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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 σ^3, λ^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 π -framework. The coordination ability of the P-center allows coordination-driven assembly of two molecular PAHs **5** onto a Au^I 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...).¹ 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 π -conjugated system or/and by the proper choice of lateral aliphatic substituents.² An alternative appealing strategy involves the incorporation of heteroatoms (N,³ O,⁴ S,⁵ B⁶) within the conjugated sp^2 -carbon backbones of PAHs. Surprisingly, no fully planarized P-containing PAHs have been described yet,⁷ although σ^3, λ^3 -P-derivatives have proven to be powerful platforms for π -conjugated scaffold molecular engineering. For example, both HOMO-LUMO gap and supramolecular organization of phosphole-modified π -systems can be readily controlled using the versatile reactivity (nucleophilicity, coordination ability) of the σ^3, λ^3 -P-centers.⁸ 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...) ^{1a} with pentaphenylphosphole derivatives failed due to the presence of the reactive phosphorus heterocycle. Only photocyclization appeared to be a suitable synthetic method,⁹ and the fused biphenyl[*b,d*]thioxophosphole **1**¹⁰ (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.¹¹ Derivative **1** (³¹P NMR: δ = +58.7 ppm) was obtained using the classic Fagan-Nugent heterole route¹² followed by sulfurization. Photocyclization of **1** during twenty hours using the Katz-modified method,¹³ 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, CH₂Cl₂), 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 ³¹P chemical shifts are typical for thioxophosphole derivatives (³¹P NMR: **2**, δ = +51.6 ppm; **3**, δ = +46.0 ppm), and the simplicity of the ¹H NMR spectrum of **3** is consistent with a highly symmetric skeleton (See SI).

Scheme 1. Synthesis of σ^3, λ^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,¹⁴ and the valence angles around the sp^2 -C atoms vary from 114.3° to 125.5°. The σ^4, λ^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.^{8a} 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 π -dimers (Figure 1a) with an intermolecular distance (3.45 Å),¹⁵ similar to that observed in other benzo-coronenes or in graphite.¹⁴

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 desulfurize¹⁶ the phosphole ring to obtain a functionalisable σ^3, λ^3 -P-dibenzophosphapentaphene. Treatment of thioxophosphole **3** with methyltriflate afforded phospholium **4** (^{31}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 σ^3, λ^3 -analog **5** by treatment with the nucleophilic $\text{P}(\text{NMe}_2)_3$ phosphane (Scheme 1). This σ^3, λ^3 -dibenzophosphapentaphene **5** was isolated in 50% yield as an air stable yellow powder moderately soluble in THF or CH_2Cl_2 . Its ^{31}P NMR chemical shift ($\delta = -2.9$ ppm) is an usual value for phosphole derivatives^{8a} 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^I-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 σ^3, λ^3 -P-center within the PAH framework allows a molecular engineering to be readily performed.

Scheme 2. Chemical derivatization of σ^3, λ^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_2Cl_2 . 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).^{1a} Neutral σ^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 λ_{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^{-1} ; **3**, $\Delta\nu = 1072$ cm^{-1} ; **7**, $\Delta\nu = 1355$ cm^{-1}) 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^{-1}) 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 ^a		fluorescence ^a		redox potentials ^c	
	λ_{abs} [nm]	$\log \epsilon$	λ_{em} [nm]	Φ_f^b	E^{ox}_1 [V]	E^{red}_1 [V]
3	514	4.04	544	0.21	0.71	-1.70 ^d
4	569	3.95	669	0.03	1.01	-1.04
5	472	4.34	489	0.80	0.44	<-2.10
6	524	4.11	549	0.52	0.77	-1.71 ^d
7	554	4.00	599	0.19	0.97	-1.31 ^d
8	508	4.14	537	0.08	0.75	-1.67 ^d

^aIn CH_2Cl_2 (10^{-5}M). ^bMeasured relative to fluorescein (NaOH, 0.1 M), $\Phi_{\text{ref}} = 0.9$. ^cIn CH_2Cl_2 with $\text{Bu}_4\text{N}^+\text{PF}_6^-$ (0.2 M) at a scan rate of 100 mVs^{-1} . Potentials vs ferrocene/ferrocenium. ^dreversible 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)¹⁷ were performed.¹⁸ This theoretical study shows that the long-wavelength UV-Vis absorption of PAHs **3-7** mainly results from the HOMO-LUMO transition.¹⁹ These frontier orbitals are similar throughout the series **5-7** (**5**, Figure 2c-d; **3-7**, Figure S14). These π -MOs are highly delocalized on the sp^2 -carbon skeletons with a significant contribution of the respective phosphole ring orbitals (Figure S15).²⁰ 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 σ^4 -P containing neutral and cationic systems, increasing also the antiaromatic character of these heteroles.^{8h,21} 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.²⁰ Overall, these experimental and theoretical data show that local chemical modification of the P-moiety of dibenzophosphaphentaphenes 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 CH_2Cl_2 (10^{-5}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 σ^3, λ^3 -dibenzophosphaphentaphenes **5** on an Au^{I} ion (Figure 3). Complex **8** (Scheme 2) was reacted with AgOTf^{22} and free ligand **5**, affording the new complex **9** (^{31}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).²³ The P-Au-P fragment is linear (P-Au-P, 180.0°) 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 π - π interactions between coordinated dibenzophosphaphentaphenes take place (π - π distances, $3.50 \text{ \AA}$) affording infinite columns of π -stacked complex **9** (Figure 3).¹⁵ Considering the rich coordination chemistry of phosphole derivatives,^{8a} 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 Au^{I} -complex **9** and view of the infinite columns along the crystallographic b axis.

In conclusion, the synthetic route to the first planar σ^3, λ^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 π -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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