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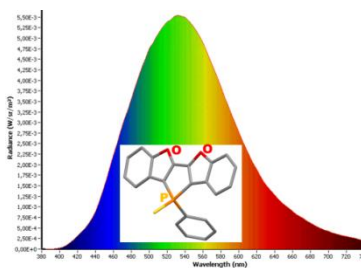
Benzofuran fused phosphole: synthesis, electronic and electroluminescence properties

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ABSTRACT



A synthetic route to novel benzofuran fused phosphole derivatives 3-5 is described. These compounds showed optical and electrochemical properties that differ from their benzothiophene analog. Preliminary results show that 4 can be used as emitter in OLEDs illustrating the potential of these new compounds for opto-electronic applications.

π -Conjugated organic systems are highly versatile materials for the development of efficient electronic devices.¹ In particular, a great variety of S-containing π -conjugated derivatives based on the thiophene scaffold have proven to be very efficient semi-conducting materials for opto-electronic devices (Organic Light Emitting Diodes (OLED), Organic Solar Cells (OSC), and Field Effect Transistors (OFET)).² In the last years, other

heteroles appeared as appealing building blocks for the tailoring of conjugated materials since they possess electronic properties that markedly differ from those of thiophene. For example, the aromatic character of furan and phosphole is less pronounced than in thiophene, resulting in an increased exocyclic conjugation ability of

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(1) a) K. Müllen, U. Scherf, (Eds.), *Organic Light Emitting Devices: Synthesis Properties and Applications*, Wiley-VCH, Weinheim, Germany **2006**; b) Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. *Chem. Rev.* **2009**, *109*,

5868; c) Usta, H.; Facchetti, A.; Marks, T. J. *Acc. Chem. Res.* **2011**, *44*, 501.

(2) (a) Roncali, J. *Chem. Rev.* **1997**, *97*, 173; (b) Mishra, A.; Ma, C.-Q.; Bäuerle, P. *Chem. Rev.* **2009**, *109*, 1141. For specific reviews on OSC, OFET and OLEDs : (c) Thomson, B.C.; Fréchet, J.M.J. *Angew. Chem. Int. Ed.* **2008**, *47*, 58. (d) Allard, S. Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. *Angew. Chem. Int. Ed.* **2008**, *47*, 4070. (e) Gather, M. C.; Köhnen, A.; Meerholz K. *Adv. Mater.* **2011**, *23*, 233.

their π -systems.³ Stable furan-containing π -systems **A** and α -oligofurans⁴ **B** showing promising results as active layer in organic/hybrid solar cells and OFETs have been described very recently.⁵ Likewise, the use of phosphole scaffolds for constructing organic materials **A** - **C** (Figure 1) has started in the last decade.⁶ In these materials, exploiting the reactivity and coordination chemistry of the reactive P-centers allowed controlling both their HOMO-LUMO gap and solid-state organization.⁷ Indeed, this unique molecular engineering afforded conjugated P-derivatives that can be used as advanced materials in OLEDs, including white-emitting devices or for the development of fibers, gels and liquid crystals.⁸ Derivatives of type **A** or **C** associating phosphole and thiophene moieties have been widely investigated.⁶ In contrast, mixed phosphole-furan compounds are quite rare. Only linear systems **A** are known to date and these compounds display moderate emission property, precluding their use in optoelectronic devices.⁹ Therefore, we have been interested by P,O-based acenes associating phosphole and furan rings since structure rigidification generally improves the emission properties of π -conjugated organic systems.

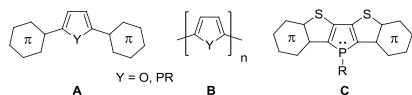


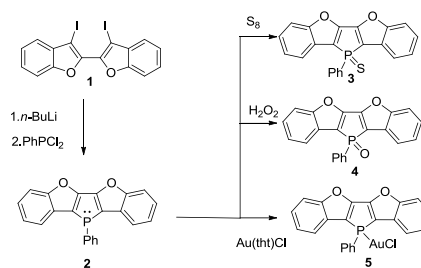
Figure 1: Phosphole based π -conjugated systems **A**, **B** and **C**.

In this paper, we describe the synthesis, structure, and electronic properties of the first mixed phosphole-furan acene **2** (Scheme 1). Proper derivatization of this scaffold using the reactivity of the σ^3, λ^3 -P center afforded compounds exhibiting good thermal stability and high emission quantum yields. These appealing properties have been exploited for the fabrication of OLEDs.

In order to design stable mixed furan-phosphole π -systems, the fused heteroacenic structure **2** (Scheme 1) was targeted since the benzofuran moiety exhibits a good

stability due to the annelation of the two aromatic rings. The target compound **2** was synthesized by using a modified synthetic procedure reported by Baumgartner *et al.* for the preparation of mixed thiophene-phosphole heteroacenes **C** (Figure 1).^{6b,7f} The iodo-substituted benzofuran **1** was subsequently treated with 2 equivalents of *n*-BuLi and one equivalent of PhPCl_2 at -78°C affording compound **2** (Scheme 1) (^{31}P NMR: -44.0 ppm). Since σ^3, λ^3 -phospholes are generally too sensitive toward oxygen to be used as material in OLEDs, this compound was derivatized in good yields by *in situ* oxidation into thiooxophosphole **3** (^{31}P NMR: $+17.0$ ppm) and oxophosphole **4** (^{31}P NMR: $+11.9$ ppm) (Scheme 1). The corresponding gold complex **5** (^{31}P NMR: -8.0 ppm) was also readily prepared by reacting **2** with $\text{AuCl}(\text{tetrahydrothiophene (tht)})$ (see Scheme 1). These novel air-stable derivatives were purified by column chromatography and fully characterized by multinuclear NMR spectroscopy and high-resolution mass spectrometry (HR-MS).

Scheme 1: Synthetic routes to furan-phosphole derivatives **2-5**



These results show that the P-center of the mixed furan-phosphole **2** retains the versatile reactivity of phosphole derivatives. It is interesting to note that the ^{13}C NMR chemical shifts of the phosphole rings of furan derivatives **3-5** are markedly different from those of their thiophene analogs of type **C** (Figure 1 and SI), suggesting that the

(3) (a) Salzner, U.; Lagowski, J. B. P.; Pickup, G.; Poirier, R. A., *Synth. Met.* **1998**, *96*, 177; (b) Cyranski, M. K.; Krygowski, T. M.; Katritzky, A. R. Von Ragué Schleyer, P. J. *Org. Chem.* **2002**, *67*, 1333.

⁴ (a) Gidron, O.; Diskin-Posner, Y.; Bendikov, M. *J. Am. Chem. Soc.* **2010**, *132*, 2148; (b) Bunz, U. H. F. *Angew. Chem. Int. Ed.* **2010**, *49*, 5037.

⁵ (a) Mitsui, C.; Tsuji, H.; Sato, Y.; Nakamura, E. *Chem. As. J.* **2012**, *7*, 1443. (b) Mitsui, C.; Soeda, J.; Miwa, K.; Tsuji, H.; Takeya, J.; Nakamura, E. *J. Am. Chem. Soc.* **2012**, *134*, 5448. (c) Walker, B.; Tamayo, A. B.; Dang, X.-D.; Zalar, P.; Seo, J. H.; Garcia, A.; Tantiwivat, M.; Nguyen, T.-Q. *Adv. Funct. Mater.* **2009**, *19*, 3063. (d) Wu, C.-C.; Hung, W.-Y.; Liu, T.-L.; Zhang, L.-Z.; Luh, T.-Y. *J. Appl. Phys.* **2003**, *93*, 5465; (e) Aleveque, O.; Frere, P.; Leriche, P.; Breton, T.; Cravino, A.; Roncali, J. *J. Mater. Chem.* **2009**, *19*, 3648; (f) Woo, C. H.; Beaujuge, P. M.; Holcombe, T. W.; Lee, O. P.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2010**, *132*, 15547; (g) Lin, J. T.; Chen, P.-C.; Yen, Y.-S.; Hsu, Y.-C.; Chou, H.-H.; Yeh, M.-C. *P. Org. Lett.* **2008**, *11*, 97.

⁶ (a) Hissler, M.; Dyer, P. W.; Réau, R. *Coord. Chem. Rev.* **2003**, *244*, 1; (b) Baumgartner, T.; Réau, R. *Chem. Rev.* **2006**, *106*, 4681.

⁷ (a) Bouit, P.-A.; Escande, A.; Szűcs, R.; Szieberth, D.; Lescop, C.; Nyulászi, L.; Hissler, M.; Réau, R. *J. Am. Chem. Soc.* **2012**, *134*, 6524; Ren, Y.; Kan, W. H.; Henderson, M. A.; Bomben, P. G.; (b) Berlinguette, C. P.; Thangadurai, V.; Baumgartner, T. *J. Am. Chem. Soc.* **2011**, *133*, 17014; (c) Deschamps, E.; Ricard, L.; Mathey F. *Angew. Chem. Int. Ed.*

Engl. **1994**, *33*, 1158. (d) Matano, Y.; Nakashima, M.; Imahori, H. *Angew. Chem. Int. Ed.* **2009**, *48*, 4002; (e) Yavari, K.; Moussa, S.; Ben Hassine, B.; Retailleau, P.; Voituriez, A.; Marinetti, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 6748. (f) Dienes, Y.; Eggenstein, M.; Kárpáti, T.; Sutherland, T. C.; Nyulászi, L.; Baumgartner, T. *Chem. Eur. J.* **2008**, *14*, 9878. (g) Fukazawa, A.; Hara, M.; Okamoto, T.; Son, E.-C.; Xu, C.; Tamao, K.; Yamaguchi, S. *Org. Lett.* **2008**, *10*, 913. (h) Fukazawa, A.; Yamada, H.; Yamaguchi, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 5582. (i) Weymiers, W.; Zaal, M.; Slootweg, J. C.; Ehlers, A. W.; Lammertsma K. *Inorg. Chem.* **2011**, *50*, 8516.

⁸ (a) 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; (b) Fave, C.; Cho, T.-Y.; Hissler, M.; Chen, C.-W.; Luh, T.-Y.; Wu, C.-C.; Réau, R. *J. Am. Chem. Soc.* **2003**, *125*, 9254; (c) Joly, D.; Tondelier, D.; Deborde, V.; Delaunay, W.; Thomas, A.; Bhanuprakash, K.; Geffroy, B.; Hissler, M.; Réau, R. *Adv. Funct. Mater.*, **2012**, *22*, 567, (d) Ren, Y.; Baumgartner, T. *Dalton Trans.* **2012**, *41*, 7792.

⁹ (a) Matano, Y.; Saito, A.; Fujita, M.; Imahori, H. *Heteroatom Chem.*, **2011**, *22*, 457; (b) Deschamps, E.; Ricard, L.; Mathey F. *Heteroatom Chem.*, **1991**, *2*, 377; (c) Tran Huy, N. H.; Lu, Y.; Nien Ah Qune, L. F.; Mathey, F. *J. Organomet. Chem.*, DOI 10.1016/j.jorganchem.2012.08.032

different electronic properties (π -donor ability and electronegativity) of the O and S atoms strongly influences the electronic distribution within the fused frameworks.^{7f}

The structures of **3-5** were determined by X-Ray diffraction. Since no solid-state structure of fused heteropentacene gold-complex is known to date, the discussion will focus on this compound. This study confirmed the proposed structure and shows that the conjugated system including the five conjugated rings is fully planar (Figure 2a). As already observed for other Au^I-phosphole complexes, the P-Au-Cl fragment is not linear (P-Au-Cl = 173°).^{8b} The phosphorus atom exhibits a distorted tetrahedral geometry with usual P-C bond lengths (1.79 Å). It is interesting to note that the furan rings display a dissymmetric character. The single C-O and double C=C bonds within the PCCO path are quasi-similar (1.36±1 Å) and notably shorter than their benzo-counterpart (1.40 Å). This dissymmetry suggests that the O-atom is effectively conjugated with the P-C=C double bond substituted by an electron-withdrawing σ^3, λ^4 -P moiety (see Table S1). Two features are worth noting. Firstly, this structural molecular feature is observed for all compounds **3-5** (see Figure S4, S5 and table S1), having similar backbone and withdrawing σ^3, λ^4 -P moieties. Secondly, this effect is not observed for the corresponding thiophene-thiooxophosphole derivatives **C** (Figure 1) characterized by X-ray diffraction studies,^{7f} showing that the impact of replacing S by O within this planar conjugated platform. Remarkably, complex **5** crystallizes as dimers which are closely packed due to a combination of both π - π interactions (π - π distances, 3.40 Å) and aurophilic interaction ($d_{\text{Au-Au}}$ = 2.99 Å) (Figure 2b).¹⁰ Furthermore, these dimers are engaged in intermolecular π - π interactions (d = 3.55 Å) resulting in the formation of infinite π -stacked columns (Figure 2c).

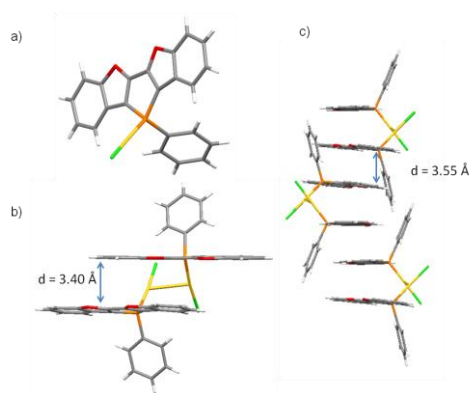


Figure 2: (a) View of crystallographic structure of **5**, (b) view of the dimers and (c) view of the packing along the x axis.

¹⁰ No proof of formation of these Au-Au interaction in solution was observed

¹¹ Note that the absence of intramolecular interaction might be detrimental to the charge transport in the device.

In contrast to what is observed with P,S-monomers **C** (Figure 1), the thiooxo and -oxo-phospholes **3,4** do not organize in the solid state via π - π interactions (see SI). This information is of prime importance for further incorporation of the compounds in OLEDs devices, since intermolecular π - π interactions induce strongly modified solid state emission behavior.¹¹

Optical properties of **3-5** were studied in CH₂Cl₂ by means of UV-Vis absorption and fluorescence (Figure 3, S7 and Table 1). The three compounds show broad absorption in the visible range (λ_{max} = 380 nm, see Figure S7) attributed to a π - π^* transition of the conjugated backbone confirmed by density functional theory calculations (DFT) at the B3LYP/6-31+G (d, p) level (Figure 3). The substitution of the P atom only weakly modifies the optical transitions. Compared to their thiophene analogs **C**, **3-5** display slightly blue shifted transition.^{7f} This observation is also in accordance with the measurements showing a reduced HOMO-LUMO gap in the oligo-thiophene series compared to its oligofuran analog.⁴ The effect of the P-environment is more pronounced on the emission properties of **3-5** (Figure 3). A gradual decrease of the maximal emission wavelength is observed in the series **4-3-5**, as already observed on phosphole oligomers.^{12,8b} P-substitution also affects the fluorescence quantum yield (Table 1). Notably, **4** and **5** display high quantum yield (65-73%), making these derivatives good candidates for use as emitters in light-emitting device. Furthermore, the solid-state emission matches the emission in diluted solution as shown Figure 4 in the case of **4**.

Table 1. Photophysical and electrochemical data.

	λ_{abs} ^a [nm]	log ϵ	λ_{em} ^b [nm]	Φ_f ^c	E^{ox}_1 ^d [V]	E^{red}_1 ^d [V]
3	391	4.4	480	0.03	+1.09	-2.06 ^e
4	390	4.3	491	0.65	+1.20	-2.08 ^e
5	380	4.5	470	0.73	+1.17 ^e	-2.03 ^e

^aIn CH₂Cl₂ (10⁻⁵M). ^bIn CH₂Cl₂ (10⁻⁵M) with (λ_{ex} = 370 nm). ^c Measured relative to quinine sulfate (H₂SO₄, 1 N), Φ_{ref} = 0.546. ^dIn CH₂Cl₂ with Bu₄N⁺PF₆⁻ (0.2 M) at a scan rate of 100 mV s⁻¹. E^{ox} (E^{red}) = 1/2(E^{pc} + E^{pa}) for reversible or quasi-reversible process, otherwise E^{ox} (E^{red}) = (E^{pa}). Potentials vs ferrocene/ferrocenium. ^equasi-reversible process.

Redox properties of **3-5** were studied by means of cyclic voltammetry (CH₂Cl₂, 0.2 M Bu₄NPF₆, v = 100 mV.s⁻¹). All compounds display amphoteric redox character with oxidation and reduction waves at relatively low potentials (Table 1). Typically, **3** display an irreversible oxidation wave (E^{ox} = +1.09 V vs Fe) and a quasi-reversible reduction wave (E^{red} = -2.06 V vs Fe). P-substitution has a weak impact on the redox properties, as illustrated by the

¹² Hay, C.; Hissler, M.; Fischmeister, C.; Rault-Berthelot, J.; Toupet, L.; Nyulaszi, L.; Réau, R. *Chem. Eur. J.* **2001**, *7*, 4222.

data presented in Table 1. Compared to its thiophene analog, **3-5** display lower oxidation and reduction potential, with a global increase of the electrochemical gap.^{7f} These data fit with the observed general trend that exchanging sulfur for oxygen in conjugated five-membered oligomers results in changes such as increasing the HOMO-LUMO gap and lowering the oxidation potential.⁴

Since the compounds **3-5** are developed as emitter for OLEDs, it was of interest to investigate their thermal stability. The compounds **3** and **4** display decomposition temperature above 250°C and a melting point at 220°C indicating good thermal stabilities which is a critical issue for device stability and lifetime. Note that compound **5** is less thermally stable than its analogs **3** and **4** with decomposition temperature of 240°C.

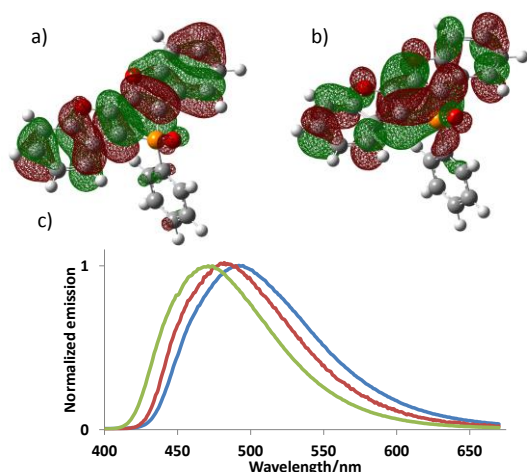


Figure 3: a) HOMO of **4**, b) LUMO of **4**, c) Normalized emission spectra in CH₂Cl₂ of **3** (red), **4** (blue) and **5** (green).

Taking in account the thermal stabilities and the physical properties of compounds **3-5**, only compound **4** was used as emitting material (EM, pure or doped in a DPVBi matrix) in multilayered OLEDs having a classical structure (indium tin oxide (ITO) / copper phthalocyanine (CuPc) (10 nm) / N,N'-diphenyl-N,N'-bis (1-naphthylphenyl) -1,1'-biphenyl-4,4'-diamine (α -NPB) (50 nm) / EM (15 nm) / 4,4'-bis (2,2'-diphenylvinyl) biphenyl (DPVBi) (35 nm) / bathocuproine (BCP) (10 nm) / tris(8-hydroxyquinolino)aluminium (Alq₃) (10 nm) / LiF (1.2 nm) / Al (100 nm) configuration, see Figure S9). In a first device **A**, mixed phosphole-furan **4** was used as pure emitter. In this case, the emission wavelength (λ_{EL} = 532 nm) is red-shifted by ca 40 nm compared to the solid-state photoluminescence of **4** (Figure 4). However, the increase of the current density does not impact the emission wavelength of device **A** (see Figure S10, S12), proving that this emission is not due to degradation of the material. In this device, luminance and external quantum efficiency are moderate (Table 2). It is believed that charge transport in **4** is low, causing this low efficiency. Derivative **4** was then

used as dopant in a DPVBi matrix (doping rate 3.6 % w, device **B**). In this case, the electroluminescence wavelength which is not affected by the increase of the current density, matches the emission of **4** in the solid state (Figure 4, Figure S13). The emission of DPVBi is not observed, indicating a quantitative energy transfer from the DPVBi to the emitter **4**. The external quantum efficiency of the device is close to the one of the DPVBi reference. In this case, the efficacy of the device is not limited by the charge transport of **4**, which explains the better properties of device **B** compared to device **A**.

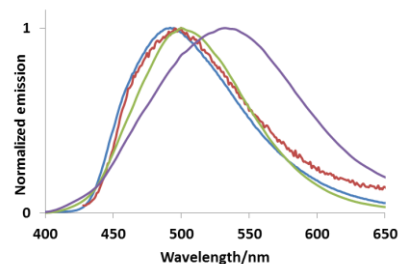


Figure 4: Photoluminescence of **4** in solution (CH₂Cl₂, 10⁻⁵ M) (blue) and in the solid state (red); Electroluminescence of device **B** (green) and device **A** (purple).

Table 2. Electroluminescent performance of devices **A** and **B**

Device	λ_{EL} [nm]	V_{on}^a [V]	B_{30}^b [cd.cm ⁻²]	EQE_{30}^b [%]	Power ^b efficiency [lm.W ⁻¹]	x^b	y^b
A	532	5.66	175	0.45	0.33	0.32	0.47
B	500	5.70	854	2.29	1.55	0.22	0.43

^a Measured for B = 0.1 cd.m⁻². ^b Measured at 30 mA.cm⁻²

In conclusion, three novel benzofuran fused phosphole heteroacenes **3-5** were synthesized and fully characterized. These P,O-containing acenes display distinct properties compared to their S-analogs. The high emission quantum yields of **4** associated with good thermal stability allowed the use of this novel scaffold in OLED emitting in the blue-green region.

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