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Visible Chromophore Phosphines as Functional Elements of Luminescent Metallopolymers

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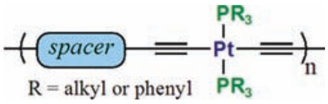
A general modular route to fluorophore-linked diphosphines from (4-iodophenyl)P(O)Ph_2 is described. The preparation of chromophoric diphosphine (**LHP1**) proceeded readily using this route. **LHP1** was employed to prepare luminescent metallopolymers of platinum (**P1**) and palladium (**P2**) exhibiting modest degrees of polymerization (13−14) and extents of polymerization (~97%). **P1** and **P2** appear to be the first metallopolymers polymerized via a visible-absorbing/emitting diphosphine. The photophysical properties of these novel materials are discussed.

Conducting metallopolymers (CMPs)[1] and oligomers incorporating platinum acetylides have yielded significant insight into the nature of the triplet excited state[2−4] and are promising materials for organic light emitting diodes (OLEDs) and photovoltaics.[5] The platinum acetylide CMPs whose photophysics have been most thoroughly studied typically include phosphines to fill out the coordination sphere of platinum, but they do not serve a significant optical role beyond typical steric and electronic influences (Chart 1). Herein we report our efforts to harness the ubiquitous phosphines to serve a functional role as visible-absorbing elements of CMPs formed as coordination polymers. As a first step in this direction, we sought to prepare a bifunctional visible-absorbing phosphine that could subsequently be utilized in the preparation of luminescent metallopolymers of metals such as palladium and platinum. There have been surprisingly few reports on fluorophore-appended phosphines, particularly those with absorption in the visible spectrum, and even fewer transition-metal complexes of visible-absorbing chromophoric phosphines. A recent review provides a comprehensive survey of phosphorus-containing chromophores.[6]

Chart 1. General Form of Platinum Acetylide CMPs



The synthetic route for preparing the first visible chromophoric phosphine in the current study, **LHP1** (Scheme 1), was selected to allow for the modular assembly of various mesogen-spaced diphosphines. For this purpose, (4-iodophenyl)-P(O)Ph_2 was prepared as a versatile precursor amenable to a variety of palladium-catalyzed coupling methodologies. Surprisingly, (4-iodophenyl)P(O)Ph_2 does not appear to have been reported previously (full characterization and structures determined by single-crystal X-ray diffraction are provided in the Supporting Information). Sonogashira coupling of 1,4-diethynyl-2,5-dihexyloxybenzene[7] with (4-iodophenyl)-P(O)Ph_2 proceeded smoothly to give the phosphine oxide **LHPO**. The fluorophore in **LHPO** (highlighted in red in Scheme 1) was selected for the initial study because it is a small-molecule model for poly(*p*-phenyleneethynylene), an organic semiconducting polymer that has found extensive utility in plastic electronics technologies. The incorporation of *n*-hexyloxy side chains should provide some solubility to polymeric materials in organic solvents. **LHPO** was readily reduced by $HSiCl_3$ to give **LHP1** following standard conditions.[8] Both **LHP1** and **LHPO** are bright-yellow-orange-to-red solids with intense fluorescence in solution (see the spectra in Figure 1), and their photophysical properties are summarized in Table 1. Although the λ_{max} and λ_{em} wavelengths are similar for the two materials, one notable difference is the significantly lower photoluminescence quantum yield (Φ) of **LHP1** (0.32) compared to that of **LHPO** (0.62). On the basis of previous studies on fluorophore-derivatized phosphines,[9] the diminished Φ of **LHP1** is most likely

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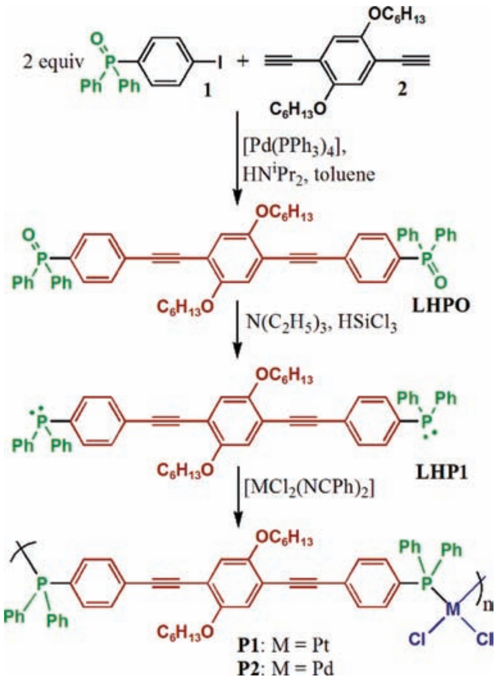
Scheme 1. Synthetic Route Used To Access Phosphine **LHP1** and Metallopolymers **P1** and **P2**



attributable to a photoinduced-electron-transfer (PET)-type quenching mechanism involving the phosphorus lone pair. The photoluminescence lifetimes are on the order expected for fluorescence from small organic molecules.

When **LHP1** was reacted in a 1:1 ratio with $[\mathrm{MCl_2(NCPh)_2}]$ (M = Pd, Pt) in dichloromethane at room temperature, we believe that high-molecular-weight coordination polymers **P1** and **P2** were produced, as evidenced by the formation of rigid, fluorescent yellow-orange gels over the course of polymerization. Unfortunately, the gels could not be readily redissolved in common organic solvents. Because diphosphine-polymerized coordination polymers are capable of ligand exchange with monophosphines,[10] our initial strategy to pull the polymers into solution was to add small amounts of $\mathrm{PMe_3}$ as end-capping units to the preformed gels to lower the average degree of polymerization. Although this method was moderately successful, we were unable to fully solubilize the samples by this route. To overcome the solubility issue associated with high molecular weight, we repeated the polymerization with a $[\mathrm{MCl_2(NCPh)_2}]$/**LHP1** ratio of 1:1.1 to define an upper limit for the statistical molecular weight. This yielded the soluble bright-yellow polymers **P1** and **P2** that were used in subsequent studies. The ^{31}P NMR shift (23.9 ppm) for **P2** is similar to that of both *trans*-$[\mathrm{PdCl_2(PPh_3)_2}]$ (24.2 ppm) and *cis*-$[\mathrm{PdCl_2(PPh_3)_2}]$ (22.4 ppm),[11] making absolute assignment of the configuration difficult from this data. The ^{31}P NMR shift (15.0 ppm) and $^1J_{\mathrm{Pt-P}}$ (3660 Hz) for **P1**, however, are much more similar to those of *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ (15.3 ppm, 3673 Hz)[12] than *trans*-$[\mathrm{PtCl_2(PPh_3)_2}]$ (19.8 ppm, 2637 Hz),[13] strongly suggesting that the metallopolymers feature a *cis* coordination mode of **LHP1** in **P1**, as represented in Scheme 1.

Table 1. Select Photophysical Data for **LHPO**, **LHP1**, **P1**, and **P2**

	$\lambda_{\max}$ (nm)	log ε	λ_{emit} (nm)	Φ	τ
LHPO	381	4.62	432	0.620 ± 0.002	1.7 ns
LHP1	376	4.29	426	0.320 ± 0.035	1.25 ns
P1 (Pt)	384	3.59	434	0.088 ± 0.010	107 ps
P2 (Pd)	378	3.59	431	0.0210 ± 0.0002	NA

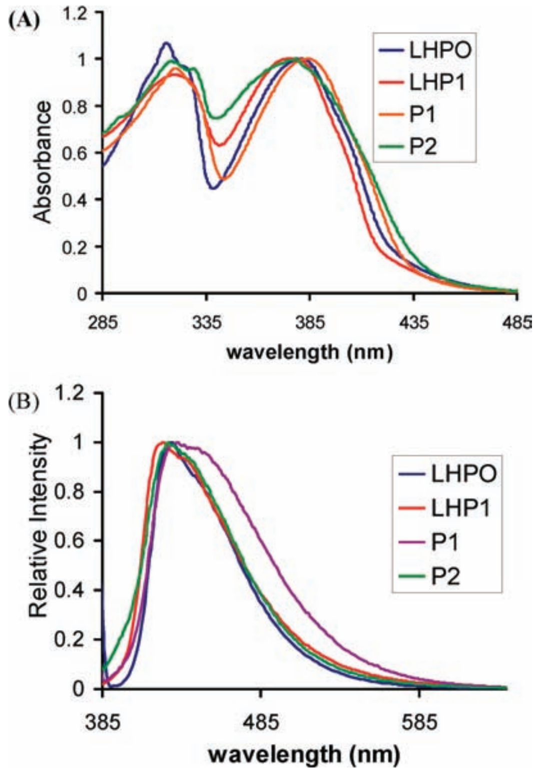


Figure 1. Normalized absorption (A) and photoluminescence (B) spectra for **LHPO**, **LHP1**, **P1** and **P2**.

Attempts to estimate the number-average molecular weight (M_n) of **P1** and **P2** by gel permeation chromatography under various conditions were unsuccessful. This is an issue that has been previously observed for coordination polymers[14] and is presumably due to the high polarity of the compounds and potentially reversible coordination of phosphines. By applying standard NMR end-group analysis techniques[15] adapted to ^{31}P NMR following previous methods for phosphorus-containing polymers,[16] we were able to estimate M_n values for **P1** (15 000 g mol^{-1}) and **P2** (17 000 g mol^{-1}). These values correspond to modest average degrees of polymerization of 13 and 14, respectively. Assuming an extent of reaction of unity (100% yield), an average degree of polymerization of 21 is expected for the comonomer stoichiometry used. Utilizing the reactant ratio and observed average degrees of polymerization in the general Carother's

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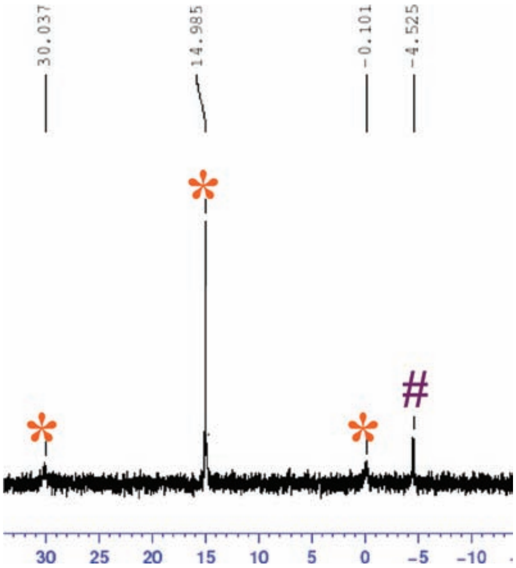

Figure 2. ^{31}P NMR spectrum of **P1** with resonances attributed to platinum-coordinated P atoms (*) and uncoordinated terminal phosphines (#).

equation[17] allows us to calculate a respectable extent of reaction of ~0.97 for both **P1** and **P2**. The ^{31}P NMR spectrum of **P1** (Figure 2) shows especially well-defined resonances attributable to main-chain platinum-coordinated P atoms (15.0 ppm) and uncoordinated end-group P atoms with a chemical shift (−4.5 ppm) nearly identical with that of **LHP1** (−4.6 ppm). The ^{31}P NMR resonances for end groups in **P2** are very close to those of the coordinated, main-chain P atoms near 24 ppm (^{31}P NMR spectrum provided in the Supporting Information), indicating that the end groups have oxidized in air during workup and manipulation of the solutions.

The photophysical properties of **P1** and **P2** are summarized in Table 1, and their absorption and photoluminescence spectra are overlaid with those of **LHP1** and **LHPO** in Figure 1. λ_{max} and λ_{em} of the polymers are not significantly different from those of **LHP1**, with only a small shoulder to the red distinguishing **P1** from the other nearly coincident photoluminescence spectra in Figure 2B, and all materials exhibit an optical band gap (estimated from the peak onset in the absorption spectrum) of about 2.7 eV. These similarities are expected because, regardless of what atoms are bound or coordinated to the P atom, they are not in direct π conjugation with the fluorophore π system. It is also important to note that phosphorus lone pairs do not participate in the π system to the same extent[18−20] as do nitrogen lone pairs.[21,22] It follows that coordination to a metal center does not lead to dramatic spectral wavelength shifts, and this observation is also in line with the trend observed in other chromophoric phosphine complexes.[9] The polymers **P1** and **P2** do have lower Φ values than **LHP1**, even though coordination to a metal center eliminates the lone-pair-derived PET as a possible quenching mechanism. In this case, the diminished Φ is due to the heavy-atom effect, whereby highly polarizable heavy elements such as platinum and palladium are classic fluorescence quenchers.[23−25] The lifetime of **P1** (Table 1) is also worth noting; platinum-containing materials are often of interest as triplet-emissive (phosphorescent) materials because of the ability of platinum to facilitate intersystem crossing via enhanced spin−orbit coupling.[26] In the current case, however, the Pt atom is not an integral part of the luminophore, and thus the lifetime observed correlates with simple fluorescence derived from the **LHP1**-centered π system. The lifetime of **P2** (Table 1) was difficult to acquire reliably because of its very low intensity, so it is not reported here.

Despite the low Φ values for **P1** and **P2**, these materials may prove to be useful components in applications where luminescence is not needed (i.e., electrochromics) or even undesirable (i.e., photovoltaics). We also anticipate that the further elaboration of the metal centers with additional π systems in place of the chloro substituents may provide materials capable of interesting energy-transfer processes.

In conclusion, a modular synthesis easily extendable to various chromophoric phosphines has been described, and the utility of these phosphines in the preparation of luminescent metallopolymers has been demonstrated. The preparation of a series of chromophoric phosphines and their metal complexes is currently underway.

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Supporting Information Available: X-ray crystallographic data in CIF format, experimental details, ^{1}H, ^{31}P, and ^{13}C NMR spectra, absorption and photoluminescence spectra, and an ORTEP drawing of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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