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Phosphorus as a carbon copy and as a photocopy: New conjugated materials featuring multiply bonded phosphorus*

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Abstract: Phosphaalkenes ($RP{=}CR_2$) and diphosphenes ($RP{=}PR$) are main group analogues of alkenes ($R_2C{=}CR_2$). Molecules featuring such multiply bonded phosphorus functionalities often display structural features and chemical reactivities that mimic their purely organic counterparts, lending credence to the claim that these compounds are "carbon copies". We have been expanding this analogy to include oligomers and polymers with extended conjugation that directly involve P=C and P=P units. Many of these materials, however, display little or no photoluminescence (PL). This article summarizes our efforts to understand P=C and P=P photobehavior and to produce materials having significant PL that mimic or "photocopy" the PL properties of the phosphorus-free systems. Recent materials based on benzoxaphospholes (BOPs), benzobisoxaphospholes (BBOPs), and higher analogues having significant fluorescence quantum yields are covered.

Keywords: conjugation; fluorescence; main group chemistry; multiple bonds; phosphorus; photochemistry; polycyclic aromatics; synthesis.

INTRODUCTION

Phosphorus has often been called a "carbon copy" because compounds having p-p π bonds between P and C atoms (or between two P atoms) are structurally and chemically similar to related systems with comparable multiple bonds between carbon atoms [1]. For example, phosphaalkenes ($RP{=}CR_2$) and diphosphenes ($RP{=}PR$) display many similarities to olefins ($R_2C{=}CR_2$). Likewise, phosphaalkynes ($P{\equiv}CR$) behave like acetylenes ($RC{\equiv}CR$) in many ways [2,3].

Part of the reason for these parallels lies in the fact that phosphorus and carbon have comparable electronegativities, making bonds between phosphorus and carbon relatively nonpolar. This situation is quite unlike that observed for the more well studied nitrogen analogues of olefins, imines ($RN{=}CR_2$), or diazenes ($RN{=}NR$). In these latter molecules the polarity of the CN bond and/or the domination of the lone pairs on nitrogen in highest occupied molecular orbitals (HOMOs) stands in contrast to the related properties of the "carbon copies". Some of these relationships and their impacts on frontier molecular orbitals of basic $H_nE{=}EH_n$ molecules (E = C, N, or P) are shown in Fig. 1. In all of these molecules the lowest unoccupied molecular orbital (LUMO) is π^* in character. Importantly, for the series $H_2C{=}CH_2$, $H_2C{=}PH$, $HP{=}PH$, one observes (a) decreasing π–π^* gaps and (b) comparably ener-

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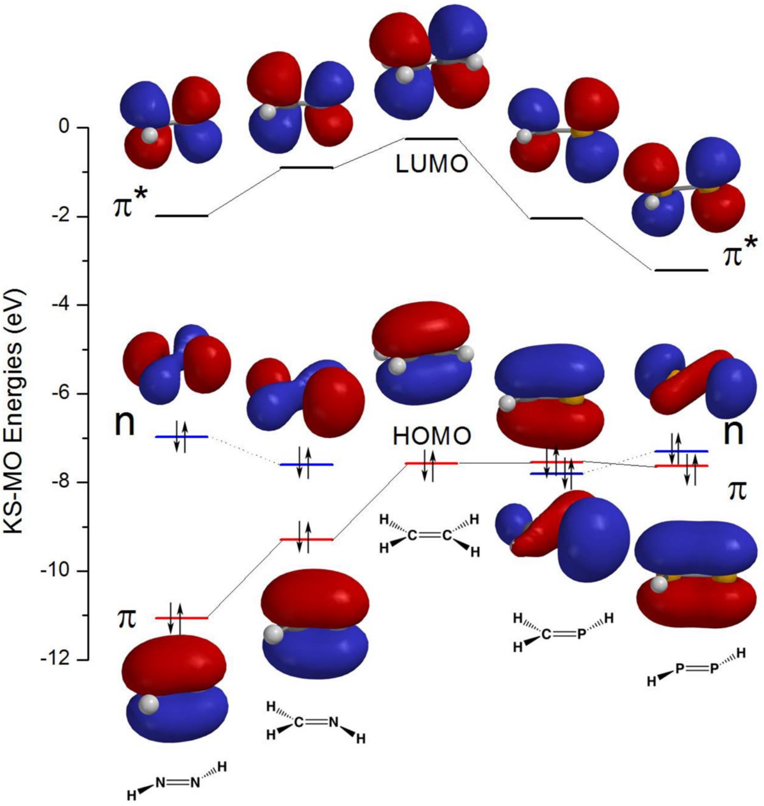


Fig. 1 Relationships between frontier orbitals of $H_nE=EH_n$ compounds (E = N, C, or P, n = 0, 1, or 2), results are based on density functional theory (DFT) calculations (B3LYP/6-31G*).

getic π-orbitals. For the series $H_2C=CH_2$, $H_2C=NH$, HN=NH, one observes (a) increasing π–π* gaps and (b) increasingly stabilized π orbitals. For the latter series of nitrogen-containing compounds the nitrogen lone pairs play a dominant role in the HOMOs. In contrast, for P=C and P=P bonded compounds, the n- and π-orbitals are close in energy.

Many groups have exploited the "carbon copy" analogy to create a wealth of compounds having multiply bonded low-coordinate phosphorus atoms. Our group [4,5] and the Gates group [6–9] have been working, however, to extend this analogy to macromolecules. Chart 1 displays several examples of polymeric materials having phosphaalkene linkages in π-conjugation along the main chain. Each of these materials is related to the important class of organic conjugated polymers poly(phenylenevinylene)s (PPVs). As anticipated, these "*phospha*-PPVs" display red-shifted π–π* transitions compared to analogous phosphorus-free polymers, and are light yellow to orange colored solids.

A common feature of conjugated materials is a reduced HOMO–LUMO gap, which gives rise to their ability to interact with UV and visible light. Light absorption by molecules can lead to various events, such as isomerization, photo-induced reactions, generation of heat, or re-emission of light (fluorescence or phosphorescence). Small-molecule analogues of *E*-**P1** and *E*-**P2**, such as **PA-1** (Fig. 2), undergo photochemical *E*–*Z*-isomerization [10].

A small isosteric molecular analogue of *E*-**P3**, the diphosphene DmpP=PDmp (and related terphenyl protected diphosphenes [11,12]), does not appear to undergo photochemical *E*–*Z*-isomerization or irreversible photoreaction, for that matter. By contrast, the diphosphene Mes*P=PMes* undergoes both photochemical *E*–*Z*-isomerization and cyclometallation of a vicinal CH bond (Scheme 1) [13,14].

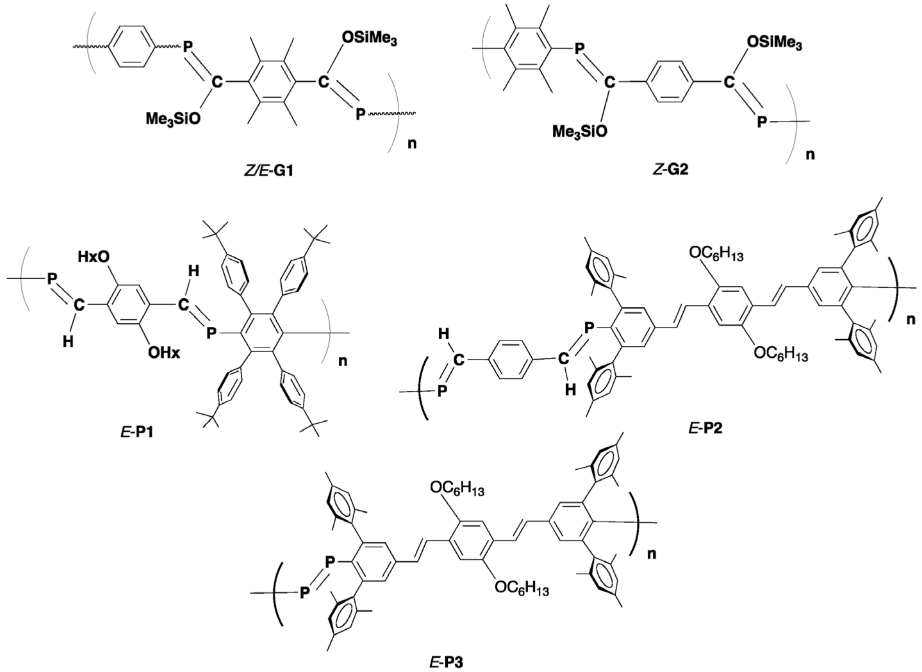


Chart 1 Some conjugated polymers with participatory P=C and P=P units.

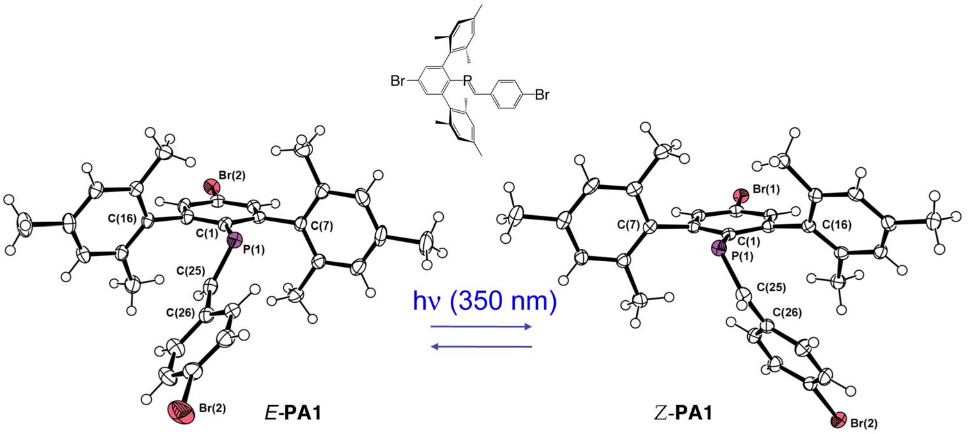
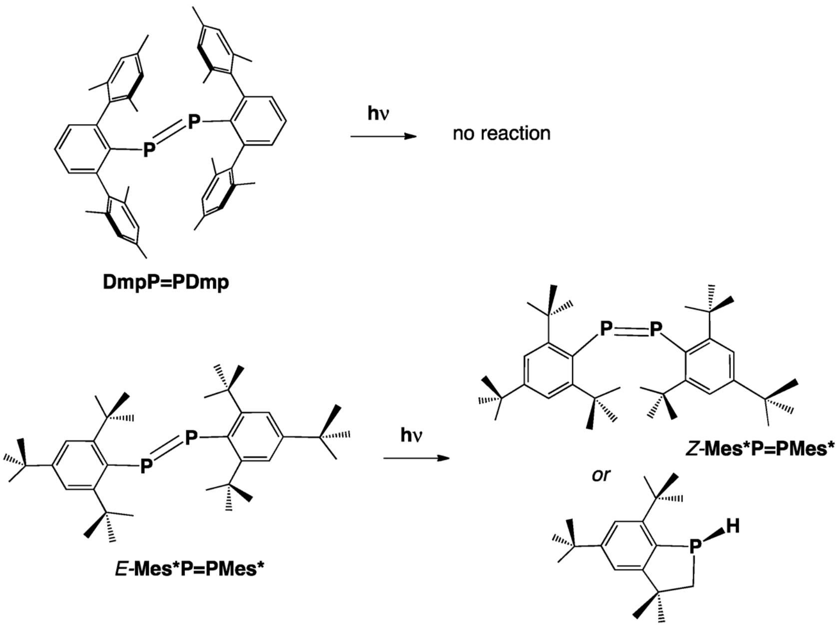


Fig. 2 Photoisomerization of a phosphaalkene.

These two examples illustrate the influence of the nature of the specific sterically demanding group can have upon the photophysical properties of multiply bonded phosphorus compounds.

Surprisingly, the above phosphaalkenes and diphosphenes display little or no PL. This observation stands in contrast to many examples of phosphorus-free conjugated molecules and polymers (e.g., stilbene). In fact, most examples of compounds having P=C or P=P linkages exhibit little or no photoluminescence (PL). Our groups have thus become interested in studying this apparent inability for phosphorus to act as a "photocopy" of olefins in greater detail.



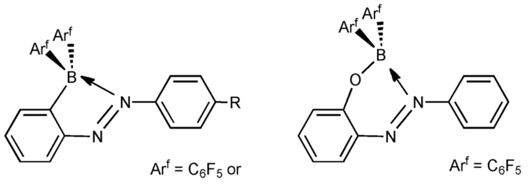
Scheme 1

ATTEMPT TO "TURN ON" DIPHOSPHENE FLUORESCENCE

Phospha-PPVs have two main attributes that distinguish them from PPVs (a) a phosphorus atom having a lone pair of electrons and (b) bulky substituents on the phenyl rings. Several factors can decrease emission yields in conjugated materials. These include the presence of lone pairs on phosphorus and the specific geometry of phosphorus compounds [15]. The lone pair of electrons on phosphorus in phosphaalkenes and diphosphenes might thus cause fluorescence quenching. Another possibility is that changes in the excited-state geometry cause rapid relaxation, as is known for alkenes [16].

In this regard, it is useful to make comparisons to compounds having C=N bonds, since they also feature a lone pair of electrons on a heteroatom of the double bond and have been the object of extensive photophysical studies. Benzalanilines (ArN=C(H)Ar) and azobenzenes (ArN=NAr) are often not fluorescent, owing to fast intersystem crossing to ($S_1^* \rightarrow T_1^*$) promoted by structural reorganization of the excited states. This effect is amplified by the presence of the lone pair(s) on the nitrogen atom. Azobenzene also has a rich history of photochemistry and is often used as a component of photo switches as it readily isomerizes between its *E*- and *Z*-forms. Protonation or intramolecular hydrogen bonding to the N-lone pairs can have a significant impact on the energetics of $n\pi^*$ excited states and raise PL efficiencies.

These concepts were pulled together and used to direct the successful synthesis of very fluorescent azobenzenes (Chart 2) [17,18]. These particular molecules features lone-pair acceptor moieties (BAr^f_2) built into the molecules that not only cap the lone pairs but also tether the two *N*-aryl groups and form a heterocyclic ring. The PL efficiency of one of these novel species was increased by a factor of 30000 relative to the parent azobenzene (Chart 2, AzB-1, $Ar^f = C_6F_5$). This achievement was attributed to both the increased rigidity of the molecule (prevention of *E*–*Z*-isomerization), through the intramolecular Lewis acid–base interaction, and to the inversion of the $^1(n,\pi^*)$ and $^1(\pi,\pi^*)$ states in energy.



AzB-1 **AzB-2**

Chart 2

The synthesis of analogous diphosphenes and phosphaalkenes having chelating Lewis acids is underway in our labs. To investigate the possibility of simply capping the lone pairs and turning on fluorescence we have explored the reaction of the diphosphene Mes*P=PMes* (Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$) with (THT)AuCl [19]. These reactions afforded either the mono-gold adduct Mes*P{AuCl}=PMes* or the di-gold adduct Mes*P{AuCl}=P{AuCl}Mes* (Fig. 3, top). Both of these gold diphosphene complexes were structurally characterized, and their structures were compared to the original structure of Mes*P=PMes*. Interestingly, very little change in the overall geometries of the diphosphenes was observed (Fig. 3, bottom). Even more interesting was the finding that the P=P bond lengths in the gold complexes are *shorter* [1.975(5) and 2.003(4)Å] than that in the free diphosphene. Neither of the gold

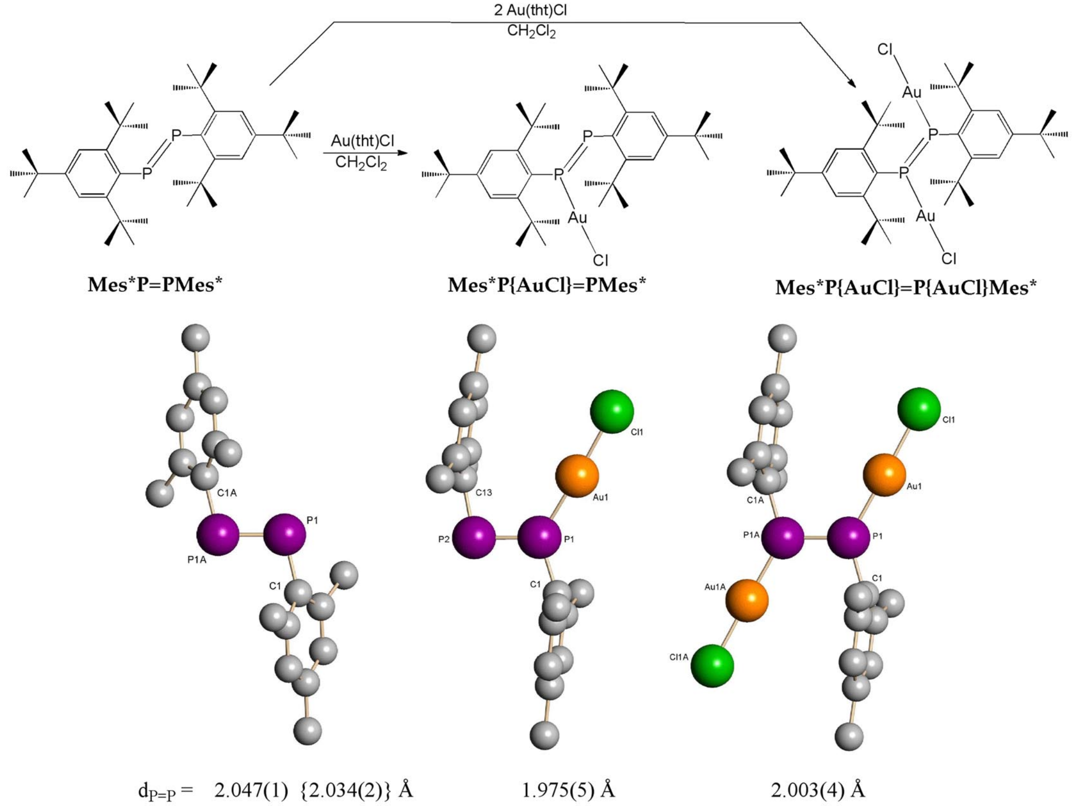


Fig. 3 Synthesis of AuCl adducts of diphosphene Mes*P=PMes* (top) and comparison of structures of Mes*P=PMes*, and Mes*P{AuCl}=PMes*, Mes*P{AuCl}=P{AuCl}Mes* (bottom, all hydrogen atoms and methyl carbon atoms omitted for clarity). Also note that two P=P bond lengths are listed for Mes*P=PMes*, as the original structure was more recently repeated at higher resolution [20].

adducts, however, showed significant fluorescence, indicating that one may need to also control the rigidity of the system to promote excited-state emission over energy loss via thermal processes.

DETAILED PHOTOPHYSICS OF A DIPHOSPHENE

In parallel collaborative studies with Cather Simpson's group (The Photon Factory at the University of Auckland, New Zealand), we have also been using a combination of ultrafast pulsed laser spectroscopy techniques and high-level quantum mechanical methods (DFT, CASSCF, and CASPT2) to better understand the photophysics of diphosphenes [11,21,22]. Most recently, femtosecond (10^{-15} s) transient absorption spectroscopy (fsTRA) has been used to provide snapshots of the UV/vis absorption spectrum of the evolution of the excited states of the DmpP=PDmp molecule (Fig. 4, upper) [21].

TRA is a pump-probe method in which the molecule of interest is first excited with a short (~100 fs) laser pulse in resonance with one of the excited states of the molecule. Then, at some time delay later, the UV/vis absorption spectrum is measured using a second short laser pulse. In our experiments, this second pulse has undergone a nonlinear optical transformation into a supercontinuum (white-light) spectrum, approximately 100 fs in duration. The results are presented as a difference spectrum, in which the baseline, ground-state UV/vis absorption spectrum, has been subtracted. The kinetics of the negative (bleach, stimulated emission) and positive (transient absorption) signals provide insight into the dynamical evolution of the molecular system—on the time scale of nuclear motion.

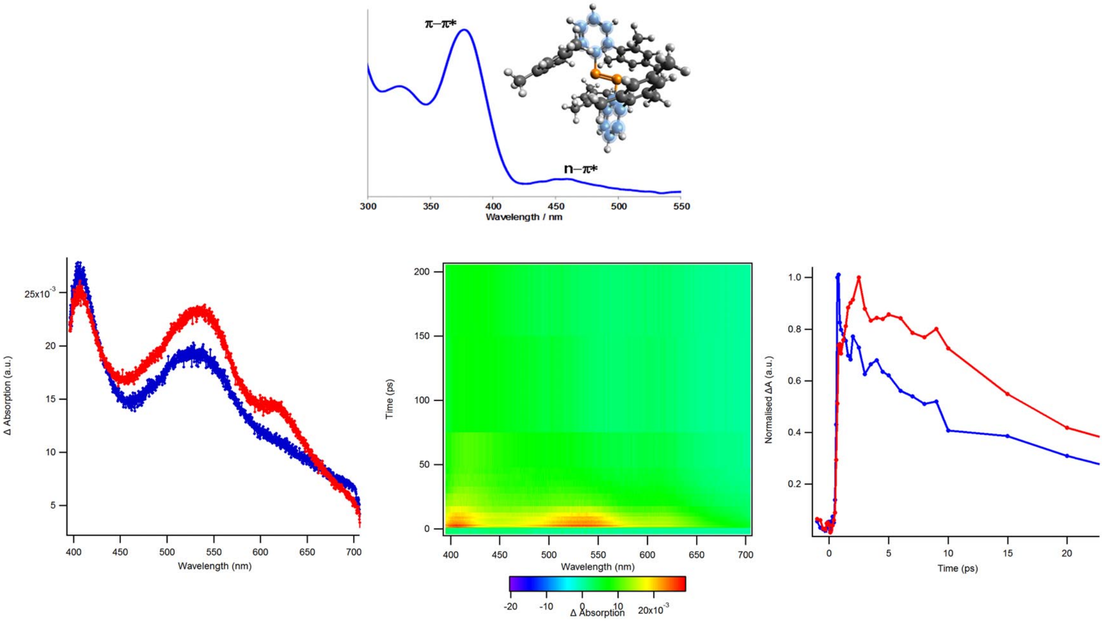


Fig. 4 UV/vis spectrum (upper) and transient absorption spectra (lower) of DmpP=PDmp. The panel on the lower left is the transient absorption difference spectrum at early (upper, red) and later (lower, blue) times. These spectra are generated by "slicing" the two-dimensional plot in the center horizontally at two different times. The panel on the lower right shows the time-dependent signal at two wavelengths. The blue trace is the kinetics in the 650–700 nm region, and the red traces show the kinetics of the more intense signal at 500–600 nm. The two kinetic traces have been normalized to emphasize the rapid rise and decay of the blue trace, and the slower rise of the red trace. In the data analysis, these evolving difference spectra and kinetic data are fit using soft and hard modeling to extract the line shapes, UV/vis absorption wavelengths and lifetimes of excited transient intermediates, and thereby obtain insight into the photochemical and photophysical mechanisms.

When DmpP=PDmp is photoexcited to the S_1 (n_+–π*) and S_2 (π–π*) states (Fig. 4, upper), transient absorption signals indicate very rapid relaxation through the excited states of the system (Fig. 4, lower). The data corroborate the absence of irreversible photochemistry in this system; the molecule returns to S_0 on a sub-nanosecond timescale. The S_2 state appears as a rapidly rising absorption at the red edge of the spectrum. This absorption signature decays with a lifetime of 275 fs, into a series of transient bands between about 450 and 650 nm that rise exhibit a mirror rise time. Calculations upon the Ph-P=P-Ph model structure at the CASSCF(8,6)/6-31G** and CASPT2(8,6)/6-31G**//CASSCF(8,6)/6-31G** levels are consistent with this assignment, and indicate that transition is relatively intense, and peaked further into the near IR. That is, our signal reflects only the higher energy tail of the signal. The n-π* (S_1) state has no appreciable absorption in the 400–700 nm detection window. This state decays rapidly into an intermediate with a very similar spectrum in the 450–650 nm region to that seen with S_2 excitation. The complete active-space calculations are also entirely consistent with the experimental results. The calculated S_1 state is predicted to show no transitions with appreciable oscillator strengths within the visible range of the spectrum.

It appears that when the DmpP=PDmp molecule is excited into the two major bands localized on the P=P moiety—the S_1 (n–π*) and S_2 (π–π*)—the subsequent evolution back to the S_0 ground state is through a common intermediate. The current working hypothesis includes a rapid intersystem crossing to the energetically low-lying triplet manifold. Preliminary quenching experiments support the availability of the T_1 and T_2 at lower energy. The transitions are rapid, probably due to an efficient coupling through El-Sayed's rules and the heavy atom (phosphorus) effect. Ultrafast time-resolved resonance Raman experiments are currently underway to more firmly assign the transient intermediate bands to individual evolving structures.

NEW STRATEGIES FOR P=E BONDS

Compounds having multiple bonding involving heavier main group elements tend to be more reactive because they possess π-bonds that are weaker than those found in olefins. This fact, coupled with the fact that the atoms are also larger (more accessible) means that many possible compounds are prone to self-dimerization or redistribution reactions that convert the combination of σ- and π-bonds within P=E multiply bonded compounds to compounds having purely σ-bonds. Most multiply bonded phosphorus compounds thus contain sterically encumbered groups on the phosphorus atom to impart kinetic stability (e.g., steric inhibition to self dimerization) to these systems. The presence of large substituents, however, can have deleterious consequences on π-conjugation. The challenges are even greater when designing conjugated compounds and materials with multiple P=E bonds. For example, the structure of a diphosphaalkene in the solid state (Fig. 5) displays significant displacement of the atoms (in color) from an all-planar configuration, thus limiting the desired π-conjugation in this system [23].

In a clever use of design strategy, the Eind ligand (Fig. 6, **A**) was used to enforce a geometry optimal for π-conjugation for two Si=P units across a phenyl ring [24]. Computational and photophysical studies support a highly conjugated system. Interestingly, the diphosphasilene is also weakly emissive in the solid state.

Acetylenes offer another approach to extending conjugation with P=E bonds, where orientational effects become unimportant. The two phosphaalkene units in the diphosphosphaalkene shown in Fig. 6 (**B**) can communicate across the anthracene bridge [25]. This red-colored material showed two reduction waves in cyclic voltammetry experiments, indicative of electronic coupling of the two P=C units.

These two examples show ideal orientations for maximizing π-conjugation between two distant P=E units. Unfortunately, they do not offer easy opportunities for extending the conjugation in a linear fashion so as to open the doors to π-conjugated polymers containing P=E bonds. Each system is "terminated" by bulky aromatic cores that are not in plane with the P=E units. Another approach is necessary.

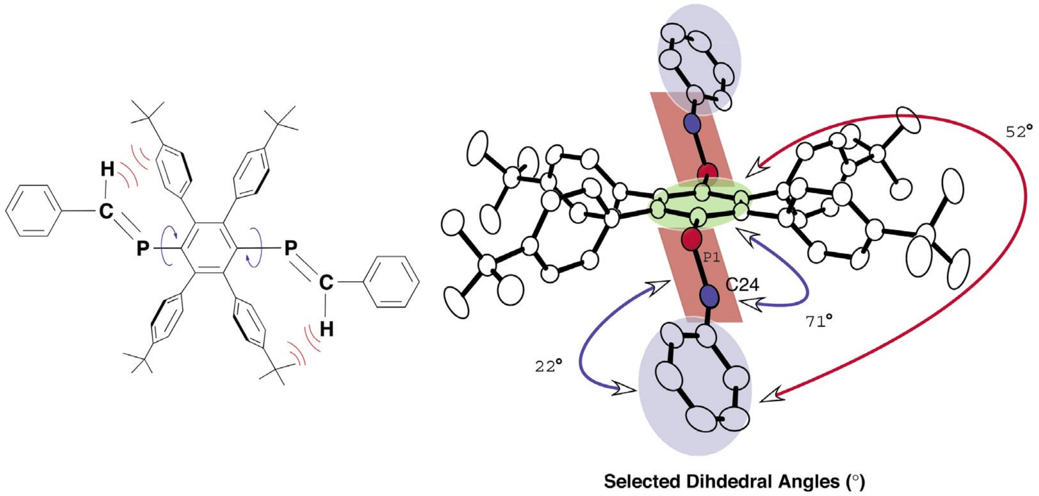


Fig. 5 Distortions in a diphosphaalkene caused by steric clashes.

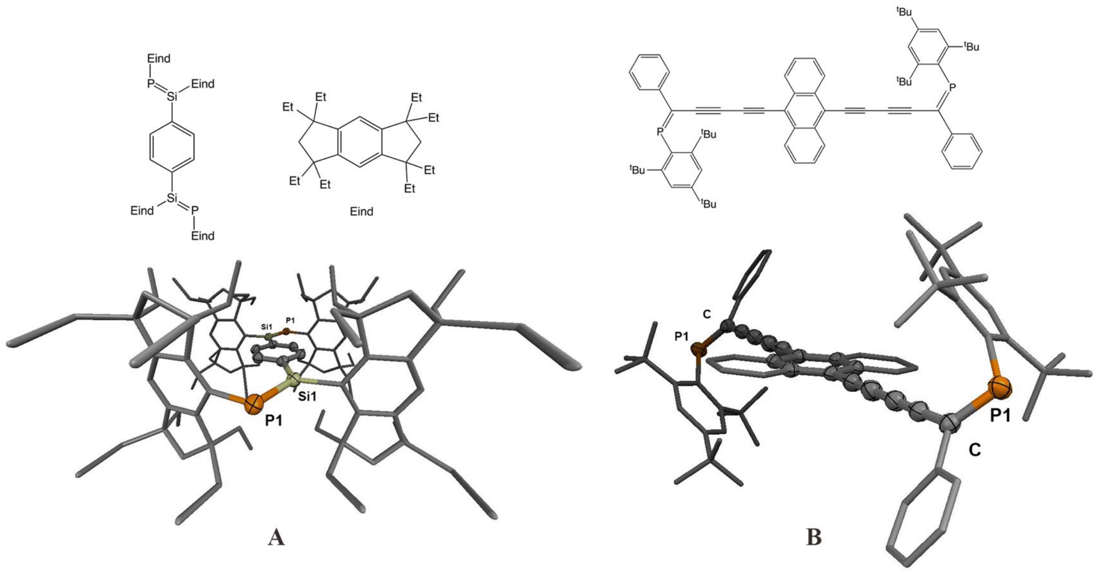
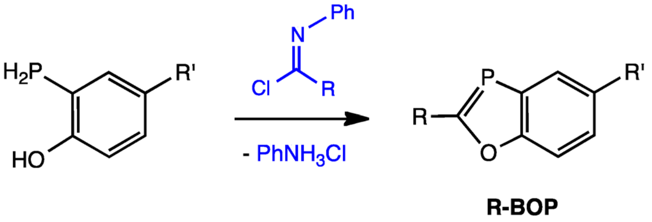


Fig. 6 Two examples of highly conjugated systems featuring two P=E units [24,25].

Early reports on benzoxaphospholes (BOPs)

Heinicke and co-workers first reported synthesis of 1,3-benzoxaphospholes (**R-BOP**, Scheme 2) in the early 1980s [26–28]. These simple-looking heterocyclic systems are surprisingly stable; they display far greater stability than many of their acyclic counterparts and, furthermore, do not require the extreme steric protection other stable multiply bonded low-coordinate phosphorus compounds demand. In addition, as the P=C bond is locked within a five-membered ring fused to the phenyl ring, the P=C unit is held in an optimal orientation for π-conjugation. Even more important for our goals is the fact that BOPs having R = aryl are very fluorescent.



Scheme 2 Synthesis of BOPs.

We thus set out to expand on the synthesis, and undertake some deeper physical studies, of these compounds [29,30]. Their PL was recorded, and lifetimes of the excited states confirmed their fluorescent nature. Under UV light the compounds emit blue light, and λ_{em} is relatively insensitive to variation of X unit (X = H, Me, Cl, Br, OMe) in a series of compounds where R = *p*-X-C_6H_4. Impressively, some of the materials have quantum yields as high as 60 %. The quantum yields were not solvent-dependent, but were affected by the nature of the R group, with R = alkyl having very low quantum yields. To the best of our knowledge, these materials are the only known compounds having bona fide P=C pπ-pπ bonds that display significant PL emission. This fact is truly exceptional, considering that hundreds (if not thousands) of compounds having P=C bonds are known [1,31].

What makes a compound like Ph-BOP fluorescent while standard phosphaalkenes are not? Embedding the P=C unit within a constrained ring certainly reduces conformational flexibility and likely leads to fewer avenues for excited-state decay through conformational relaxation. Computational studies (DFT/BLY3P 6-31G*) on Ph-BOP highlight also some similarities to unconstrained P=C systems, and some significant differences. Figures 7 and 8 show selected frontier orbitals for Ph-BOP and an acyclic model compound PhP=C(H)Ph. First, the HOMOs and LUMOs of both compounds are predominantly P=C π and π* in character, respectively. While each structure has a PC bond length shorter than that observed for typical PC single bond lengths (ca 2.22 Å), the bond distance for Ph-BOP is longer than that of PhP=C(H)Ph (1.736 vs. 1.696 Å). We explain this fact by resonance effects due to the presence of the oxygen atom, and to the smaller bond angles at phosphorus imposed by the five-membered ring (which in turn changes p-orbital contribution to σ bonding).

The phosphorus lone pair is found at the HOMO (–4) for Ph-BOP, substantially lower in energy than the HOMO (by 2.1 eV). The situation for PhP=C(H)Ph is a bit more complicated. The nonplanar conformation of this molecule leads to mixing of the phosphorus lone pair with the two sets of aromatic p-orbitals that occur throughout HOMOs –1 to –4. Such extensive n–π mixing could facilitate quenching by the phosphorus lone pair. In addition, twisting or isomerization about the P=C bond could promote intersystem crossing to triplet states. We are currently undertaking TDDFT studies of these materials to better understand the nature of the excited states that are emissive.

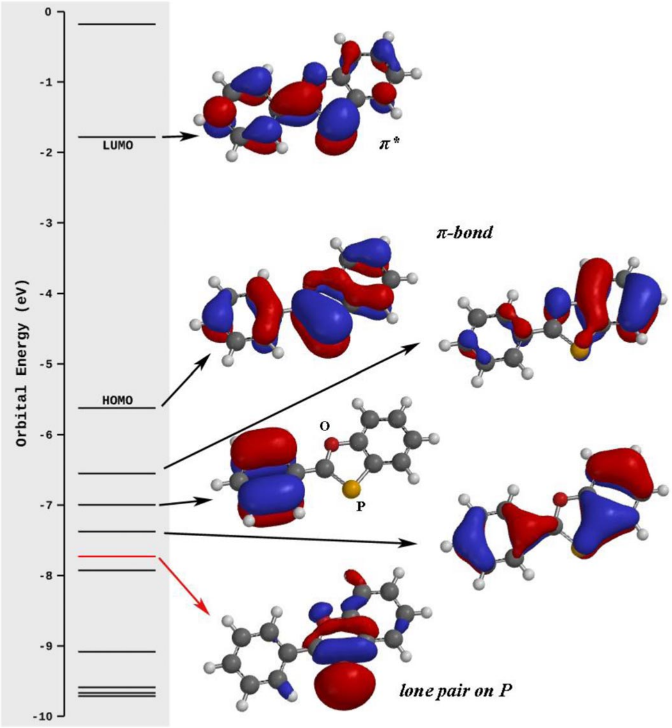


Fig. 7 Selected frontier orbitals and energies for Ph-BOP (DFT/BLY3P 6-31G*).

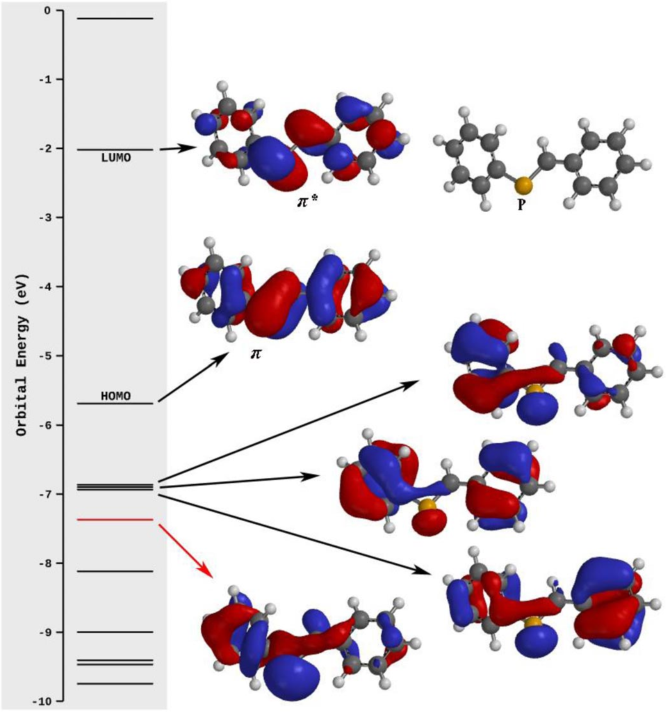
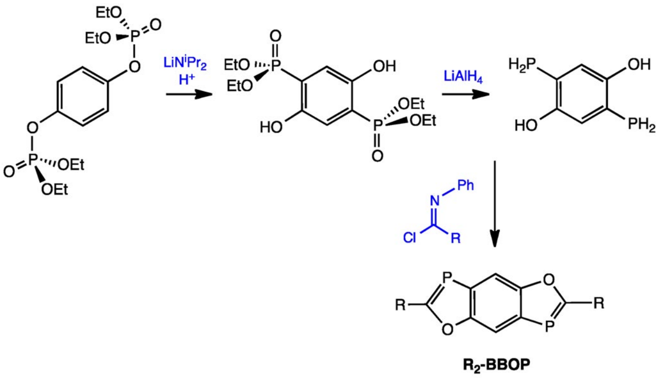


Fig. 8 Selected frontier orbitals and energies for PhP=C(H)Ph (DFT/BLY3P 6-31G*).

New benzobisoxaphospholes (BBOPs)

While R-BOPs display impressive PL properties, and can be considered “photocopies” of analogous olefinic compounds, we are interested in expanding the scope of this class of materials. Our first targets were the doubly functionalized benzene systems R_2-BBOPs (Scheme 3) [30]. The synthesis required development of a new diphosphinohydroquinone, which turned out to be relatively easy to prepare from hydroquinone in a few steps.



Scheme 3 Synthesis of BBOPs.

BBOPs were isolated as colorless solids that exhibited blue fluorescence when excited in the UV. Quantum yields were again higher for R = aryl (up to 27 %), than for R = alkyl (3–4 %). Computational studies showed that the nature of the frontier orbitals were in general alignment with those obtained for BOPs. As anticipated, BBOPs were found to have smaller HOMO–LUMO gaps due to the greater degree of conjugation in these systems. Electrochemical studies of BBOPs display two sets of behavior [29]. For R = aryl, two electrochemical reductions are observed, the first of which is reversible (Fig. 9, left). For R = alkyl, a single reversible reduction process was observed. By contrast, BOPs

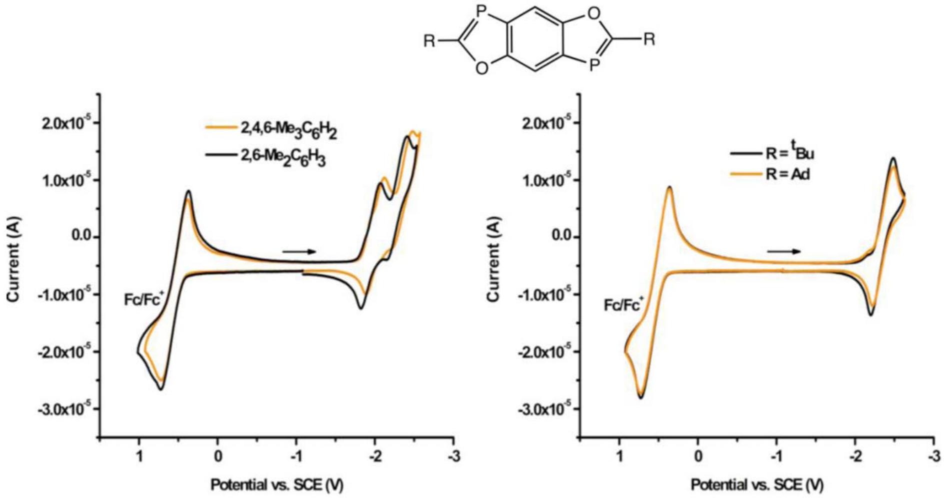


Fig. 9 Comparison of cyclic voltammetry for BBOPs (scan rate 0.1 V/s, referenced to Cp_2Fe/Cp_2Fe^+, $^nBu_4NBF_4$ in THF).

showed a single reversible reduction process when R = aryl, but no waves when R = alkyl (Fig. 9, right). These experimental data are consistent with the computational data that predict that BBOPs offer lower-lying LUMOs and greater ease of reduction, especially for R = aryl.

Naphthoxaphospholes (NOPs)

The above results suggested that continuation of the progression would lead to other interesting molecules with even smaller HOMO–LUMO gaps and significant PL. Indeed, parallels can be drawn for these higher analogues and pentacenes (Chart 3).

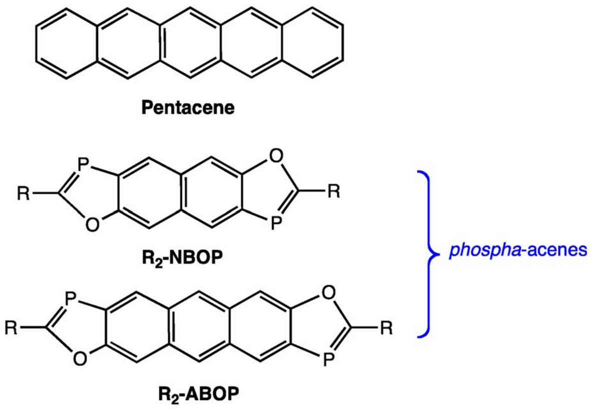
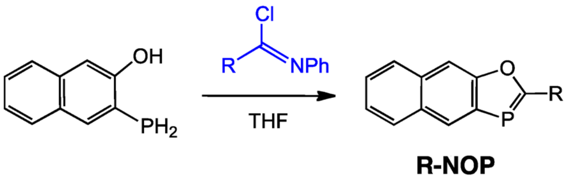


Chart 3

Pentacenes are drawing increased attention in molecular electronics as solid-state semiconducting materials [32–38]. Access to analogous materials having P=C bonds with lower lying π*-orbitals should provide new compounds with high electron affinity. Hence, we have developed the synthesis of NOPs (Scheme 4) as first routes towards new potential *phospha*-acenes [39].



Scheme 4 Synthesis of NOPs.

Like the preceding syntheses, the target compounds were accessible via condensation reaction of an appropriate hydroxyphosphinoarene, in this case 3-phosphino-2-naphthol being required. NOPs were isolated as either crystalline white (R = alkyl) or yellow (R = aryl) solids [39]. The R-NOPs displayed $^{31}P\{^{1}H\}$ NMR shifts between 72.8–86.6 ppm, which are slightly upfield from similarly substituted R-BOPs. Unlike for BOPs and BBOPs, all NOPs (R = both alkyl and aryl) were reasonably fluorescent with quantum yields ranging from 0.12 to 0.26. The two types of R-BOPs display slightly different fluorescence, however. The alkyl derivatives emit more of a cyan color, while the aryl derivatives emit blue (Fig. 10, left). Electrochemical investigations of these R-NOPs (R = aryl) reveal quasi-reversible reductions at –1.8 to –1.9 V vs. SCE in THF.

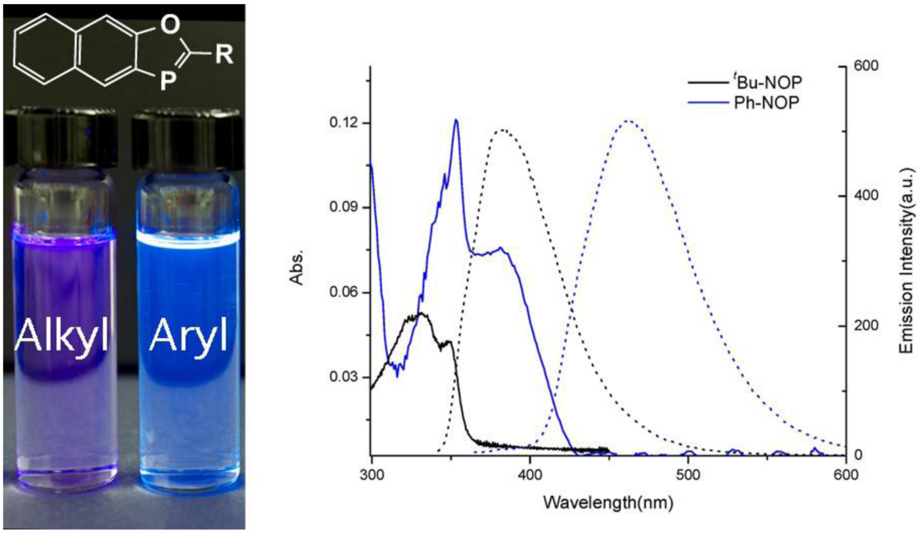


Fig. 10 Absorption and emission of R-NOPs.

Naphthobisoxaphospholes (NBOPs) and beyond

With the above successes in hand, we have moved on to tackle synthesis of other *phospha*-acenes. The next obvious target would be R_2-NBOP (Chart 3). While we are in the process of preparing that particular material, we have recently prepared an isomer 2,7-di-phenyl-naphtho[1,2-*d*:5,6-*d*]bisoxaphosphole (Fig. 11) [40]. This extended BOP derivative also fluorescences ($\Phi_F = 0.63$, $\lambda_{F,max}$ 422 nm) under

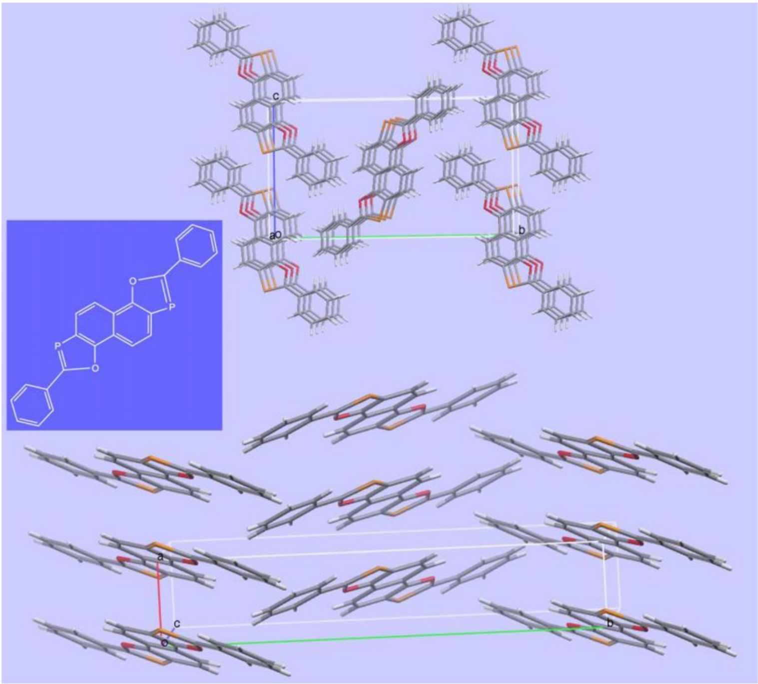


Fig. 11 Packing of a *phospha*-acene in the crystal lattice.

UV-irradiation. The structure was determined by single-crystal X-ray diffraction methods, and the results reveal that the compound is essentially planar and π-stacks in columns parallel to the *a*-axis with only 3.49 Å separating the molecules (Fig. 11). Analysis of the solid-state packing is relevant to the electronic properties of such materials in semiconducting applications.

Preliminary computational results show that this molecule is electronically similar to those presented above. The calculated P=C bond length of 1.736 Å agrees well with that experimentally determined [1.729(3) Å]. Again, the HOMO has significant P=C bond character, the LUMO has PC π* character, while the lone pairs on phosphorus are low in energy [n^+ combination is HOMO (–7) and n^- combination is HOMO (–8)].

CONCLUSIONS

BOPs and derivatives thus present a class of special conjugated compounds that possess p-p π P=C bonds in conjugation with aromatic systems and are also highly emissive materials. These facts earn them the right to not only be called carbon copies, but also photocopies of phosphorus free analogues.

Despite these examples of photocopies, there are many examples of multiply bonded compounds that would seem to have properties in common with the present compounds and offer other examples of compounds with significant PL. We have recently prepared Ph-BOP-^{t}Bu$_2$ (Chart 4) as a BOP analogue that should display enhanced air and water stability due to the bulky *tert*-butyl group that flanks the low coordinate phosphorus atom [41]. While this compound does indeed have greater stability towards air and water, it was surprising that the fluorescence quantum yields drops to 0.12 compared to 0.57 and 0.55 for Ph-BOP-R (Chart 4, R = H or ^{i}Pr, respectively). The presence of additional alkyl substituents at selected positions can have significant impact on emissive properties of these systems. Benzazaphospholes (R-BAPs, Chart 4) are close analogues to R-BOPs. They have received much more study than R-BOPs, yet none appear to have been noted to be fluorescent. A better understanding of the factors that turn on or shut down fluorescence in these materials may allow us to design and synthesize new “photocopies” that are based on other low-coordinate multiply bonded phosphorus compounds and polymers.

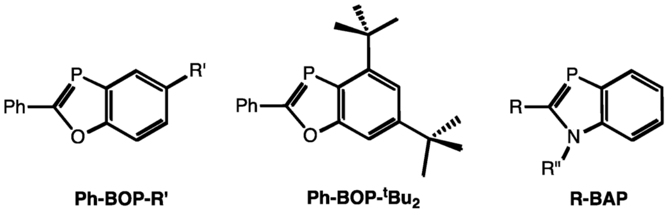


Chart 4

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