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# A Guide for the Design of Functional Polyaromatic Organophosphorus Materials

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Abstract: The impact of integrating six-membered phosphorus heterocycles into poly(hetero)aromatic materials is investigated. Mechanistic studies reveal the key synthetic requirements for embedding the latter phosphorus heterocycles in polyaromatic molecules. DFT calculations indicate that introducing six-membered phosphorus rings into π-extended molecules induces a particular electron distribution over the π-extended system. Electrochemical investigations confirm that inserting six-membered phosphacycles into polyaromatics triggers ambipolar redox behavior. Steady-state spectroscopy reveals that fusing pyrroles with phosphoruscontaining polyaromatic molecules induces fluorescence quantum yields as high as 0.8, whereas transient absorption spectroscopy demonstrates that fusing thiophenes promote the formation of nonemissive triplet-excited states. As a whole, the optoelectronic properties of fused phosphorus-containing materials give rise to promising performances in photoelectrochemical cells. Moreover, Xray analyses confirm that the 3D arrangement in the solid state of polyaromatic systems containing six-membered phosphorus rings can be tailored by the post-functionalization of the phosphorus center. Altogether, this investigation set the bedrock for the design of generation of highly functional polyaromatic а new organophosphorus materials keeping control over their electrochemical properties, fluorescence features, photo-induced excited states and 3D molecular arrangement.

#### Introduction

Polyaromatic materials play a fundamental role in organic electronic applications such as field-effect transistors,<sup>[1]</sup> lightemitting devices,<sup>[2]</sup> solar cells<sup>[3]</sup> and sensors.<sup>[4]</sup> The particularities of these materials involve an extended mantle of  $\pi$ -electrons formed by the efficient overlap of *p* atomic orbitals. As a result, many polycyclic aromatics exhibit semiconductor behavior,<sup>[1e]</sup> excellent charge-transport properties<sup>[5]</sup> and the capacity to

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photo- and/or electrogenerate light.<sup>[2]</sup> Importantly, the latter properties are strongly sensitive to the perturbation of the materials' electron cloud. Thus, diversifying the nature of the atomic orbitals involved in the  $\pi$ -electron cloud with heteroatoms has become a promising strategy to modulate the optoelectronic properties of polycyclic aromatics for functional applications.

To this end, increasing research interest has been devoted to integrating phosphorus rings into polyaromatic materials. The most investigated phosphorus systems for materials applications are based on phospholes.<sup>[6]</sup> These non-planar five-membered heterocycles were first synthesized in the 1950's.<sup>[7]</sup> However, it was only at the beginning of the 21<sup>st</sup> century when the groups of Réau<sup>[8]</sup> and Baumgartner<sup>[9]</sup> independently laid the foundation for the development of phosphole-based systems for materials applications. Thus, based on a large number of investigations developed over the last fifteen years,<sup>[6]</sup> it is currently established that: a) extending the conjugation of five-membered phosphorus rings provides highly stable materials.<sup>[8,10]</sup> b) the integration of phospholes into π-extended systems leads to high fluorescence quantum yields (QYs)<sup>[11]</sup> and c) phosphole-based systems behave primarily as electron acceptors.<sup>[12]</sup> Moreover, shedding light on the high synthetic versatility of  $\lambda^3$ - $\sigma^3$  phosphorus centers of phospholes triggered an extensive development of organophosphorus materials;  $\lambda^3$ - $\sigma^3$  phosphorus centers possess a variety of selective post-functionalization reactions that provide unique means to tailor the materials' optoelectronic properties for practical applications. As a result, organophosphorus materials containing five-membered phosphorus heterocycles have led to important breakthroughs in fields such as liquid crystals,[13] OLEDs.<sup>[14]</sup> cells,<sup>[15]</sup> solar electrochromic materials<sup>[13a,16]</sup> and sensors,<sup>[17]</sup> just to name a few.

On the other hand, the six-membered analogues, phosphabenzenes ( $\lambda^3$ -phosphines), were first prepared in the 1960's.<sup>[18]</sup> Surprisingly, the application of six-membered phosphorus heterocycles has been, to date, mostly limited to coordination chemistry<sup>[19]</sup> and homogeneous catalysis;<sup>[19h-k]</sup> they have been barely employed in materials applications.[1e,20] Notwithstanding, phosphabenzenes possess appealing properties that clearly distinguish them from both phospholes and their heterocyclic analogues, pyridines.<sup>[20]</sup> They are highly aromatic<sup>[21]</sup> and present a particular orbital level distribution with a low-lying LUMO<sup>[19a,20]</sup> that converts them into electron acceptors.<sup>[22]</sup> Thus, six-membered phosphorus heterocycles intuitively open up new possibilities in materials science. However, only few polyaromatic materials based on these heterocycles have been reported to date.<sup>[1e]</sup> Examples are the phospha-rhodamine<sup>[23]</sup> and the phospha-fluorescein,<sup>[24]</sup> which possess a fused  $\pi\text{-extended}$  framework and a  $\lambda^{5}\text{-}\sigma^{4}\,\text{phosphorus}$ center. These molecules illustrate the potential of six-membered phosphorus rings for materials applications, in particular, as potential pH sensors for biological media<sup>[23]</sup> and in vivo biomarkers.<sup>[24]</sup> Simultaneously, we reported a new synthetic protocol to access novel polyaromatic systems containing a

versatile  $\lambda^3 - \sigma^3$ phosphorus the center: i.e. phosphaphenalenes.<sup>[25]</sup> This procedure demonstrated to be highly versatile; it enabled phosphorus-containing six-membered rings to be fused with a wide variety of aromatic systems, from electron-rich heterocycles to aromatic hydrocarbons and electron-deficient rings. However, hitherto, the potential of polycyclic materials containing six-membered phosphorus units is still far from being fully revealed; there is a lack of systematic investigations that provide the crucial parameters for the development of phosphorus-doped polyaromatic materials with improved optoelectronic properties.

This motivated us to investigate the key aspects to set the bedrock for a new generation of phosphorus-containing polyaromatic materials. In particular, we targeted at addressing important open questions such as: a) which are the key synthetic parameters to incorporate phosphorus-containing six-membered rings into polyaromatic structures? b) Which type of (hetero)cycles must be integrated into the polyaromatic organophosphorus materials to obtain the best optoelectronic properties? c) Which phosphorus post-functionalization should be employed to control the 3D molecular arrangement of the phosphorus-containing polyaromatic materials? In other words, with this investigation we aimed to establish a guide for the design of a new generation of functional polyaromatic organophosphorus materials.

#### **Results and Discussion**

To this end, we first investigated the key requirements to integrate six-membered phosphorus rings into  $\pi$ -extended aromatic systems. As mentioned above, we recently reported a new non-catalyzed synthetic protocol for the cyclization of naphthalene-substituted chlorophosphane (PCI) to obtain fused phosphaphenalene derivatives; first insights into the reaction mechanism revealed a S<sub>E</sub>Ar to be at work.<sup>[25]</sup> However, further investigations on the chlorophosphane intermediate are required to benchmark the latter cyclization towards  $\pi$ -extended polyaromatic systems.



Scheme 1. Potential Routes A and B to access fused six-membered phosphorus heterocycles from chlorophosphane derivatives.

Thus, to analyze the key features of the PCI derivatives (**P-A**, **P-B**) for the cyclization to occur, we investigated Routes A and B (Scheme 1). They consist of the synthesis of the PCI species from haloaromatics via organolithium derivatives and subsequent cyclization; Route A and B differ on the position of the PCI.

First insights on the latter routes came experimentally. While Route A led to a wide synthetic versatility, giving rise to fused six-membered phosphorus heterocycles with electron acceptors, electron donors and aromatic hydrocarbons, surprisingly, Route B under the same cyclization conditions provided unsuccessful results. DFT calculations provided the explanation for this observation. We considered the formation of the carbonphosphorus bond during the cyclization as the rate-determining step; i.e. the transformation from **P-A/B** to **I-A/B**. This can be seen as a S<sub>E</sub>Ar in which the phosphorus atom acts as an electrophile or as a S<sub>N</sub>2 on the phosphorus atom, where the aryl group acts as nucleophile and the chloride as leaving group.

Within the former scheme, the rate-determining step is the formation of a  $\sigma$ -intermediate (Wheland complex),<sup>[26]</sup> in which a positive charge develops in the aromatic ring, with a concomitant loss of aromaticity. This  $\sigma$ -intermediate can evolve either spontaneously or through a process with a small energetic barrier to give the final phosphorus ring by the abstraction of one proton by the chloride group, previously released in the formation of **P-A/B**. The transition states (TS) associated with the formation of the  $\sigma$ -intermediate are shown in the Figure 1a and 1b (see Figure S1 for the complete profile associated with different systems).



Figure 1. Main geometrical features and Gibbs activation barriers of the transition states associated with the carbon-phosphorus bond formation of: a) I-A from P-A and b) I-B from P-B, computed at the B3LYP-D3(PCM)/6-311+G(D) level of theory. Energies are given in kcal mol<sup>-1</sup>, distances in Å and angles in degrees.

Our results show that **P-B** of Route B is less reactive than **P-A**, Route A. This is reflected by the higher computed Gibbs barriers for the corresponding transition states **TS1b** and **TS1a** (Figure 1); 35.8 and 28.3 kcal·mol<sup>-1</sup>, respectively. According to Hammond's postulate, the geometry of the transition state will resemble the unstable positively charged Wheland complex; i.e. the stabilization of the evolving positive charge should determine the feasibility of the process.

In I-A, the positive charge delocalizes more efficiently over the phenyl and naphthyl moieties (Scheme S1) leading to a stabilizing effect reflected in a lower Gibbs activation barrier of

ca. 10 kcal mol<sup>-1</sup>. In turn, in **I-B**, the charge only delocalizes over the naphthyl moiety (Scheme S1). The latter justifies the higher activation barrier found not only in Route B, but also in the formation of fused phospholes via ortho-aryl chlorophosphane derivatives (Figure S1). It is worth highlighting that  $\pi$ -extended derivatives with electron-rich aromatics such a thiophenes favor the cyclization reaction as reflected by the lower Gibbs activation barriers (see Figure S1 for details).

All in all, the investigations of the cyclization mechanism by theoretical calculations reveal that, importantly, an extensive delocalization of the cationic intermediate is imperative for the non-catalyzed phosphorus cyclization to occur. In other words, the nature of the central PCI moiety (red color in Routes A and B, Scheme 1) is key to obtain fused polyaromatic molecules with six-membered phosphorus heterocycles.  $\pi$ -Extended systems such as naphthalene are required to delocalize the evolving positive charge of the Wheland intermediate and to ultimately render fused heterocycles. Smaller systems such as phenyl do not lead to the non-catalyzed formation of six-membered phosphorus cycles.

After analyzing the reaction mechanisms to obtain fused phosphorus-containing structures, we focused our efforts on reporting the key aspects that could modulate the optoelectronic properties of phosphorus-based extended systems. In particular, we centered our investigations on a series of polycyclic derivatives that differ either in the nature of the fused aromatic rings or in the functionalization of the phosphorus center (Chart 1). Thus, we distinguished six different groups of compounds: molecules of Group A contain a thiophene fused through different patterns. Compounds 4 and 5, Group B, present a substituted thiophene fused through different patterns, too. Molecules of Group C differ in the type of the fused electron-rich heterocycles; i.e. furan, pyrrole and benzothiophene, a πextended moiety. Group D is represented by six-membered phosphorus rings fused with aromatic hydrocarbons and Group E is composed of polycyclic systems fused with an electrondeficient pyridine heterocycle. Finally, Group F consists of molecules 12, 13 and 14, which differ in their phosphorus functionalization.

To better comprehend the optoelectronic properties of the phosphorus-containing derivatives, we first gathered information on their electronic nature. In particular, the aromaticity provides insights on the electronic distribution of the fused system. Among the different computational criteria, despite being a continuous source of controversy,[27] Nucleus-independent Chemical Shift (NICS) obtained by calculating the absolute magnetic shielding at a point of interest<sup>[27a]</sup> has been one of the most employed aromaticity probes. Thus, we calculated the NICS values at the ring critical points and at 1 Å above; i.e. NICS(0) and NICS(1), respectively. The results are shown in Table S1 and represented in Charts 2 and Figure S2. It is important to highlight that these theoretical studies are aimed at providing the NICS(0) and NICS(1) values for the relative comparison of systems and not to validate the employed standard methodologies as such.

Surprisingly, fusing six-membered phosphorus heterocycles with other (hetero)cycles confers them positive NICS values (Table S1), which suggest an anti-aromatic character. The same is true for six-membered phosphorus heterocycles fused only with naphthalene (see the tricyclic phosphaphenalenes **B** and **C** Figure S2).

This is in stark contrast with the non-fused analogues, phosphabenzenes (phosphinnes) (NICS(1) = -10.1 ppm),<sup>[28]</sup> which exhibit 84% of the aromaticity of the benzene (NICS(0) = -8.1 ppm, NICS(1) = -10.2 ppm),<sup>[20]</sup> or naphthalene (NICS(0) = -8.5 ppm, NICS(1) = -10.7 ppm).<sup>[21,27]</sup>



Chart 1. Phosphaphenalene derivatives considered for this study.

The fused (hetero)cycles impact the (anti)aromatic character of the phosphorus ring. The trends from the NICS(0) and NICS(1) values differ slightly, presumably due to the larger sigma contribution in the NICS(0) values. Thus, for the phosphorus heterocycles with a pentavalent phosphorus atom, considering the side of the molecule with the oxygen atom, the highest NICS(0) value, +5.1 ppm, is reached when fusing a benzene moiety (compound **9**), whereas the highest NICS(1), +1.91 ppm, is found in the thiophene derivative **2**. In turn, the lowest NICS(0) and NICS(1) are obtained by fusing the phosphorus heterocycle with furan (compound **6**, NICS(0) =

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+3.53 ppm) or benzene (compound **9**, NICS(1) = +0.55 ppm, Table S1). Likewise phosphole-based polycyclic compounds,<sup>[29]</sup> the anti-aromatic character does not expand to the fused rings; in agreement to the Clar's rule,<sup>[30]</sup> the outer rings have greater aromatic character in all cases.

The valence of the phosphorus center commonly affects the aromaticity of the ring; phospholes turn from slightly aromatic to antiaromatic when switching the phosphorus center from the trivalent to the pentavalent form.<sup>[6a,31]</sup> In contrast, fused sixmembered phosphorus heterocycles with either trivalent or pentavalent phosphorus centers present an anti-aromatic character; i.e. positive NICS(0) and NICS(1) values. Nevertheless, the antiaromatic character increases when oxidizing the phosphorus atom; tri- and pentavalent derivatives **12** and **3** present NICS(0) values of +3.66 and +4.94 ppm, and NICS(1) of +0.12 and +1.0 ppm, respectively (Table S1).



Chart 2. Aromaticity (NICS(0) values in ppm) of compounds 3, 6, 9 and 12 computed at the PBE0/6-311+G(d) level of theory. Bottom: color scale in ppm.

In addition to the aromaticity, we calculated the properties of the molecular orbitals (MOs) of **1-12** (Figures S3-S5 and Table S2). The results revealed a significant impact of the nature and substitution pattern of the fused ring into the MOs' energy (Chart 3). Within the Groups A-E, whereas the pyridine-containing **11** exhibits the lowest LUMO level, -2.48 eV, the highest HOMO level, -5.72 eV, is given by the pyrrole derivative **7** (see Chart 3 and Table S2).

In particular, the position of the heteroatom of the fused ring has a stronger impact on the LUMO than the HOMO energy. Thus, the LUMO increases from -2.32 to -2.06 eV within the Group A when moving into the series from **1** to **3**, respectively. The peripheral functionalization also affects the MOs' energies. Both the LUMO and HOMO increase when introducing, for

instance, a side alkyl chain into 1 and 2 to form derivatives 4 and 5. Comparing compound 1 with the molecules of Group C reveals that the band gap decreases in the order 6>7>1; i.e. with the aromaticity of the fused ring (aromaticity of furan<pyrrole<thiophene). In turn, higher electron-donating capacity of the peripheral ring also leads to a decrease of the band gap (8<1). Furthermore, it decreases with the number of fused aromatic hydrocarbons (see 9 and 10) and substantially increases when incorporating electron-poor heterocycles such as pyridines, compound 11 (see Table S2). The valence of the phosphorus center also affects the MOs' energies. However, in stark contrast with phospholes, the reduction of the phosphorus center decreases the band gap. From the oxide derivative 3 to the reduced analogue 12, the fused polycyclic molecule transforms into a better electron donor; i.e. the HOMO level is higher in energy. In turn, the band gap decreases from 4.00 to -3.92 eV.



Chart 3 Frontier MOs' distribution for 1-12, B3LYP/6-31+G(d) level of theory.

To further investigate the electronic properties of the fused systems, we turned to electrochemical measurements. To that end, we representatively selected a derivative with high HOMO level, compound 7; derivatives with low-lying LUMO orbitals, compounds 8 and 11, and derivatives 3, 12 and 13, which only differ in the functionalization of the phosphorus atom. The voltammograms obtained by cyclic (CV), differential pulse (DPV) and square wave (SWV) voltammetries are shown in Figures 2 and S6.

Overall, polyaromatics containing six-membered phosphorus rings possess a rich electrochemistry (Table S4). Except **11** (Figure S6), all compounds present an ambipolar redox behavior; i.e. they possess both electrochemical reduction and oxidation processes. This is in line with the redox properties of unfunctionalized phosphabenzenes.<sup>[22]</sup> Importantly, whereas the oxidation processes are irreversible, all compounds except **13** exhibit at least one fully reversible electrochemical reduction.

The nature of the fused aromatic systems affects the electrochemical potentials. Fusing phosphacycles with pyrroles (compound 7) leads to the best electron-donating properties; i.e. +1.37 V. This is in agreement with the theoretical calculations (Chart 3).

The potentials of **3**, **12** and **13**, which only differ in the functionalization of the phosphorus atom, reveal a strong impact of the phosphorus substituent into the electrochemical properties.

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As predicted by DFT calculations, the reduction of the pentavalent phosphorus center of **3** to give compound **12** improves the electron-donating capacity, from +1.66 to +1.14 V; i.e. providing a lower oxidation potential than for **7**. It is worth to note that the complexation with gold (compound **13**) predominantly reduces the reduction potential to -1.62 V, compared with -1.74 and -1.97 V for the pentavalent **3** and the trivalent **12** derivatives, respectively.



**Figure 2.** Voltammograms of **8** obtained by cyclic voltammetery (top), differential pulse voltammetry (middle) and square wave voltammetry (bottom) form acetonitrile solutions vs SCE. See Supporting Information for details.

Table 1. Photophysical properties of 1-14.

In turn, fusing the six-membered phosphorus heterocycles with  $\pi$ -extended systems such as benzothiophene (compound **8**) and electron-deficient heterocycles such as pyridines (compound **11**) provides the best electron accepting properties (lowest reduction potentials). Compound **8** presents an  $E_{red}$  at -1.41 V whereas compound **11** exhibits two reduction processes, a reversible reduction at -1.39 V and an irreversible one at -1.92 V.

Electron-acceptor materials are of utmost importance in organic electronics, particularly in research fields such as organic solar cells, organic light-emitting diodes and solar fuels;<sup>[32]</sup> the limited variety of electron-acceptor systems has converted this type of materials into a constant research objective.

In brief, the redox behavior of the fused organophosphorus materials can be tailored via the nature of the fused aromatic ring and the functionalization of the phosphorus center; electron-donating rings such as pyrroles lead to the lowest oxidation potentials whereas  $\pi$ -extended aromatics as well as electron-deficient heterocycles improve the electron accepting capacities. In turn, trivalent phosphorus centers lead to better electron-donating properties than their pentavalent analogues.

The energy distribution of the MOs defines the optical properties of the materials. Thus, to further investigate the optoelectronic properties of the organophosphorus materials, we focused on steady-state and time-resolved spectroscopies. The results are summarized in Table 1.

	Absorption					Emission					
Compd.	$\lambda_{max} \left( nm  ight)^{[a]}$	$\lambda^{calc.}_{max}$ (nm) <sup>[b]</sup>	<i>f</i> <sup>[c]</sup>	$\log \epsilon^{[d]}$	$\lambda_{max} \left( nm  ight)^{[e]}$	λ <sup>calc.</sup> <sub>max</sub> (nm) <sup>[f]</sup>	<b>f</b> <sup>[g]</sup>	$\Delta v (cm^{-1})^{[h]}$	$\tau$ 1; $\tau$ 2; $\tau$ 3 (ns) <sup>[i]</sup>	${\cal P}^{[i]}$	
1	357	365	0.337	3.79	420			4202	0.4	0.2	
2	344	349	0.32	3.91	402			4194	5.9; 0.4	0.04	
3	335	337	0.275	3.83	399	393	0.218	4788	1.1; 0.5	0.12	
4	367	375	0.368	4.08	436			4312	0.6	0.1	
5	345	351	0.089	3.90	414			4831	1.0; 0.3	0.03	
6	352	360	0.301	3.71	425			4880	4.2; 0.9	0.1	
7	367	369	0.244	3.90	450	446	0.159	5175	9.9	0.8	
8	366	372	0.466	4.14	433			4228	0.5	0.11	
9	337	337	0.336	3.89	389			3967	0.9	0.14	
10	353	375	0.262	3.84	407			3759	0.2	0.45	
11	336	337	0.329	4.04	383			3652	0.9	0.14	
12	336	335	0.275	4.04	466	480	0.232	8303	1.2	0.08	
13	336	-		3.82	399			4699	2.3; 0.7; 0.1	0.005	
14	353			3.86	418			4405	2.6; 1.1	0.07	

[a] Absorption maxima recorded from DCM solutions. [b] Computed absorption maxima at the PBE0-D3(PCM) / 6-311+G(d) level of theory. [c] Force constant of the calculated absorption maxima. [d] Molar extinction coefficient. [e] Emission maxima recorded from DCM solutions. [f] Computed emission maxima at the PBE0-D3(PCM) / 6-311+G(d) level of theory. [g] Force constant of the calculated emission maxima. [h] Stokes shift. [i] Fluorescence lifetimes. [j] Fluorescence quantum yields relative to quinine sulfate in 0.1 M H<sub>2</sub>SO<sub>4</sub>,  $\phi$  = 0.54.

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The absorption and emission maxima match the values provided by the DFT calculations (see Table 1). Molecules **1-14** absorb in the near-UV spectral region with maxima located in the range between 336-367 nm (Figure 3a and S7-9) and emit in the blue region of the visible spectrum; the color coordinates are represented in Figure 3b.



**Figure 3.** a) Normalized absorption and emission spectra of compounds 1, 7, 11 and 12 in DCM. b) Color coordinates of compounds 1-14. c) Emission color of 7 under 360 nm light illumination, obtained from a  $10^{-6}$  M DCM solution.

Monitoring the emission maxima facilitates evaluating the impact of the fused aromatic ring into the photophysical properties of the materials. In line with the absorption maxima, the emission properties (emission maxima, fluorescence lifetime and quantum yields (QYs)), vary as a function of the nature, position and functionalization of the fused heterocycles. Compound **1** presents an emission maximum at 420 nm (Figure 3a) with a significant QY of 0.2 and a mono-exponential lifetime of 0.4 ns. Within Group A (Chart 1), by changing the fusion pattern of the thiophene moiety, the emission maximum is blue shifted from 420 to 399 nm for **1** to **3**, respectively (Figure S7), whereas the QY drops to 0.12 (Table 1).

The peripheral functionalization of **1** and **2** with alkyl chains leads to a red shift of the emission features and a decrease of the QYs; i.e. **4** and **5** exhibit emission maxima at 436 and 414 nm (Figure S7), and QYs of 0.1 and 0.03, respectively.

The changes in the QYs can be attributed to an increment in the degrees of freedom. On the other hand, the type of fused

heterocycle also impacts the emission maxima; they are red shifted in the order pyrrole>benzothiophene>furan>thiophene; i.e. **7>8>6>1** (Figure S8). Importantly, incorporating pyrrole heterocycles into polyaromatic phosphorus-containing systems leads not only to the largest red shift, but also to the best photophysical properties. Compound **7** exhibits an intense blue fluorescence (Figure 3c) that maximizes at 450 nm (Figure 3a) with a QY as high as 0.8 and a long lifetime of 9.9 ns. These values make pyrrole derivatives very attractive for future optoelectronic applications. As a matter of fact, long lifetimes (usually above 5 ns) are optimum for efficient photo-induced charge transfer events.<sup>[6b]</sup>

Importantly, incorporating an increasing number of aromatic hydrocarbons increases the QYs from 0.14 to 0.45 for 9 and 10, respectively. In contrast, electron-acceptor rings such as pyridine lead to the biggest hypsochromic shifts of the emission maxima; the fluorescence of 11 maximizes at 383 nm (Figure 3a). Moreover, the functionalization of the phosphorus center strongly impacts the spectroscopic features of the organophosphorus materials. Reduction of the phosphorus center from  $\lambda^5$ - $\sigma^4$  to  $\lambda^3$ - $\sigma^3$  decreases the QY from 0.2 to 0.08 and leads to a bathochromic shift of the emission maximum, from 420 to 466 nm for 1 and 12, respectively (Figure 3a and S9). This is remarkable since, commonly, materials based on fivemembered phosphorus heterocycles exhibit the opposite scenario; the oxidation of the phosphorus center leads to a red shift of the emission properties.<sup>[12]</sup> In turn, while the gold functionalization produces the lowest QYs, <0.01, and a multiexponential decay, the quaternization of the phosphorus atom leads to a QY of 0.07 and a bi-exponential fluorescence decay (compound 14, Table 1). Notably, the emission maxima of the Groups A-F (Chart 1) linearly correlate with the calculated NICS(0) values of the six-membered phosphorus heterocycle (Figure S10). Overall, lower NICS(0) values of the fused phosphorus heterocycle lead to larger emission maxima.

The contrasting fluorescence quantum yields obtained from the different fused materials especially attracted our attention. Unlike **1** (QY = 0.2), phospholes fused with thiophenes exhibit QYs up to  $0.8^{[9]}$  On the other hand, phosphorus-based gold complexes have demonstrated outstanding performances in light-emitting diodes<sup>[14]</sup> and remarkable QYs up to  $0.75^{[11d]}$ This is in stark contrast with **13**, which possesses a QY<0.01. Thus, to provide an unambiguous explanation, we turned to pump-probe experiments; i.e. transient absorption spectroscopy. For our studies, we selected compounds **7**, **3** and **13**, which possess the highest, an intermediate and the lowest QYs, respectively. The corresponding transient spectra are shown in Figure 4.

Photoexcitation of the pyrrole-containing 7 leads to the rapid formation of the singlet-excited state, which maximizes at 500, 640, 700, 740 and 1050 nm (Figure 4a). Subsequently, the latter excited state internally converts within  $9 \pm 2$  ps into a new transient with maxima at 460 and 640 nm. These features decay with a lifetime that correlates with the fluorescence lifetime reported in Table 1; i.e. about 10 ns. In other words,



photoexcitation of 7 leads to the efficient formation of a highly emissive state, which is responsible for the outstanding QY, 0.8.

3.5



Figure 4. Differential absorption spectra obtained upon femtosecond flash photolysis (275 nm, 150 nJ) of 7 (a), 3 (b) and 13 (c) at r.t.; see figure legend for time delays (fs). Insets: Time absorption profile monitoring: for a) the internal conversion, for b) the internal conversion and the intersystem crossing, and for c) the intersystem crossing

Compound 3 led to a different scenario (Figure 4b). Upon photoexcitation, the singlet excited state features emerge with maxima at 520, 720 and 1200 nm. Rapidly, the latter decay with a lifetime of 8.8 ± 1 ps, giving rise to a new transient that maximizes at 510, 680 and 1030 nm, and whose lifetime

matches the fluorescence lifetime measured by steady-state spectroscopy; i.e. 0.5 ns. Finally, however, a new metastable transition state, characteristic for the triplet state, slowly evolves within 1030 ± 70 ps featuring a broad maximum at 580 nm and whose lifetime exceeds the time-scale of our experimental setup.

A rationale infers a dual deactivation of the singlet excited state through two competitive pathways due to the heavy atom effect from the sulfur atom of the thiophene;[34] i.e. internal conversion to an emissive state and intersystem crossing to an non-radiative triplet state. The latter is in agreement with the moderate fluorescence quantum yield of 3 (QY = 0.12) and biexponential fluorescence lifetime.

The gold complex 13, which exhibits a fluorescence quantum yield below 0.01, is in sharp contrast with 3 and 7. Initially, 13 shows the singlet excited state features with maxima at 550, 705, 740 and 1240 nm. However, instead of internally converting into an emissive state, the aforementioned features rapidly transform within 38 ± 1 ps into the corresponding triplet excited state via intersystem crossing. This is in agreement with a more efficient heavy atom effect as a result of a strong spinorbit coupling arising, presumably, from the gold atom and the sulfur of the thiophene moiety.

In brief, the presence of sulfur and especially gold atoms in polyaromatic phosphorus-containing systems leads to lower fluorescence quantum yields due to intersystem crossing. In contrast, fused pyrrole heterocycles prevent the aforementioned intersystem crossing leading to an efficient fluorescent process. Altogether, this is the first investigation of phosphorus-containing polyaromatic materials by means of transient absorption spectroscopy reported to date.



Figure 5. a) Photoresponses of 7 under on/off cycles of illumination (5s) increasing the applied bias from 0 V to +1.5 V (see Supporting Information for details). b) Averaged photoresponse as a function of the applied bias.

The electron-donating properties together with the outstanding photophysical properties of **7** motivated us to demonstrate its suitability in photoelectrochemical cells (Figure 5). In particular, we were interested in investigating the photoresponse speed of **7**; it is of great importance for a variety of optoelectronic applications such as photodetectors.<sup>[35]</sup> In a proof-of-principle setup, we drop-casted **7** onto indium tin oxide (ITO) wafers and exposed it to 5 s on-off cycles of illumination (see details in the Supporting Information). As a result, in a triethylamine solution as sacrificial electrolyte, ITO/**7** showed a fast and repeatable photoresponse (Figure 5a). From the representation of the generated photocurrent versus the applied voltage bias (Figure 5b), we established a minimum bias of around 0.5 V for the generation of photocurrent. To the best of

our knowledge, this is the first phosphorus heterocycle-based photoelectrochemical cell reported to date.

Finally, we focused on investigating suitable means toward controlling the 3D molecular arrangements by simple phosphorus functionalization. As described in the introduction, the particular geometry and the versatile functionality of  $\lambda^3$ - $\sigma^3$  phosphorus centers have led to systems exhibiting intriguing properties such as liquid crystallinity, gels and nanostructures formation, which are closely related to a particular 3D arrangement of molecules.

For our studies, we succeeded in obtaining the crystal structures of compounds **12**, **13** and **14**, which, together with **3**,<sup>[25]</sup> possess the identical framework and only differ in their phosphorus functionalization (Figure 6, Table S5). Relevant bond lengths are summarized in Table S6.



Figure 6. 3D arrangement of a) 12; b) 3 c) 13 and d) 14, deduced from X-ray spectroscopy. Framed structures indicate the unit cell. Ellipsoids at 50% probability. Hydrogens have been omitted for clarity.

Compound 12, with a  $\lambda^3 - \sigma^3$  center, presents a unit cell composed of four molecules with a somewhat random distribution. The closest intermolecular interactions have a distance of 3.22 Å (Figure 6a). Oxidation of the phosphorus atom renders a unit cell rather complex (see Figure 6b). However, closer examination reveals the formation of stacks consisting of four molecules that interact through the naphthalene moieties. The smallest intermolecular distances within the stacks are in the range of  $\pi$ -stacking interactions; i.e. 3.4 to 3.6 Å.

A more interesting 3D arrangement of molecules is attained after gold functionalization of the  $\lambda^3$ - $\sigma^3$  center (Figure 6c). In particular, 13 forms dimers through Au-Au interactions solely from molecules of opposite chirality; i.e. only R-S interactions can be identified within the crystal structure. The Au-Au distances of 3.215 Å are typical for aurophilic interactions. Within the unit cell, however, the dimeric structures are randomly distributed. The most interesting 3D features arose when quaternizing the phosphorus atom with a methyl group (compound 14, Figure 6d). To avoid interference of the counterion into the 3D arrangement, 14 was prepared with a small chloride ion (see Supporting Information). The unit cell of the latter compound appears quite simplified; it contains only a dimer formed by  $\pi$ - $\pi$  interaction, that is, with a smallest intermolecular interaction of 3.46 Å. The latter association presents, moreover, an inversion center. As a result, 14 exhibits an intriguing 3D arrangement. The dimers stack along one edge with inter-dimer interactions of 3.68 Å, leading to highly ordered 3D stacking. Related molecular ordering has demonstrated to be crucial to access, for instance, highly performing organic field effect transistors.[36]

#### Conclusions

In conclusion, fused six-membered phosphorus heterocycles possess an outstanding potential for the development of improved polyaromatic materials. Herein, we reveal the key parameters not only to synthesize new phosphorus heterocyclebased systems but also to tailor the optoelectronic properties for future practical applications. Thus, incorporating electron-rich heteroles into *π*-extended six-membered phosphorus systems leads to a bathochromic shift of the absorption and emission properties. On the other hand, aromatic hydrocarbons and electron-poor systems induce a hypsochromic shift of the absorption and emission features. The fluorescence lifetimes and quantum yields are strongly impacted by the type and substitution pattern of the fused ring. Fusing pyrroles with sixmembered phosphorus derivatives leads to the longest fluorescence lifetime (10 ns) and the highest guantum yields ( $\Phi$ = 0.8) due to the absence of intersystem crossing. In turn, whereas incorporating electron-rich heterocycles into the fused systems improve the electron-donating properties,  $\pi$ -extended and electron-deficient rings improve the electron-accepting Polyaromatic phosphorus-containing capacities. materials exhibit promising performances in a photoelectrochemical cell. Finally, the 3D molecular arrangement can be precisely

controlled by phosphorus post-functionalization; quaternized phosphorus centers with small counterions lead to the highest ordered arrangements. All in all, the investigation described herein establishes the lines for the development of new generations of polyaromatic organophosphorus materials, which are currently underway.

#### **Experimental Section**

Experimental details, synthetic procedures, theoretical calculations, UV-Vis spectra, electrochemical investigation, X-ray data and NMR spectra are included in the Supporting Information.

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#### Abbreviations

PCI, chlorophosphane; TS, transition state; NICS, nucleusindependent chemical shift; MOs, molecular orbitals; CV, cyclic voltammetry; DPV, differential pulse voltammetry; SWV, square wave voltammetry; DCM, dichloromethane; QYs, quantum yields; ITO, indium tin oxide.

**Keywords:** organophosphorus materials • six-membered phosphorus heterocycles • reaction mechanism • optoelectronic properties

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## Entry for the Table of Contents

Layout 1:

# FULL PAPER

**FULL PAPER** 

**Tracing the lines:** Detailed investigations on a series of polycyclic organophosphorus materials containing six-membered phosphorus heterocycles reveal the key parameters to synthesize functional architectures with different electrochemical behavior, fluorescence quantum yields up to 0.8 and versatile means to keep control over the nature of the photoinduced excited states and the 3D molecular arrangement in the solid state.



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