



**HAL**  
open science

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

Pierre-Antoine Bouit, Aude Escande, Rózsa Szűcs, Dénes Szieberth, Christophe Lescop, László Nyulászi, Muriel Hissler, Régis Réau

### ► To cite this version:

Pierre-Antoine Bouit, Aude Escande, Rózsa Szűcs, Dénes Szieberth, Christophe Lescop, et al.. Dibenzophosphapentaphenes: exploiting P chemistry for gap fine-tuning and coordination-driven assembly of planar polycyclic aromatic hydrocarbons.. *Journal of the American Chemical Society*, 2012, 134 (15), pp.6524-7. 10.1021/ja300171y . hal-00848165

**HAL Id: hal-00848165**

**<https://hal.science/hal-00848165v1>**

Submitted on 31 Mar 2017

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Pierre-Antoine Bouit,<sup>†</sup> Aude Escande,<sup>†</sup> Rózsa Szűcs,<sup>‡</sup> Dénes Szieberth,<sup>‡</sup> Christophe Lescop,<sup>†</sup> László Nyulási,<sup>‡</sup> Muriel Hissler\*<sup>†</sup>, Régis Réau\*<sup>†</sup>

<sup>†</sup> Sciences Chimiques de Rennes, UMR 6226 CNRS - Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex France

<sup>‡</sup> Department of Inorganic Chemistry, Budapest University of Technology and Economics, H-1521 Budapest, Hungary

## Supporting Information Placeholder

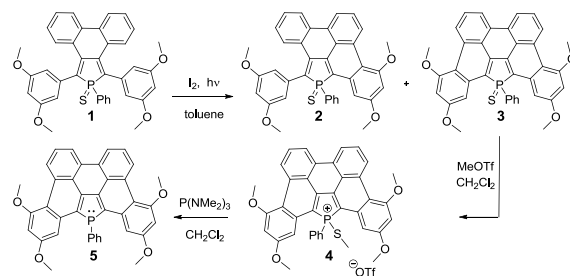
**ABSTRACT:** A synthetic route to planar P-modified polycyclic aromatic hydrocarbons (PAHs) is described. The presence of a reactive  $\sigma^3, \lambda^3$ -P-moiety within the  $sp^2$ -carbon atom scaffold allows the preparation of a new family of PAHs displaying tunable optical and redox properties. 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-

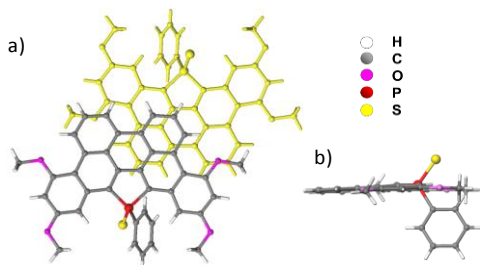
signed as a key precursor following numerous unsuccessful tries. For example, the choice of the P=S function was crucial since this P-moiety is less prone to react with *in-situ* generated protic acid than the corresponding P=O function.<sup>11</sup> Derivative **1** (<sup>31</sup>P NMR:  $\delta = +58.7$  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 benzocoronenes or in graphite.<sup>14</sup>

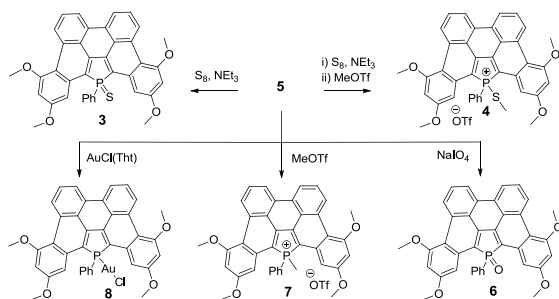


**Figure 1.** X-ray crystallographic structure of **3** with the view of the discrete dimers observed in the packing (a) view of **3** perpendicular to the  $sp^2$ -C plane (b).

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 ( $\lambda_{\max} = 472$  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).

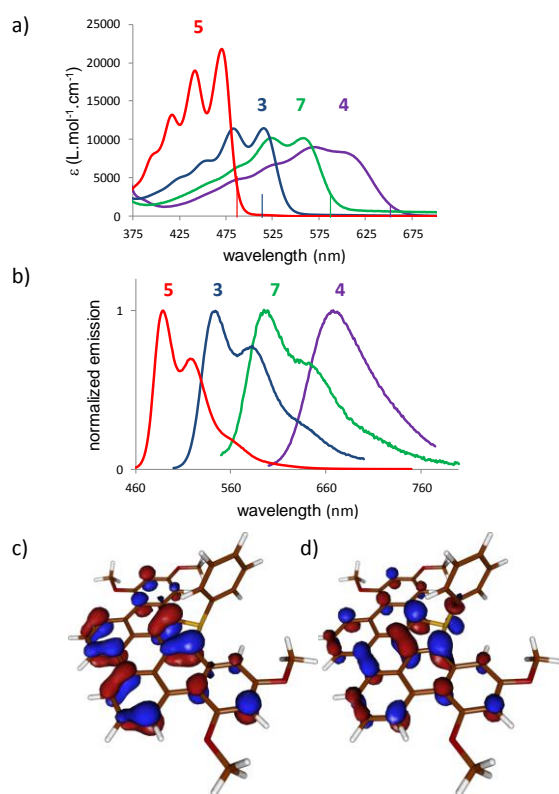
**Table 1. Photophysical and Electrochemical Data**

Compd	absorption <sup>a</sup>		fluorescence <sup>a</sup>		redox potentials <sup>c</sup>	
	$\lambda_{\text{abs}}$ [nm]	$\log \epsilon$	$\lambda_{\text{em}}$ [nm]	$\Phi_f^b$	$E^{\text{ox}}_1$ [V]	$E^{\text{red}}_1$ [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

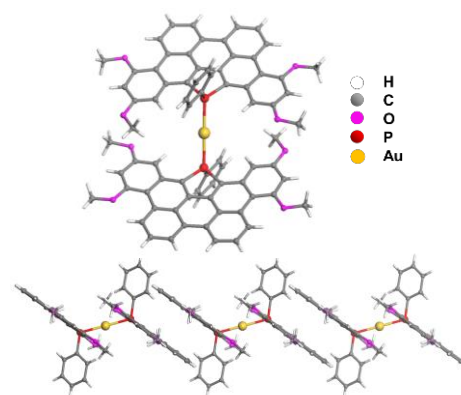
effects of the P-substituents. This explains why the shape of these orbitals is unaltered upon modifying the P-moiety (Figure S14). The LUMO is subjected to the negative hyperconjugative interaction between the  $\sigma^*_{\text{PSubstituent}}$  MO and the MOs of  $sp^2$ -carbon atoms framework. This 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 CH<sub>2</sub>Cl<sub>2</sub> (10<sup>-5</sup>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 Au<sup>I</sup> ion (Figure 3). Complex **8** (Scheme 2) was reacted with AgOTf<sup>22</sup> and free ligand **5**, affording the new complex **9** (<sup>31</sup>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°) 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 Å) 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 Au<sup>I</sup>-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>.

## AUTHOR INFORMATION

Corresponding Author

\* [muriel.hissler@univ-rennes1.fr](mailto:muriel.hissler@univ-rennes1.fr); [regis.reau@univ-rennes1.fr](mailto:regis.reau@univ-rennes1.fr)

## ACKNOWLEDGMENT

This work is supported by the Ministère de la Recherche et de l'Enseignement Supérieur, the Centre National de la Recherche Scientifique (CNRS), the Institut Universitaire de France (IUF) and the Région Bretagne. COST CM0802 (Phoscinet) and TAMOP-4.2.2/B-10/1-2010-0009 are also acknowledged.

## REFERENCES

- (1)(a) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267; (b) Wu, J. S.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718; (c) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119; (d) Pisula, W.; Feng, X.; Müllen, K. *Chem. Mater.* **2010**, *23*, 554.
- (2)(a) Pisula, W.; Feng, X.; Müllen, K. *Adv. Mater.* **2010**, *22*, 3634; (b) Yan, X.; Li, L.-S. *J. Mater. Chem.* **2011**, *21*, 3295.
- (3)(a) Draper, S. M.; Gregg, D. J.; Madathil, R. *J. Am. Chem. Soc.* **2002**, *124*, 3486; (b) Draper, S. M.; Gregg, D. J.; Schofield, E. R.; Browne, W. R.; Duati, M.; Vos, J. G.; Passaniti, P. *J. Am. Chem. Soc.* **2004**, *126*, 8694;

- (c) Wu, D. Q.; Pisula, W.; Enkelmann, V.; Feng, X. L.; Müllen, K. *J. Am. Chem. Soc.* **2009**, *131*, 9620; (d) Davis, N. K. S.; Thompson, A. L.; Anderson, H. L. *J. Am. Chem. Soc.* **2011**, *133*, 30; (e) Fogel, Y.; Kastler, M.; Wang, Z.; Andrienko, D.; Bodwell, G. J.; Müllen, K. *J. Am. Chem. Soc.* **2007**, *129*, 11743; (f) Wu, D.; Pisula, W.; Enkelmann, V.; Feng, X.; Müllen, K. *J. Am. Chem. Soc.* **2009**, *131*, 9620; (g) Wu, D. Q.; Feng, X. L.; Takase, M.; Haberecht, M. C.; Müllen, K. *Tetrahedron* **2008**, *64*, 11379; (h) Gregg, D. J.; Fitchett, C. M.; Draper, S. M. *Chem. Commun.* **2006**.
- (4) Wu, D.; Pisula, W.; Haberecht, M. C.; Feng, X.; Müllen, K. *Org. Lett.* **2009**, *11*, 5686.
- (5)(a) Martin, C. J.; Gil, B.; Perera, S. D.; Draper, S. M. *Chem. Commun.* **2011**, *47*, 3616; (b) Feng, X.; Wu, J.; Ai, M.; Pisula, W.; Zhi, L.; Rabe, J. P.; Müllen, K. *Angew. Chem. Int. Ed.* **2007**, *46*, 3033; (c) Gorodetsky, A. A.; Chiu, C.-Y.; Schiros, T.; Palma, M.; Cox, M.; Jia, Z.; Sattler, W.; Kymissis, I.; Steigerwald, M.; Nuckolls, C. *Angew. Chem. Int. Ed.* **2010**, *49*, 7909; (d) Benshafut, R.; Rabinovitz, M.; Hoffman, R. E.; Ben-Mergui, N.; Müllen, K.; Iyer, V. S. *Eur. J. Org. Chem.* **1999**, *1999*, 37.
- (6)(a) Hatakeyama, T.; Hashimoto, S.; Seki, S.; Nakamura, M. *J. Am. Chem. Soc.* **2011**, *133*, 18614; (b) Zhou, Z.; Wakamiya, A.; Kushida, T.; Yamaguchi, S. *J. Am. Chem. Soc.* **2012**, DOI: 10.1021/ja211944q.
- (7) A curved  $\pi$ -extended triarylphosphine was recently described: Hatakeyama, T.; Hashimoto, S.; Nakamura, M. *Org. Lett.* **2011**, *13*, 2130.
- (8)(a) Baumgartner, T.; Réau, R. *Chem. Rev.* **2006**, *106*, 4681; (b) Matano, Y.; Saito, A.; Fukushima, T.; Tokudome, Y.; Suzuki, F.; Sakamaki, D.; Kaji, H.; Ito, A.; Tanaka, K.; Imahori, H. *Angew. Chem. Int. Ed.* **2011**, *50*, 8016; (c) Bruch, A.; Fukazawa, A.; Yamaguchi, E.; Yamaguchi, S.; Studer, A. *Angew. Chem. Int. Ed.* **2011**, *50*, 12094; (d) Ren, Y.; Kan, W. H.; Henderson, M. A.; Bomben, P. G.; Berlinguette, C. P.; Thangadurai, V.; Baumgartner, T. *J. Am. Chem. Soc.* **2011**, *133*, 17014; (e) Graule, S.; Rudolph, M.; Vanthuyne, N.; Autschbach, J.; Roussel, C.; Crassous, J.; Réau, R. *J. Am. Chem. Soc.* **2009**, *131*, 3183; (f) Nohra, B.; Graule, S.; Lescop, C.; Réau, R. *J. Am. Chem. Soc.* **2006**, *128*, 3520; (g) Chen, H.; Delaunay, W.; Yu, L.; Joly, D.; Wang, Z.; Li, J.; Wang, Z.; Lescop, C.; Tondelier, D.; Geffroy, B.; Duan, Z.; Hissler, M.; Mathey, F.; Réau, R. *Angew. Chem. Int. Ed.* **2012**, *51*, 214; (h) Benkő, Z.; Nyulászi, L. *Aromatic Phosphorus Heterocycles. In Aromaticity in Heterocyclic Compounds*. Krygowski, T. M.; Cyransky, M. K. (Editors). Vol 19 in *Topics in Heterocyclic Chemistry* (Gupta R. R. (Series Editor) Springer, Heidelberg, 2009. pp. 27-83.
- (9) Fadhel, O.; Szieberth, D.; Deborde, V.; Lescop, C.; Nyulászi, L.; Hissler, M.; Réau, R. *Chem. Eur. J.* **2009**, *15*, 4914.
- (10) Related bithienyl[b,d]phospholes were recently described: Matano, Y.; Miyajima, T.; Fukushima, T.; Kaji, H.; Kimura, Y.; Imahori, H. *Chem. Eur. J.* **2008**, *14*, 8102.
- (11) Protonation of the strongly polarized P=O function is the first step towards decomposition of the phosphole ring.
- (12) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310.
- (13) Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769.
- (14) Herwig, P. T.; Enkelmann, V.; Schmelz, O.; Müllen, K. *Chem. Eur. J.* **2000**, *6*, 1834.
- (15) The  $\pi$ - $\pi$  distances were obtained measuring the distances between the mean planes including all the C and P atoms of the planar scaffold of two neighboring molecules.
- (16) Omelańczuk, J.; Mikołajczyk, M. *Tetrahedron Lett.* **1984**, *25*, 2493.
- (17) A systematic study showed that TD-DFT with the B3LYP functional provides good results for vertical excitation energies of organic molecules: Jacquemin, D.; Wathelot, V.; Perpète, E. A.; Adamo, C. *J. Chem. Theory Comput.* **2009**, *5*, 2420.
- (18) DFT calculations were performed using the Gaussian 03 suite of programs Frisch, M. J. *et al.* Gaussian 03, Revision C.02; Gaussian, Inc.: Wallingford CT, 2004. The MO-s were visualized by the MOLDEN program (Schaffenaar, G.; Noordik, J.H. *J. Comput.-Aided Mol. Design* **2000**, *14*, 123-134.). Complete reference of Gaussian 03 and more details of the calculations are given in the SI.
- (19) The contribution of the HOMO-LUMO excitation is 0.65 for all the molecules investigated, coefficients from other electron configurations being smaller than 0.12.
- (20) Hay, C.; Hissler, M.; Fischmeister, C.; Rault-Berthelot, J.; Toupet, L.; Nyulászi, L.; Réau, R. *Chem. Eur. J.* **2001**, *7*, 4222.
- (21) Nyulászi, L.; Holloczki, O.; Lescop, C.; Hissler, M.; Réau, R. *Org. Biomol. Chem.* **2006**, *4*.
- (22) Escallé, A.; Mora, G.; Gagosz, F.; Mézailles, N.; Le Goff, X. F.; Jean, Y.; Le Floch, P. *Inorg. Chem.* **2009**, *48*, 8415.
- (23) A 'squeeze' treatment was necessary to remove the scattering contribution of highly disorder CH<sub>2</sub>Cl<sub>2</sub> molecules and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> counterions that could not be satisfactory modeled, see SI.