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# Dibenzophosphapentaphenes: Exploiting P-chemistry for gap fine-tuning and coordination-driven assembly of planar polycyclic aromatic hydrocarbons.

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## Supporting Information Placeholder

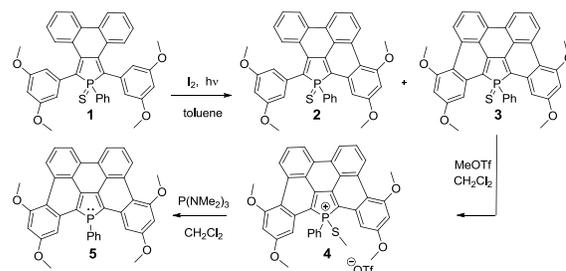
**ABSTRACT:** A synthetic route to planar P-modified polycyclic aromatic hydrocarbons (PAHs) is described. The presence of a reactive  $\sigma^3, \lambda^3$ -P-moiety within the  $sp^2$ -carbon atom scaffold allows the preparation of a new family of PAHs displaying tunable optical and redox properties. Their frontier MO's are derived from the corresponding phosphole MO's and show extended conjugation with the entire  $\pi$ -framework. The coordination ability of the P-center allows coordination-driven assembly of two molecular PAHs **5** onto a Au<sup>1</sup> ion.

Polycyclic aromatic hydrocarbons (PAHs), like benzocoronenes or nanographenes, are of great potential in molecular electronics for the development of efficient opto-electronic devices (solar cells, field-effect transistors...).<sup>1</sup> The possibility of performing molecular engineering of PAHs using the power of organic chemistry is a key towards these applications. Indeed, PAHs' HOMO-LUMO gap and supramolecular assembly can be controlled through size-modification of the  $\pi$ -conjugated system or/and by the proper choice of lateral aliphatic substituents.<sup>2</sup> An alternative appealing strategy involves the incorporation of heteroatoms (N,<sup>3</sup> O,<sup>4</sup> S,<sup>5</sup> B<sup>6</sup>) within the conjugated  $sp^2$ -carbon backbones of PAHs. Surprisingly, no fully planarized P-containing PAHs have been described yet,<sup>7</sup> although  $\sigma^3, \lambda^3$ -P-derivatives have proven to be powerful platforms for  $\pi$ -conjugated scaffold molecular engineering. For example, both HOMO-LUMO gap and supramolecular organization of phosphole-modified  $\pi$ -systems can be readily controlled using the versatile reactivity (nucleophilicity, coordination ability) of the  $\sigma^3, \lambda^3$ -P-centers.<sup>8</sup> Herein, we report that this approach based on P-chemistry can be extended to planar P-modified PAHs, with the synthesis of dibenzophosphapentaphenes. Of particular interest, exploiting the reactivity of the P-center allows a straightforward gap fine-tuning of this novel family of PAH derivatives. Furthermore, these compounds can be coordinated to metal ions, offering an unprecedented way of assembling PAHs using coordination chemistry.

The synthesis of P-containing PAHs using classical approaches (Scholl reaction, thermolysis...) <sup>1a</sup> with pentaphenylphosphole derivatives failed due to the presence of the reactive phosphorus heterocycle. Only photocyclization appeared to be a suitable synthetic method,<sup>9</sup> and the fused biphenyl[*b,d*]thioxophosphole **1** (Scheme 1) was finally de-

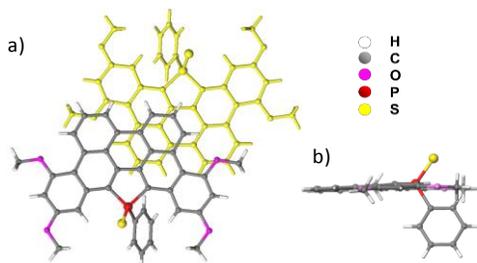
signed as a key precursor following numerous unsuccessful tries. For example, the choice of the P=S function was crucial since this P-moiety is less prone to react with *in-situ* generated protic acid than the corresponding P=O function.<sup>11</sup> Derivative **1** (<sup>31</sup>P NMR:  $\delta = +58.7$  ppm) was obtained using the classic Fagan-Nugent heterole route<sup>12</sup> followed by sulfurization. Photocyclization of **1** during twenty hours using the Katz-modified method,<sup>13</sup> afforded a mixture of the mono-cyclized derivative **2** and the fully-cyclized target dibenzophosphapentaphene **3** (Scheme 1). Increasing the reaction time did not improve the yield of **3**. Both compounds are air stable, soluble in usual organic solvents (THF, CH<sub>2</sub>Cl<sub>2</sub>), and were isolated in pure form (yields: **2**, 50%; **3**, 20%) after purification by chromatography. The two products were fully characterized by NMR spectroscopy and high-resolution mass spectrometry (HRMS). Their <sup>31</sup>P chemical shifts are typical for thioxophosphole derivatives (<sup>31</sup>P NMR: **2**,  $\delta = +51.6$  ppm; **3**,  $\delta = +46.0$  ppm), and the simplicity of the <sup>1</sup>H NMR spectrum of **3** is consistent with a highly symmetric skeleton (See SI).

## Scheme 1. Synthesis of $\sigma^3, \lambda^3$ -dibenzophosphapentaphene **5**



The definitive proof for the proposed structure was given by an X-ray diffraction study performed on single crystals of **3** (Figure 1). The  $sp^2$ -carbon atoms framework is planar (maximum deviation from the mean C- $sp^2$  plane, 0.15 Å) and the P-atom lies within the  $sp^2$ -C plane (Figure 1b). The C-C bond lengths range from 1.35 Å to 1.49 Å, as observed in prototype benzocoronene derivatives,<sup>14</sup> and the valence angles around the  $sp^2$ -C atoms vary from 114.3° to 125.5°. The  $\sigma^4, \lambda^5$ -phosphorus atom has a pyramidal shape (Figure 1b) with usual valence angles, and the C-C and C-P bond lengths within the phosphole ring are classic.<sup>8a</sup> This solid state structure shows that **3** possesses all the characteristic structural features of both PAH and phosphole derivatives. In the solid state, **3** forms

discrete head-to-tail  $\pi$ -dimers (Figure 1a) with an intermolecular distance (3.45 Å),<sup>15</sup> similar to that observed in other benzo-coronenes or in graphite.<sup>14</sup>

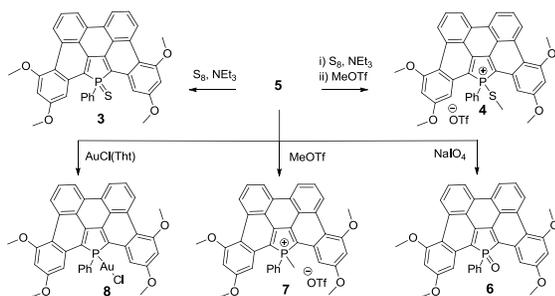


**Figure 1.** X-ray crystallographic structure of **3** with the view of the discrete dimers observed in the packing (a) view of **3** perpendicular to the  $sp^2$ -C plane (b).

Having constructed the P-modified PAH backbone, the next step was to desulfurize<sup>16</sup> the phosphole ring to obtain a functionalisable  $\sigma^3, \lambda^3$ -P-dibenzophosphapentaphene. Treatment of thioxophosphole **3** with methyltriflate afforded phospholium **4** (<sup>31</sup>P NMR,  $\delta = +50.1$  ppm), which was isolated as a purple solid in 60% yield (Scheme 1). Derivative **4**, which is the first isolated phospholium ion bearing a P-S bond, is remarkably air and moisture stable in solution and in the solid state. The solid state structure of this cationic dibenzophosphapentaphene **4** (Figure S12) is superimposable to that of its neutral precursor **3**, showing that chemical modifications of the P-moiety do not alter the planar  $sp^2$ -carbon backbone. Phospholium **4** was then converted into its  $\sigma^3, \lambda^3$ -analog **5** by treatment with the nucleophilic P(NMe<sub>2</sub>)<sub>3</sub> phosphane (Scheme 1). This  $\sigma^3, \lambda^3$ -dibenzophosphapentaphene **5** was isolated in 50% yield as an air stable yellow powder moderately soluble in THF or CH<sub>2</sub>Cl<sub>2</sub>. Its <sup>31</sup>P NMR chemical shift ( $\delta = -2.9$  ppm) is an usual value for phosphole derivatives<sup>8a</sup> and the proposed structure is consistent with its NMR and MS data (see SI).

The P-center of compound **5** retains a versatile reactivity as illustrated by its transformations into oxidized phospholes (thioxophosphole **3**, oxophosphole **6**), phospholiums **4** and **7**, and neutral Au<sup>I</sup>-complex **8** in almost quantitative yields (Scheme 2). These compounds exhibit the expected multinuclear NMR and MS data (see SI). Overall, a family of neutral and cationic dibenzophosphapentaphenes derivatives **3-8** has been prepared (Scheme 2). This nicely illustrates that introducing a reactive  $\sigma^3, \lambda^3$ -P-center within the PAH framework allows a molecular engineering to be readily performed.

**Scheme 2.** Chemical derivatization of  $\sigma^3, \lambda^3$ -dibenzophosphapentaphene **5**.



In order to evaluate the impact of the P-modifications on the electronic properties of these PAHs, the optical and electrochemical properties of dibenzophosphapentaphenes **3-8**

were investigated in CH<sub>2</sub>Cl<sub>2</sub>. The absorption spectrum of dibenzophosphapentaphene **5** consists in a large and structured band in the visible range ( $\lambda_{\text{max}} = 472$  nm, Table 1), that displays the typical PAHs-like hyperfine structure (Figure 2a).<sup>1a</sup> Neutral  $\sigma^4$ -P derivatives **3**, **6** and **8** (Scheme 2) exhibit red-shifted absorption spectra with similar shape and absorption maxima (Table 1, Figure 2a). A larger bathochromic shift is observed with P-alkyl and P-S phospholium salts **7** and **4** (Table 1). Remarkably, the absorption spectra of this family of dibenzophosphapentaphenes **3-8** (Scheme 2), having the same polycyclic aromatic C-skeleton but different P-moiety, vary over a wide range covering almost the entire visible spectrum (Figure 2a). All these dibenzophosphapentaphenes are fluorescent in solution with a gradual red-shift of  $\lambda_{\text{em}}$  in the series **5/3/7/4** (Table 1, Figure 2b). The Stokes shifts are reasonably small for these rigid structures (**5**,  $\Delta\nu = 737$  cm<sup>-1</sup>; **3**,  $\Delta\nu = 1072$  cm<sup>-1</sup>; **7**,  $\Delta\nu = 1355$  cm<sup>-1</sup>) and the emission bands are structured suggesting a small rearrangement of these molecules upon photoexcitation. Therefore, their quantum yields are relatively high (> 20%, Table 1). In contrast, derivative **4** presents a larger Stokes shift ( $\Delta\nu = 2875$  cm<sup>-1</sup>) accompanied by a decrease of the fluorescence quantum yield (3%).

Analysis of the cyclic voltammetry (CV) shows that the chemical modification performed on the P-center of **5** leads to a gradual increase of the oxidation and reduction potentials in the series **5/3/7/4** (Table 1). The variation is even more pronounced for the reduction potential revealing that phospholium salts **4** and **7** display rather high electron affinity. It is noteworthy that **3**, **6**, **7** and **8** show reversible reduction waves, indicating sufficient stability in their reduced state under the measurement conditions (Table 1). Note that the evolution of the Redox potentials within the **5/3/7/4** series is consistent with the decrease of the optical gap (Figure 2a).

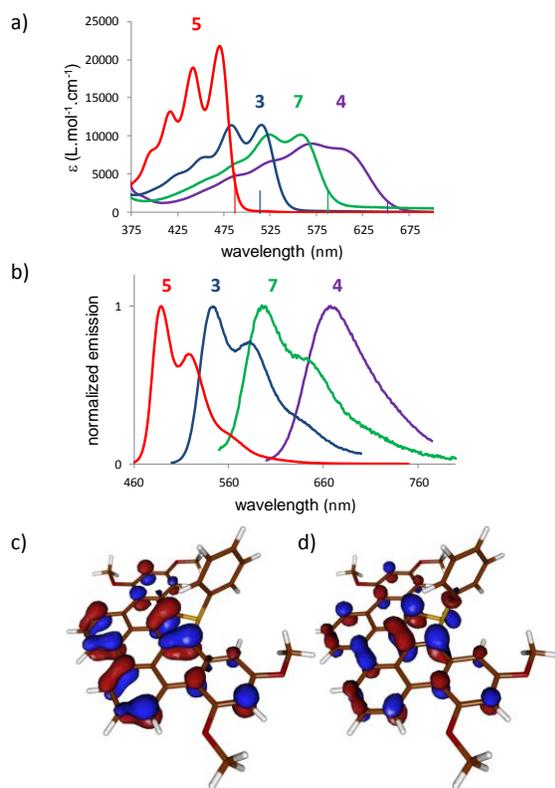
**Table 1. Photophysical and Electrochemical Data**

Compd	absorption <sup>a</sup>		fluorescence <sup>a</sup>		redox potentials <sup>c</sup>	
	$\lambda_{\text{abs}}$ [nm]	log $\epsilon$	$\lambda_{\text{em}}$ [nm]	$\Phi_f^b$	E <sup>ox</sup> <sub>1</sub> [V]	E <sup>red</sup> <sub>1</sub> [V]
<b>3</b>	514	4.04	544	0.21	0.71	-1.70 <sup>d</sup>
<b>4</b>	569	3.95	669	0.03	1.01	-1.04
<b>5</b>	472	4.34	489	0.80	0.44	<-2.10
<b>6</b>	524	4.11	549	0.52	0.77	-1.71 <sup>d</sup>
<b>7</b>	554	4.00	599	0.19	0.97	-1.31 <sup>d</sup>
<b>8</b>	508	4.14	537	0.08	0.75	-1.67 <sup>d</sup>

<sup>a</sup>In CH<sub>2</sub>Cl<sub>2</sub> (10<sup>-5</sup>M). <sup>b</sup>Measured relative to fluoresceine (NaOH, 0.1 M),  $\phi_{\text{ref}} = 0.9$ . <sup>c</sup>In CH<sub>2</sub>Cl<sub>2</sub> with Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> (0.2 M) at a scan rate of 100 mVs<sup>-1</sup>. Potentials vs ferrocene/ferrocenium. <sup>d</sup>reversible process

To get more insights into the electronic properties of these novel P-modified PAHs, time-dependent DFT calculations (B3LYP/6-31+G\* level of theory)<sup>17</sup> were performed.<sup>18</sup> This theoretical study shows that the long-wavelength UV-Vis absorption of PAHs **3-7** mainly results from the HOMO-LUMO transition.<sup>19</sup> These frontier orbitals are similar throughout the series **5-7** (**5**, Figure 2c-d; **3-7**, Figure S14). These  $\pi$ -MOs are highly delocalized on the  $sp^2$ -carbon skeletons with a significant contribution of the respective phosphole ring orbitals (Figure S15).<sup>20</sup> The HOMO, which has a nodal plane on the phosphorus atom, is influenced by the inductive

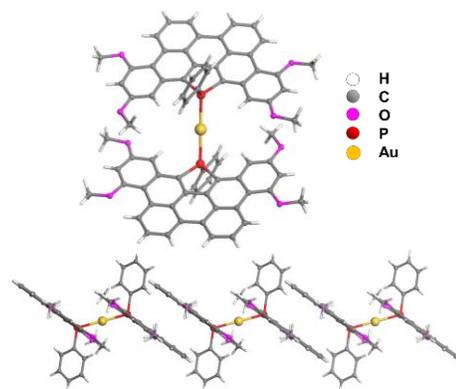
effects of the P-substituents. This explains why the shape of these orbitals is unaltered upon modifying the P-moiety (Figure S14). The LUMO is subjected to the negative hyperconjugative interaction between the  $\sigma^*_{\text{PSubstituent}}$  MO and the MOs of  $sp^2$ -carbon atoms framework. This results in the stabilization of this empty level for  $\sigma^4$ -P containing neutral and cationic systems, increasing also the antiaromatic character of these heteroles.<sup>8h,21</sup> This influence of the P-substituent can be nicely seen through the increasing weight of the P-atom in the LUMO (Figure S14), especially for cationic systems **4** and **7**, which exhibit the highest reduction potentials (Table 1). It is interesting to note that the effect of P-substitution on the electronic properties and frontier orbitals of these P-modified PAHs follows the same trend than the parent phosphole.<sup>20</sup> Overall, these experimental and theoretical data show that local chemical modification of the P-moiety of dibenzophosphapentaphenes is a powerful mean to fine-tune the gap of these novel family of planar PAH derivatives.



**Figure 2.** UV-Vis absorption and TD-DFT simulated spectra (vertical lines) (a); normalized emission (b) of **3** (blue), **4** (purple), **5** (red) and **7** (green) in  $\text{CH}_2\text{Cl}_2$  ( $10^{-5}\text{M}$ ); Frontier Kohn-Sham MOs (HOMO, c; LUMO, d) of **5**.

The reactive P-center of **5** also offers an unprecedented way of organizing PAHs using coordination chemistry, as illustrated by the assembly of two  $\sigma^3, \lambda^3$ -dibenzophosphapentaphenes **5** on an  $\text{Au}^{\text{I}}$  ion (Figure 3). Complex **8** (Scheme 2) was reacted with  $\text{AgOTf}^{22}$  and free ligand **5**, affording the new complex **9** ( $^{31}\text{P}$  NMR,  $\delta = +40.8$  ppm). An X-ray diffraction study confirmed the unique structure of complex **9** in which two PAHs are coordinated to a metal ion (Figure 3).<sup>23</sup> The P-Au-P fragment is linear (P-Au-P,  $180.0^\circ$ ) and the two highly planar C-skeletons of **5** exhibit an *anti*-conformation with respect to the P-Au-P moiety (Figure 3). Interestingly, the packing of **9** is deeply modified compared to derivatives **3** or **4**. Intermolecu-

lar  $\pi$ - $\pi$  interactions between coordinated dibenzophosphapentaphenes take place ( $\pi$ - $\pi$  distances,  $3.50 \text{ \AA}$ ) affording infinite columns of  $\pi$ -stacked complex **9** (Figure 3).<sup>15</sup> Considering the rich coordination chemistry of phosphole derivatives,<sup>8a</sup> the fact that **5** behaves as a classic two-electrons P-donor toward metal centers opens an avenue for coordination-driven assembly of phosphorus-modified PAHs.



**Figure 3.** X-ray crystallographic structure of  $\text{Au}^{\text{I}}$ -complex **9** and view of the infinite columns along the crystallographic b axis.

In conclusion, the synthetic route to the first planar  $\sigma^3, \lambda^3$ -P-modified PAH is described. The presence of a reactive P-moiety within the C-skeleton allows a facile synthesis of a new family of PAHs with tunable optical and electrochemical properties using a single precursor. This molecular engineering of PAHs based on P-chemistry and their assembly using coordination chemistry shows the potential of modifying planar  $\pi$ -extended frameworks by organophosphorus fragments.

## ASSOCIATED CONTENT

**Supporting Information.** Experimental procedures, NMR data, X-ray crystallographic data and CIF files for **3**, **4** and **9**. HOMO and LUMO plots and energies for **3-7** and the related 1-methylphospholes and complete ref 18. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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