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Phosphorus Can Also Be a “Photocopy”

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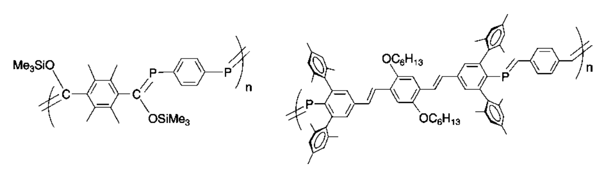
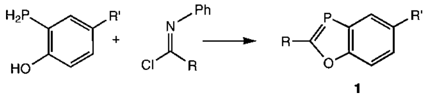
Organophosphorus compounds featuring p−p π bonds between phosphorus and carbon display close similarities to related materials having corresponding carbon−carbon π bonds, and thus, phosphorus has come to be called a “carbon copy”.[1a] While many properties are mirrored between the two sets of compounds, there remain some that are not reflected when C═C units are replaced by P═C (or P═P) units. The widespread attention on π-conjugated polymers for applications in areas such as molecular electronics, sensors, organic light-emitting diodes (OLEDs), and solar photovoltaics led to a recent Nobel prize awarded to the three pioneers of these materials.[2] It would thus seem natural to expect that related π-conjugated materials incorporating other sp^2-hybridized elements as participatory units could be realized. We and others have been seeking to exploit and extend the analogies between carbon and phosphorus to create extended conjugated materials,[3] such as *phospha*-PPVs (Chart 1).

These materials, however, show minimal photoluminescence relative to that displayed by materials such as poly(phenylenevinylene)s (PPVs). Nevertheless, phospholes have been shown to exhibit significant luminescence and also electroluminescence.[4] Because of their pyramidal phosphorus atoms, phospholes do not exhibit significant planarization and n−p π conjugation. Furthermore, many of the materials with interesting luminescent properties feature tetracoordinate phosphorus in which the phosphorus is often oxidized in the form of P═E functionalities (E = O, S) or by formation of AuCl adducts. Noting that incorporation of ring structures (and rigidity) into pendant vinyl units on phenyl rings can bring forth desirable properties, such as those found in benzodifurans and benzobisoxazoles, we now communicate the synthesis and elaboration of benzoxaphospholes and benzobisoxaphospholes that display blue fluorescence and high quantum yields for photoluminescence. These materials feature bona fide P═C p−p π bonds suitable for conjugated materials having phosphorus as a participatory atom.

Chart 1. Examples of *phospha*-PPVs



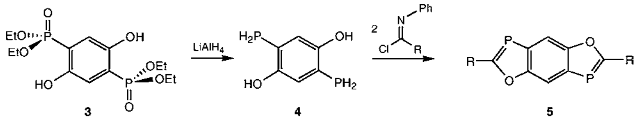
1,3-Benzoxaphospholes constitute a class of heterocycles that is a subclass of oxaphospholes and have been known for some time.[1b,5] One paper in particular piqued our interest: select benzoxaphospholes were reported to exhibit intense blue fluorescence.[5a] Though this particular facet of the report seems to have garnered little attention, it led us to examine these materials in further detail. By means of the described synthesis (the reaction of 2-phosphinophenols and *N*-phenyl imidoylchlorides; eq 1), some of these compounds and several new representatives were prepared. Most of these materials are distinctly fluorescent (Table 1). Measurement of the excited-state lifetimes allowed for confident assignment of the emission as fluorescence. All but the alkyl-substituted derivative **1d** displayed significant photoluminescence (PL) intensity (the PL intensity of **1d** was enhanced in MeOH relative to CH_2Cl_2).



(1)

With an eye toward the eventual synthesis of extended materials, we set out to synthesize and characterize the previously unknown benzobisoxaphospholes. The novel precursor 2,5-diphosphinohydroquinone (**4**) was readily accessed by reduction of **3** (Scheme 1), which itself can be readily accessed by an anionic double Fries rearrangement of 1,4-{OP(═O)-$(OEt)_2$}C_6H_4.[6] Reaction of **4** with 2 equiv of select imidoylchlorides led to the corresponding 2,6-substituted benzo[1,2-*d*;4,5-*d*′]bisoxaphospholes (Scheme 1, Table 1). Compounds **1** and **5** display greater air and water stability than previously reported *phospha*-PPVs.

Scheme 1



	R	% Yield	^{31}P δ (ppm)
5a	Ad	31	76.7
5b	^tBu	69	78.1
5c	2,4,6-$Me_3C_6H_2$	42	99.7
5d	2,6-$Me_2C_6H_3$	40	99.3

The benzobisoxaphospholes were characterized by ^{31}P NMR spectroscopy, and resonances near those of their simpler

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analogues were found (Scheme 1). The single-crystal structure of **5b** is shown in Figure 1. The P═C bond length of 1.694(1) Å is somewhat longer than that found in most phosphaalkenes and shorter than the P−C(2) single-bond distance of 1.782(1) Å, but consistent with such distances found in benzoxaphospholes. The angle about the phosphorus atom is 88.34(5)°. The results of a density functional theory (DFT) study of the model diphenyl-substituted benzobisoxaphosphole **5e** showed that the frontier orbitals consist largely of phosphorus−carbon π and π^* orbitals (Figure 1).

The photoluminescence data for **5a−d** are provided in Table 1 and again show that aryl-substituted analogues display much greater PL intensity than alkyl-substituted materials.

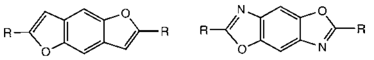
Table 1. Selected Data for Compounds

	R	R′	λ_{max} (nm)[a]	$\lambda_{F,max}$ (nm)[a]	Φ[a]	τ (ns)[b]
1a	C_6H_5	H	337	425	0.57	12.0
1b	4-ClC_6H_4	H	343	427	0.62	11.8
1c	4-$MeOC_6H_4$	H	348	437	0.63	13.5
1d	Ad	H	281[c]	426[c]	0.04[c]	9.0[c]
1e	4-BrC_6H_4	H	343	426	0.62	11.9
1f	4-MeC_6H_4	H	343	426	0.69	7.0
1g	C_6H_5	^{i}Pr	339	421	0.55	5.8
1h	4-ClC_6H_4	^{i}Pr	345	424	0.58	28.0
1i	4-$MeOC_6H_4$	^{i}Pr	351	438	0.56	25.0
1j	4-MeC_6H_4	^{i}Pr	342	429	0.56	4.8
5a	Ad	H	306	367	0.03	3.9
5b	^{t}Bu	H	304	372	0.04	4.6
5c	2,4,6-$Me_3C_6H_2$	H	337	432	0.27	3.7
5d	2,6-$Me_2C_6H_3$	H	336	436	0.22	2.3

[a] Measurements were performed in CH_2Cl_2. [b] Values were determined in hexanes. [c] Measurements were performed in CH_3OH.

The benzobisoxaphospholes thus mimic the PL characteristics of their two closest phosphorus-free analogues, benzodifurans and benzobisoxazoles (Chart 2). While studies of the former are limited in number despite the fact that they show interesting properties,[7] benzobisoxazoles, in contrast, have been extensively studied and found broad use in robust materials having high mechanical strength and important photophysical and electronic properties.[8] Preliminary electrochemical studies of **1a** and **1g** revealed reversible reductions occurring at −1.90 and −1.93 V versus SCE, respectively (see the Supporting Information), which are analogous to those reported for other phosphaalkenes and also suggests possibilities for the use of these materials as components in n-type conjugated materials.

Chart 2



In summary, we have shown that benzoxaphospholes and benzobisoxaphospholes are materials that have bona fide P═C double bonds, do indeed possess interesting and significant PL properties, and can “photocopy” the properties of other conjugated molecules. We are currently preparing extended conjugated materials for examination in applications such as OLEDs.

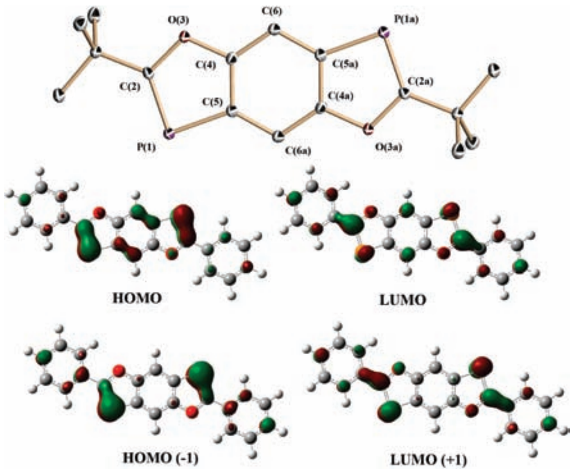


Figure 1. (top) X-ray structure of **5b** and (bottom) selected molecular orbitals (DFT B3LYP/6-31+G**) for the minimized structure of **5e**. Selected experimental bond distances (Å) and angles (deg): P(1)−C(2), 1.694(1); P(1)−C(5), 1.782(1); C(2)−P(1)−C(5), 88.34(5).

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Supporting Information Available: Experimental procedures and characterization data for all compounds and X-ray analysis data for **5a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: New York, 1998. (b) Mathey, F. *Phosphorus−Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Pergamon Press: Amsterdam, 2001.
(2) (a) Heeger, A. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2591. (b) MacDiarmid, A. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2581. (c) Shirakawa, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2575.
(3) (a) Smith, R. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **2004**, *126*, 2268. (b) Smith, R. C.; Chen, X.; Protasiewicz, J. D. *Inorg. Chem.* **2003**, *42*, 5468. (c) Wright, V. A.; Gates, D. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2389. (d) Wright, V. A.; Patrick, B. O.; Schneider, C.; Gates, D. P. *J. Am. Chem. Soc.* **2006**, *128*, 8836. (e) Geng, X.-L.; Hu, Q.; Schafer, B.; Ott, S. *Org. Lett.* **2010**, *12*, 692.
(4) Recent examples: (a) Fave, C.; Cho, T.-Y.; Hissler, M.; Chen, C.-W.; Luh, T.-Y.; Wu, C.-C.; Reau, R. *J. Am. Chem. Soc.* **2003**, *125*, 9254. (b) Baumgartner, T.; Neumann, T.; Wirges, B. *Angew. Chem., Int. Ed.* **2004**, *43*, 6197. (c) Matano, Y.; Imahori, H. *Org. Biomol. Chem.* **2009**, *7*, 1258. (d) Tsuji, H.; Sato, K.; Ilies, L.; Itoh, Y.; Sato, Y.; Nakamura, E. *Org. Lett.* **2008**, *10*, 2263. (e) Sanji, T.; Shiraishi, K.; Tanaka, M. *Org. Lett.* **2007**, *9*, 3611.
(5) (a) Heinicke, J.; Tzschach, A. *Phosphorus Sulfur Relat. Elem.* **1985**, *25*, 345. (b) Bansal, R. K.; Heinicke, J. *Chem. Rev.* **2001**, *101*, 3549.
(6) Dhawan, B.; Redmore, D. *J. Org. Chem.* **1984**, *49*, 4018.
(7) (a) Hayashi, N.; Saito, Y.; Higuchi, H.; Suzuki, K. *J. Phys. Chem. A* **2009**, *113*, 5342. (b) Tsuji, H.; Mitsui, C.; Ilies, L.; Sato, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2007**, *129*, 11902.
(8) Selected references: (a) Hu, X.-d.; Jenkins, S. E.; Min, B. G.; Polk, M. B.; Kumar, S. *Macromol. Mater. Eng.* **2003**, *288*, 823. (b) So, Y.-H.; Zaleski, J. M.; Murlick, C.; Ellaboudy, A. *Macromolecules* **1996**, *29*, 2783. (c) Mike, J. F.; Makowski, A. J.; Jeffries-El, M. *Org. Lett.* **2008**, *10*, 4915. (d) Klare, J. E.; Tulevski, G. S.; Sugo, K.; de Picciotto, A.; White, K. A.; Nuckolls, C. *J. Am. Chem. Soc.* **2003**, *125*, 6030. (e) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4556.

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