atom (within a phosphetene ring) to chirally perturb linearly fused PAHs. Hence, phosphetene is a 4-membered P-ring that, despite being barely investigated, has started to be used in the context of molecular materials and optoelectronics.[5] We describe the synthesis of four new PAHs fused to a phosphetene ring. The impact of both the polyaromatic platform and the P-ring on the structure, as well as the optical and redox properties of the compounds are investigated experimentally and using theoretical methods. Finally, we show that the stereogenic P-ring acts as an efficient chiral perturbator to induce circularly polarized luminescence of the polyaromatic system with g_{lum} of ~10^{-3}.

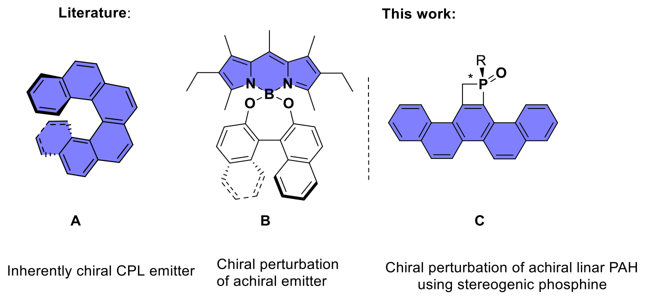

Figure 1. Examples of CPL emitters (**A-B**) and compound studied in this work (**C**) (blue part represents the fluorophore in each molecule)

To prepare phosphetenes **1-4**, Doxsee's one-pot methodology was used starting from the corresponding alkynes (Scheme 1).[6] The phosphetenes having trivalent P-centres (^{31}P NMR: ~-17 ppm) were oxidized in situ to form the corresponding phosphetene oxides (^{31}P NMR: ~+20 ppm), which can easily be handled in air. All compounds were synthesized in moderate yields (31-46%) and were fully characterized by multinuclear NMR, mass spectrometry and their structures were unequivocally confirmed by single crystal X-ray diffraction (Scheme 1). The unit cells are all composed by a racemic mixture of the two enantiomers, with the P atom as a stereogenic centre. In all these derivatives, the P-ring is a distorted square (Table S2) with usual

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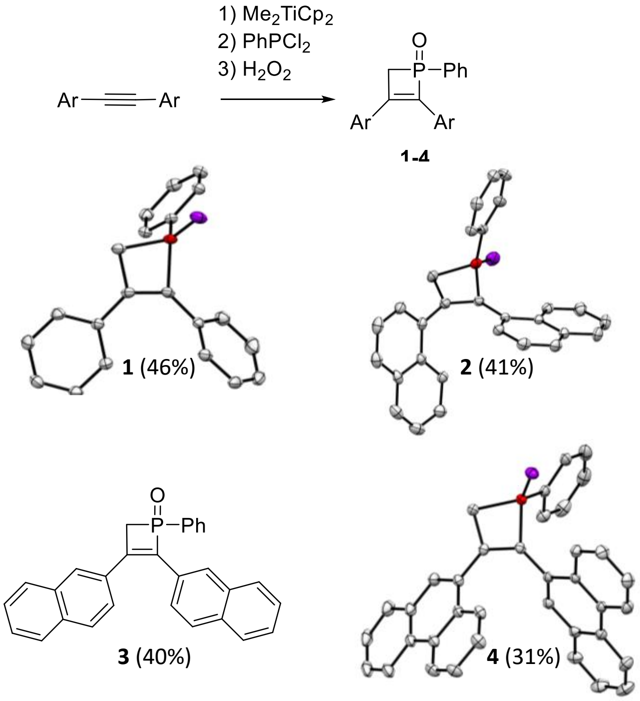
bond distances and angles for phosphetenes.[5] The lateral aryl groups are twisted from the plane of the P-ring. Such a structural property will have an impact on the conjugation in the systems (*vide infra*). No intermolecular interactions were observed in the packing.



Scheme 1. Synthesis route to **1-4** and X-ray structures of **1-2**, **4.** Hydrogen atoms are omitted for clarity and thermal ellipsoids are set at 50% probability.

The optical properties (absorption/emission) of compounds **1-4** were investigated in diluted DCM solutions (c = 5.10^{-6} $mol.L^{-1}$, Fig. 2 and Table S4). **1-4** display large UV-vis absorption bands in the visible range that were attributed by TD-DFT to π–π* transition (HOMO-LUMO) without significant contribution from the P-atom (Table S10). Due to the rotation of the aryl group, in solution several conformers may coexist, which is supported by DFT calculations: except for **1**, conformers having similar energies were found for **2-4**, and these isomers have slightly different absorption wavelengths. As expected, the extension of the π-skeleton leads to a bathochromic/hyperchromic shifts. All derivatives are also luminescent in diluted solution and show broad and unstructured emission in the blue region, with a large Stokes shift (Table S4 and Fig. 2). These emissions display a lifetime in the range of the ns (Table S5).

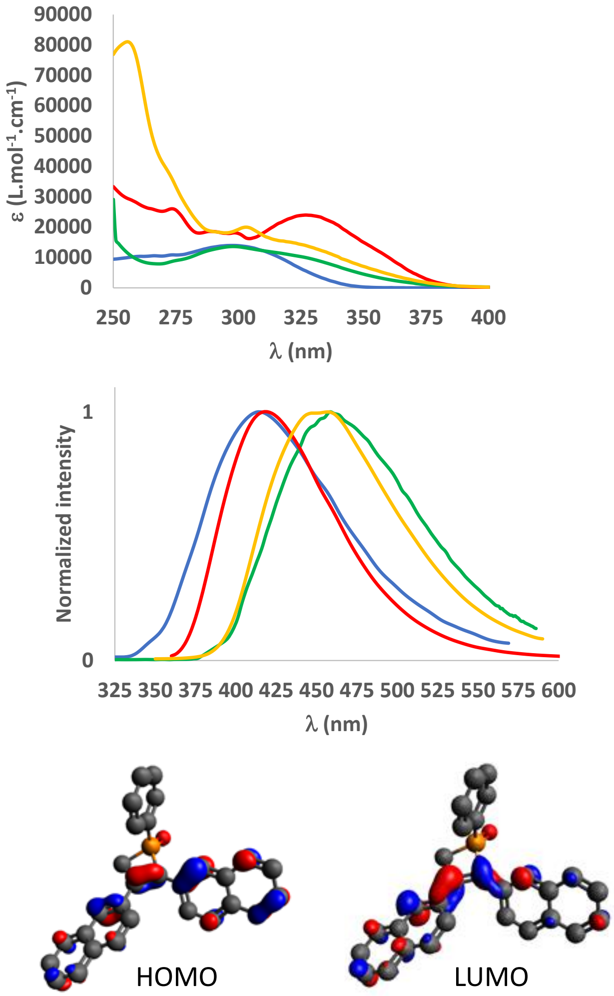
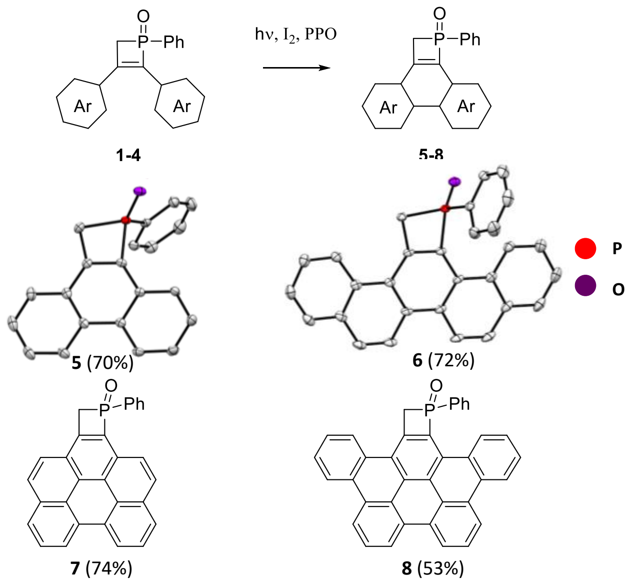


Figure 2. UV-Vis absorption (up) and normalized emission spectra (middle) of **1** (blue), **2**(green), **3**(orange) and **4** (red) in DCM (c = 10^{-6} M). HOMO and LUMO of **3** (down) (calculations at the B3LYP-D3/6-31G* level).

The molecular structures of **1-4**, with their heterocycle-substituted stilbene backbones, makes them ideal synthons to promote photoinduced intramolecular cyclization. Indeed, the reaction of **1** and **2** in the "Katz" conditions (hν, I_2, propylene oxide)[7] leads to the formation of phenanthrene- (**5**, Scheme 2) and picene-substituted phosphetene oxides (**6**, Scheme 2) in good yields (70-72%). In the case of **3-4**, the reaction does not stop after the first cyclization, and a second cyclization occurs to yield planar PAH substituted phosphetene **7** and **8** (74%-83%).[8] All the derivatives were fully characterized by multinuclear NMR, mass spectrometry and the structure of **5** and **6** were further confirmed by X-ray diffraction (Scheme 2). Again, the structures consist in a racemic mixture of enantiomers and the geometry of the P-ring is not significantly altered by the cyclization. In these systems, the polyaromatic scaffold is mostly planar (maximal deviation from the mean polyaromatic plane in **6**: 0.14 Å). The NICS(0) patterns confirm that these PAHs nicely agree with Clar's criterion (Table S6-S9) despite the presence of the P-heterocycle. No intermolecular interactions based on π-stacking of the PAH framework can be observed in the packing.



Scheme 2. Synthesis route to **5-8** and X-ray structures of **5-6.** Hydrogen atoms are omitted for clarity and thermal ellipsoids are set at 50% probability.

The presence of an electron-withdrawing P=O markdly impacts the redox properties. Compared to the purely hydrocarbon analogs, the cyclic voltammetry measurements revealed that **6-8** display monoelectronic quasi-reversible reduction waves at moderated potential (E_{red}~-2.2V vs Fc, see Table S4 and Fig. S44). This redox behaviour arises from the presence of the electron-deficient phosphine oxide moiety directly attached to the PAH backbone.[9]

The optical properties (absorption/emission) of **5-8** have been investigated in diluted DCM solutions ($c = 5.10^{-6}$ mol.L^{-1}, Fig. 3 and Table S4). The UV-vis absorption spectra of **5-8** are in marked contrast with those of their precursors **1-4**. Indeed, they all display finely structured absorption bands in 300-440 nm range, characteristic for PAHs derivatives (Fig. 3). Actually, the effect of the P-ring on the absorption is limited compared to the purely hydrocarbon analogues.[10] As expected, the extension of the π-backbone in the series leads to bathochromic shifts. TD-DFT calculations for **5** show satisfactory agreement with the experimental data (Table S12, Fig. S46): the excitations have strong multi reference characters, e.g. the first excitation belong to a mixed HOMO-1 to LUMO and HOMO to LUMO+1 transitions. However, for compounds **6-8** various TD-DFT methods fail in describing the spectra, meaning that even the patterns cannot be properly simulated. Thus, ACD(2) calculations were applied, which not only predict a correct pattern, but also offer acceptable quantitative agreement (Table S12, Fig. S46-S53). Based on these data, the sets of low energy peaks with low intensities in the spectra of **5-8** belong to the vibrational fine structures of the lowest energy excitations. Again, the P-atom is practically not involved in any of these transitions. Importantly, however, the orbitals are not symmetric when compared to the C2v symmetric parent compounds without flanking phosphetene rings. As Fig. 3 shows, the orbital contributions not only indicate asymmetric pattern along the linear chain, but also on the two sides of the quasi plane of the molecules. As it will be shown below, this will affect the chiroptical properties, because the asymmetries in the lobes differ among the different orbitals, offering a slight charge transfer character. The emission spectra also strongly differ from the precursors as finely structured emission bands with very low Stokes shifts are observed (Fig. 3 and Table S4). The lifetime is one order of magnitude higher compared to their precursors (~10 ns, Table S5), but remain in the range of purely fluorescent compounds. The luminescence is again highly similar to that of the purely hydrocarbonated analogs.[10] The trend in emission wavelengths in the series agrees with that observed in absorption. These compounds all display high quantum yields (35-62%), in agreement with their rigid polyaromatic structures.

In conclusion, four new phosphetene-substituted PAHs (either linear (**5-6**) or extended planar (**7-8**) were prepared and these compounds demonstrate intense emission in solution characteristic of PAH derivatives.

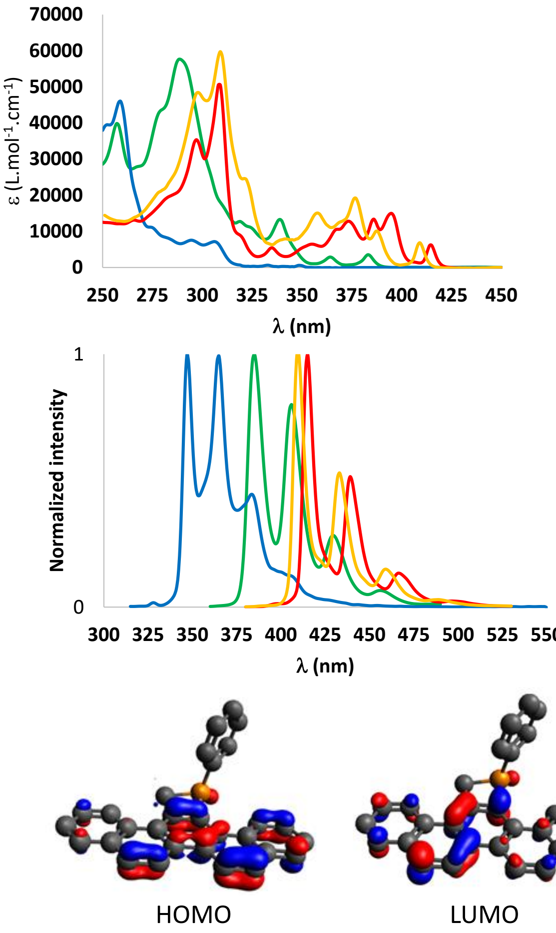


Figure 3. UV-Vis absorption (up) and normalized emission spectra (middle) of **5** (blue), **6** (green), **7** (red) and **8** (orange) in DCM (c = 10^{-6} M). HOMO and LUMO of **6** (down) (calculations at the B3LYP-D3/6-31G* level).

As mentioned previously, the P-atom in these systems is stereogenic. To investigate the effect of the chirality on the optical properties, enantiopure samples (with ee > 99,5%) of linearly fused derivatives **5-6** were obtained via HPLC using a chiral stationary phase (see ESI). The absolute configuration of (R)-**5** and (R)-**6** was assigned using their X-ray diffraction structure (Fig. S32 and S34).

Electronic circular dichroism (ECD) was recorded in diluted DCM solutions. (R)-**5** and (S)-**5** (respectively (R)-**6** and (S)-**6**) displayed ECD with the expected mirror-image relationship (Fig. 4). For example, (R)-**6** shows various positive ECD bands (Δε = +15 at 258 nm, Δε = +19 at 298 nm), negative bands (Δε = -16 at 290 nm, De = -16 at 338 nm and Δε = -7 at 380 nm). Interestingly, **5** and **6** present quite remarkable CPL (Fig. 4) with g_{lum} ~ 9 10^{-4} at 370 nm for **5** and g_{lum} ~ 1.1 10^{-3} at 408 nm for **6**, in agreement with their g_{abs} values (for example, g_{abs}(**5**) =~2.10^{-3} at 345 nm, and g_{abs}(**6**) =~9.9 10^{-3} at 340 nm and =~1.5 10^{-3} at 380 nm). These values are typical for organic CPL emitters[2] but are rather unexpected as the P-atom has a very weak impact on the electronic properties (*vide supra*).[11] This clearly shows that the chiral perturbation induced by the presence of the stereogenic P-atom triggers the CPL activity of linear PAHs.

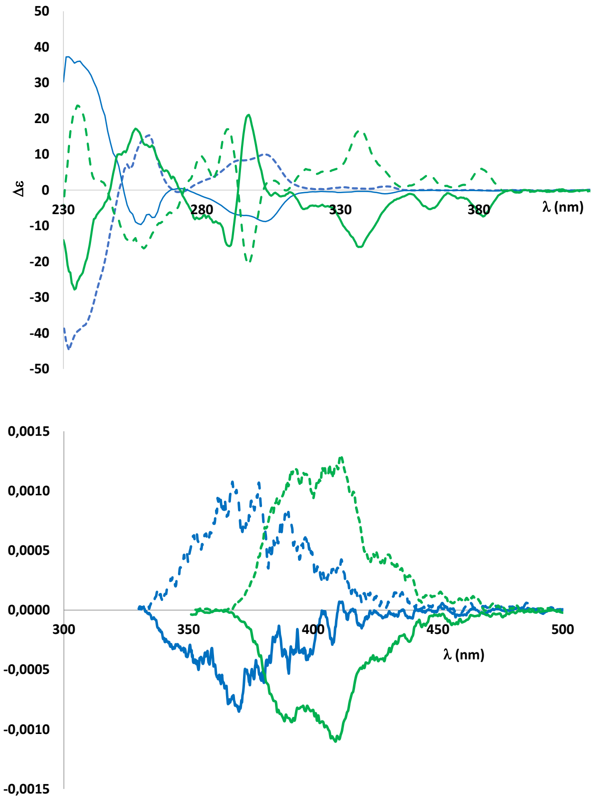


Figure 4. ECD spectra (up) and CPL spectra (down) of (R)-**5** (blue dotted), (S)-**5** (blue), (R)-**6**, (green dotted) (S)-**6** (green) (up) in diluted DCM at 10^{-5} M

In conclusion, four new polyaromatic fluorophores fused to a phosphetene ring **5-8** have been synthesized. These compounds exhibit the typical optical properties of polyaromatic compounds, such as structured absorption, and fluorescence with very low Stokes shift. The presence of the P atom (phosphine oxide) generates quasi-reversible electrochemical properties as well as chirality. The enantiopure samples **5-6** showed significant CPL emission induced by the chiral perturbation of the stereogenic P-center. Although the flanking four membered rings are not extensively involved in the HOMO and LUMO (or any other near-lying orbitals), their chiral characters induce asymmetry in the relevant orbitals, resulting in chiroptical properties. This observation opens many perspectives in the field of organic materials with chiroptical properties, given the diversity of chiral phosphines and P-rings.

ASSOCIATED CONTENT

Supporting Information. Synthetic procedure, complete characterizations, X-ray crystallographic data and CIF files, computational details and Cartesian coordinates. The following files are available free of charge.

Author Contributions

The manuscript was written through contributions of all authors.

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