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Luminescent materials containing multiple benzoxaphosphole units

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A series of bisbenzoxaphospholes and a trisbenzoxaphosphole have been prepared and characterized. These extended π -conjugated heterocyclic phosphalkenes display significant fluorescence in solution having quantum yields between 0.12–0.85. The solid state structure of a bisbenzoxaphosphole reveals evidence for extended conjugation, as do DFT calculations.

Organic π -conjugated materials have been intensively studied due to their promise for use as active materials in optoelectronic applications such as sensors, organic light-emitting diodes and photovoltaic cells.¹ Much of this work has been focused on efficiently modifying the structures of conjugated materials for obtaining desired functions in electronic devices. Incorporation of heteroatoms (N, P, S, O, Si, *etc.*) into the backbone of conjugated materials is one strategy to yield novel properties.² Conjugated materials integrating phosphorus atoms have received increasing attention since they display remarkably different electronic properties from purely organic systems.³ Our group⁴ and others^{3b,5} have been very interested in replacing one or more C=C entities with P=C bonds ($p\pi-p\pi$) in conjugated materials to produce new materials having reduced HOMO-LUMO gaps and increased redox activity.⁶ Most recently we have explored the chemistry of 1,3-benzoxaphospholes (**R-BOP** and **R-BOP***) and their fused ring relatives, as exemplified in Chart 1. These particular heterocyclic phosphalkenes offer in comparison to acyclic phosphalkenes (a) enforced coplanarity of P=C bonds with attached aromatic residues, (b) greater air and water stability (without the requirement for sterically demanding protecting groups), and (c) unique fluorescent properties.⁷ In this communication we report on the successful synthesis and characterization of highly fluorescent linked bis- and trisbenzoxaphospholes.

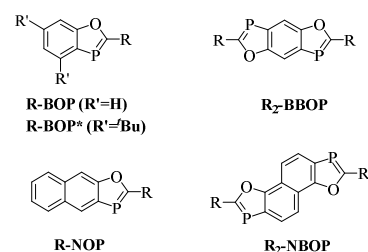
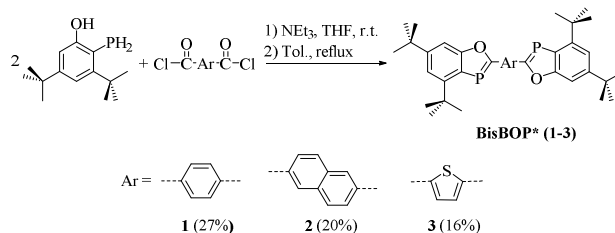


Chart 1

A series of bisbenzoxaphospholes (**BisBOP***, Scheme 1) with various linkers were synthesized by dehydrocyclization reactions.⁸ Specifically, 3,5-di-*tert*-butyl-2-phosphinophenol⁹ (*t*-butyl groups enhance air-stability and solubility) was first reacted with aryl dicarbonyl dichlorides in the presence of triethylamine at room temperature overnight. After removal of a white precipitate and solvent, the mixtures were refluxed in toluene (several days for **1** and **2**, overnight for **3**) to produce **1–3** as the major products. Extraction with hexanes and filtration through basic alumina, followed by evaporation of solvent afforded **BisBOP*** as yellow (**1** and **2**) or red (**3**) solids in modest yields (16–27%).



Scheme 1

The ³¹P{¹H} NMR chemical shifts of **BisBOP*** are located between 91–95 ppm, ca. 2–5 ppm downfield from Ph-BOP*, which are consistent with the presence of the benzoxaphosphole functionality.⁹ Compounds **1** and **2** display modest air stability in solution, degrading in CDCl₃ over a period of days. Compound **3** is much less stable (completely decomposes under similar conditions within 30 minutes).

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A colourless crystal of **1** was grown by slow evaporation from a solution of **1** in hexanes, and the result of a single crystal X-ray analysis is shown in Figure 1. There exists an inversion center within **1** that relates both halves of the molecules. The P=C bond length of 1.712 (2) Å is consistent with the P=C bond length determined in *p*-ClC₆H₄-BOP (1.712 (7) Å).¹⁰ Within the structure of **1**, the two benzoxaphosphole units are coplanar, and the central phenyl ring is canted by 18.8° with respect to these benzoxaphosphole groups. The molecules of **1** are loosely π -stacked (ca. 3.80 Å), with each molecule of **1** slipped in such a manner so as to avoid direct steric clashes of the tertiary butyl groups that would arise if the molecules of **1** sat exactly upon each other (Figure 1).

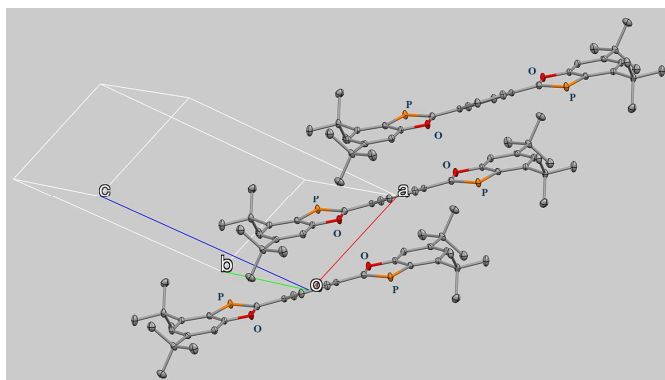


Figure 1 X-ray crystallographic structure of **1** showing the packing structure with unit lattice.

Bisbenzoxaphospholes are notably fluorescent. Upon excitation at 365 nm, they appear blue-green (**1** and **2**) or yellow (**3**) in CH₂Cl₂ solution or in the solid state. The photophysical properties of **1-3** were examined using UV-vis absorption and fluorescence spectroscopies in CH₂Cl₂ (Figure 2). The absorption spectra of **1-2** feature absorption maxima at 418 (437sh) and 412 (438sh) nm respectively, which are at longer wavelengths than observed for Ph-BOP* (345 nm), Mes₂-BBOP (337 nm), Ph₂-NBOP (387 nm) and Ph-NOP (353 nm).^{7,9} Thiophene bridged **3** has an even longer absorption wavelength (457 nm). The fluorescence emission spectrum of **1** exhibits two emission peaks at 462 and 485 nm, which are red shifted by around 40 nm compared with that for Ph-BOP* (λ_{em} = 425 nm).⁹ Compound **2** displays broad emission at around 473 (shoulder at 462 nm). For compound **3**, however, only a single broad emission centered at 533 nm is observed. The UV-vis absorption and emission spectra for **1-3** showed only slight change upon changing the solvent from CH₂Cl₂ to hexanes (supporting information). A summary of the photophysical data of **1-3** in solution is presented in Table 1. Quantification of the intensity of emission showed that compound **2** exhibits higher fluorescence quantum yield ($\Phi_F=0.50$) in CH₂Cl₂ as compared to **1** ($\Phi_F=0.31$) and **3** ($\Phi_F=0.12$).

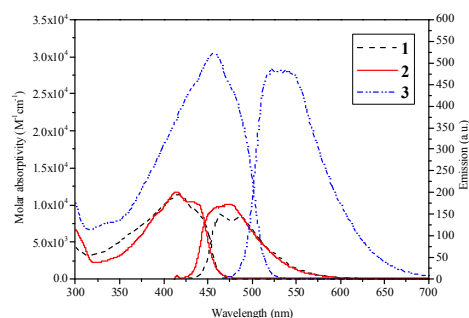


Figure 2 UV-vis absorption and fluorescence spectra of BisBOP* in CH₂Cl₂ (Conc. 0.5×10^{-6} M). Excitation wavelength for fluorescence measurements was the corresponding absorption maxima.

In order to better understand the photophysics of these compounds, DFT (6-311G+(d,p) B3LYP) studies of **1** and **3** were undertaken. The minimized structures (supporting information) feature planar structures and P=C bond lengths of 1.737 and 1.741 Å respectively. TDDFT calculations (6-311G+(d,p) CAM-B3LYP) on these structures predict absorption maxima of 414 nm ($f=1.40$) and 467 nm ($f=1.30$) in CH₂Cl₂ (IEFPCM), respectively. These transitions are largely HOMO→LUMO in character (>94%) and involve significant participation of the P=C π system. The bisbenzoxaphosphole **1** mimics the photoluminescent properties of two lighter analogues, bisbenzoxazole and bisbenzofuran (Chart 2), but note that the λ_{max} for **1** is 64-77 nm red shifted compared to these materials.¹¹ Bisbenzoxazole is a well-studied molecule for use in organic light emitting devices and chemical sensors.¹² Similarly, benzoxazoles and benzobisoxazoles have become interesting motifs for new polymeric materials.¹³

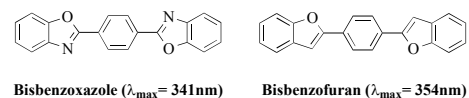
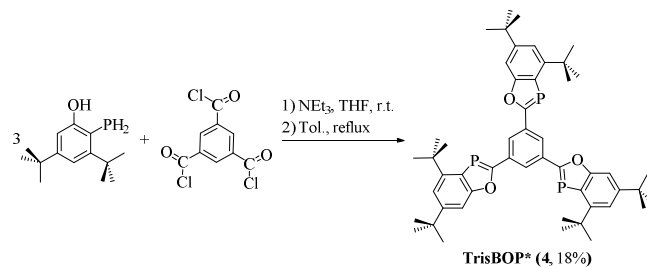


Chart 2

With successful synthesis of BisBOP*, we applied this synthetic strategy to produce a trisbenzoxaphosphole (**TrisBOP***, **4**), which contains three benzoxaphosphole units (Scheme 2). First, the reaction of 3,5-di-*tert*-butyl-2-phosphinophenol with 1,3,5-benzenetricarbonyl trichloride in the presence of triethylamine at room temperature was carried out overnight. After removal of precipitate and solvent, the mixture was refluxed in toluene for 4 days. From this reaction mixture, pure **4** was eventually isolated as a yellow solid in 18% yield. The ³¹P{¹H} NMR chemical shift appears at 94.9 ppm, which is consistent with the presence of the P=C functionality.⁷



Scheme 2

TrisBOP* **4** is also fluorescent under UV light, appearing blue. The UV-vis absorption and fluorescence of **4** in CH₂Cl₂ and hexanes are characterized (supporting information). The absorption profile and maxima of **4** are similar in CH₂Cl₂ and hexanes (Table 1). While **4** shows a red shift of 17 nm compared with λ_{max} of Ph-BOP*, **4** exhibits a 56 nm wavelength blue shift compare to BisBOP* **1**. The latter result is consistent with more effective conjugation in the *para*-substituted system.

Table 1 Photoluminescent data of **1-4**.

Compound	Solvent	λ_{max} (nm)	ϵ^{a} (M ⁻¹ .cm ⁻¹)	λ_{F} (nm)	$\Phi_{\text{F}}^{\text{b}}$
1	DCM	418	11305	462,485sh	0.31
	Hexanes	413	24968	455,481sh	0.18
2	DCM	412	11570	462sh,473	0.50
	Hexanes	407	34814	439sh,449sh,465	0.85
3	DCM	457	32283	533 ^c	0.12
	Hexanes	452	15034	509sh,537	0.22
4	DCM	362	28214	437,451sh	0.14
	Hexanes	359	28583	425,446sh	0.34
Ph-BOP* ^d	DCM	345	12110	425	0.12

Note: ^aExtinction coefficients based on absorbance at λ_{max} . ^bRelative Φ_{F} values were measured using 9,10-diphenylanthracene in cyclohexane (**1** and **2**), fluorescein in 0.1 M NaOH (**3**) and anthracene in ethanol (**4**).

In conclusion, a series of bisbenzoxaphospholes (**1-3**) and a trisbenzoxaphosphole (**4**) were synthesized by dehydrocyclization. The single crystal X-ray study documented a largely planar structure for **1**. Photoluminescence studies revealed that these materials have high fluorescence quantum yields of up to 0.85. Compared with BBOP, NOP and NBOP, novel heterocyclic phosphalkenes **1-3** have smaller HOMO/LUMO gaps and greater effective conjugation lengths. Future efforts will concentrate on design and synthesis of polymers and other extended conjugated materials having BOP units to further decrease bandgaps and tune optical properties.

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Notes and references

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Electronic Supplementary Information (ESI) available: Experimental details, X-ray analysis data for **1** (CCDC 1007938), NMR spectra, UV-vis absorption and emission spectra, and DFT calculation. See DOI: 10.1039/c000000x/

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