Spectroscopic Study of Phosphine-Substituted Oligothiophenes

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The spectroscopic behavior (solution and solid-state absorption and emission) of a series of mono-(diphenylphosphino) and bis-(diphenylphosphino) α-substituted oligothiophenes varying in length from one to three thienyl rings is described. The absorption spectra red-shift with increasing oligomer length, and the spectra of the bisphosphines are red-shifted, relative to the monophosphines that contain the same number of thienyl groups. In solution, emission from the mono- and bithienyl compounds is broad and shows a large Stokes shift, attributed to a planar excited state due to the $n{\rightarrow}\pi^*$ nature of the excitation. Emission from the terthienyl compounds shows a much smaller Stokes shift and is attributed to a thienyl-based $\pi{\rightarrow}\pi^*$ transition. In the solid state, similar effects are observed in both absorption and emission spectra. Density functional theory (DFT) calculations show that the contribution of the P lone pair to the highest occupied molecular orbital (HOMO) diminishes as the oligomer length increases, supporting the experimental results.

Introduction

Conjugated oligomers and polymers are organic materials with many interesting properties, including electronic conductivity, luminescence, and color.[1] Pendant metal groups, which can be attached using several different coordinating groups, may be used to modify the electronic and optical properties of these materials.[2−11] Our group has investigated the use of phosphine substituents as ligating groups,[12−16] which is an approach driven both by the versatility of phosphines in binding a wide variety of metals[17] and the benefit of having only a single atom (P) between the metal and conjugated backbone, facilitating strong electronic interactions. It is therefore of interest to understand the electronic behavior of phosphine-substituted oligothiophenes prior to the coordination of a metal, because this is important to help build an understanding of the behavior of corresponding metal complexes.

The electronic effects of a range of substituents both in the terminal (α) position and the internal (β) position of thiophenes and oligothiophenes have been studied.[18] However, no systematic study of the influence of phosphine substituents on the electronic properties of the conjugated backbone exists. Diarylamino-substituted oligothiophenes, ranging from one to six rings in length, have been prepared.[19] These compounds show strong bathochromic shifts, relative to the parent oligomers in both absorption and emission spectra; in addition, because nitrogen and phosphorus are Group 15 congeners, it is interesting to compare these compounds to the phosphino analogues. Here, we report the absorption and emission spectra of the series of monosubstituted and disubstituted oligothiophenes shown in Chart 1, both in solution and in the solid state as thin films. The disubstituted thiophenes are of interest because of the possibility of binding metals to the ends of these ligands, which is relevant to "molecular wire" studies with these conjugated compounds.[3]

Experimental Section

General. All reactions were performed under a nitrogen atmosphere, using standard Schlenk techniques and dry solvents.

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CHART 1
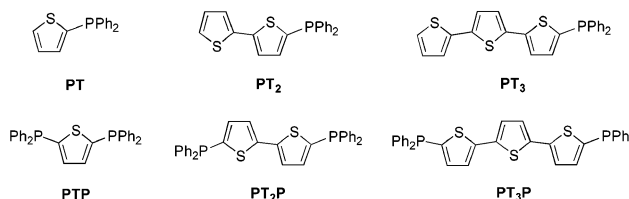
PPh$_2$Cl was purchased from Aldrich and was distilled under N$_2$ prior to use. The following compounds were made according to literature methods: 2,2′-bithiophene,[20] 2,2′:5′,2″-terthiophene,[20] **PT$_2$**,[21] **PT$_2$P**,[22] **PT$_3$**,[14] and **PT$_3$P**.[21] ^{1}H and ^{31}P{^{1}H} NMR experiments were performed on a Bruker spectrometer (models AC-200E, AV-300, or AV-400). Spectra were referenced to the residual solvent (^{1}H) or external 85% H$_3$PO$_4$ (^{31}P). Electronic spectra were obtained on a Cary model 5000 in high-performance liquid chromatography (HPLC)-grade CH$_2$Cl$_2$. Emission spectra were obtained on a Cary Eclipse in HPLC-grade hexanes. Solid-state absorption and emission spectra were obtained by casting a thin film of the compound from a CH$_2$Cl$_2$ solution onto quartz slides. Some emission spectra contain peaks from excitation overtones; these are indicated with an asterisk. Microanalyses were performed at the University of British Columbia (UBC). Density functional theory (DFT) calculations were performed using a B3LYP/6-31G* basis set that was implemented in the Spartan 02 software package.[23] Mass spectrometry was performed on a Kratos model MS50 spectrometer.

2-Diphenylphosphinothiophene (PT). A solution of thiophene (1 mL, 12.5 mmol) in 100 mL of dry Et$_2$O was cooled to 0 °C, and 9.4 mL (15 mmol, 1.6 M) *n*-butyllithium was added dropwise, using a syringe. The resulting white suspension was warmed to room temperature, stirred for 2 h, and then cooled again to 0 °C. After 2.3 mL (15 mmol) of PPh$_2$Cl was added with a syringe, the ice bath was removed and the reaction mixture was stirred overnight at room temperature. Fifty milliliters of 0.1 M HCl and crushed ice were added to the mixture, which was then extracted three times with CH$_3$Cl. The organic phases were combined, washed with saturated NaHCO$_3$

TABLE 1: Spectroscopic Data

complex	solution absorption,[a,b] λ_{max}/nm (ϵ_{max})	solid-state absorption, λ_{max}/nm	solution emission,[c] λ_{max}/nm (excitation wavelength/nm)	solid-state emission, λ_{max}/nm
PT	265 (1.0×10^4)	no distinct peak	496 (260)	475
PT$_2$	330 (1.6×10^4)	248, 333	485 (327)	478
PT$_3$	250 (1.1×10^4), 374 (2.0×10^4)	260, 375, 420 (sh)	446 (368)	480
PTP	258 (sh) (1.7×10^4), 300 (1.3×10^4)	no distinct peak	496 (300)	481
PT$_2$P	245 (sh) (2.0×10^4), 350 (2.5×10^4)	250, 353	430, 460 (343)	470
PT$_3$P	245 (2.5×10^4), 389 (3.6×10^4)	255, 395, 430 (sh)	465 (383)	507
OPTPO	258 (2.1×10^4), 266 (1.9×10^4), 273 (1.3×10^4)		315 (258), 384 (339)[a]	

[a] In CH_2Cl_2. [b] Value given in parentheses is the corresponding ϵ_{max} value, in units of M^{-1} cm^{-1}. [c] In hexanes.

solution and saturated NaCl solution, and dried with Na_2SO_4. The solvent was then removed, yielding a viscous, clear oil. This crude product was purified by column chromatography on silica gel with a 1:4 CH_2Cl_2:hexanes eluent. Two bands were isolated as viscous oils: the first was the desired product, and the second was **PTP**. Yield: 60%. Anal. Calcd for $C_{16}H_{13}PS$: C, 71.62; H, 4.88. Found: C, 71.41; H, 4.99. MS (EI) *m/z*: 268. ^1H NMR (CDCl$_3$): δ 7.58 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.41−7.29 (m, 11H), 7.1 (ddd, *J* = 4.8, 3.7, 1.2 Hz, 1H). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 18 (s).

2,5-bis(Diphenylphosphino)thiophene (PTP). A solution of thiophene (1 mL, 12.5 mmol) and tetramethylethylenediamine (TMEDA) (3.8 mL, 25 mL) in 50 mL dry hexanes was cooled to 0 °C, and 15.7 mL (25 mmol, 1.6 M) *n*-butyllithium was added dropwise, using a syringe. The ice bath was removed, the solution was heated to reflux for 30 min, and the resultant white suspension was cooled again in an ice bath. PPh$_2$Cl (4.7 mL (25 mmol)) was added with a syringe, the ice bath was removed, and the reaction mixture was stirred overnight at room temperature. Fifty milliliters of 0.1 M HCl and crushed ice were added to the mixture, which was then extracted three times with hexanes. The organic phases were combined, washed with saturated NaHCO$_3$ solution and saturated NaCl solution, and dried with Na$_2$SO$_4$. The solvent was then removed, yielding a viscous light yellow oil. This crude product was purified by column chromatography on silica gel with a 1:3 CH_2Cl_2:hexanes eluent. Two bands were isolated as viscous oils: the first was **PT**, and the second was the desired product. The oil was recrystallized in ethanol with 2% CH_2Cl_2 added to give large clear, colorless crystals. Yield: 25%. Anal. Calcd for $C_{28}H_{22}$-P$_2$S: C, 74.32; H, 4.90. Found: C, 74.58; H, 4.88. MS (EI) *m/z*: 268. ^1H NMR (CDCl$_3$): δ 7.37−7.27 (m, 10H), 7.17 (dd, *J* = 4.2, 2.3 Hz, 1H), 7.01 (ddd, *J* = 4.8, 3.7, 1.2 Hz, 1H). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 19 (s).

2,5-bis(Diphenylphosphine oxide)thiophene (OPTPO). This compound was synthesized by a modification of a literature procedure.[15] A solution of 30% H_2O_2 in H_2O (0.05 mL) was added, with stirring, to **PTP** (0.22 mmol) in 50 mL of CHCl$_3$/acetone (1:1). The mixture was stirred for 1 h, and the solvent was then removed by rotary evaporation. The crude product, a white solid, was redissolved in acetone, gravity-filtered, and precipitated in hexanes. The resulting white powder was recrystallized in H_2O, yielding small white crystals. Yield: 75%. Anal. Calcd for $C_{28}H_{22}O_2P_2S$: C, 68.57; H, 4.52. Found: C, 68.70; H, 4.65. MS (EI) *m/z* 484. ^1H NMR (CDCl$_3$): δ 7.78−7.65 (m), 7.6−7.52 (m), 7.51−7.42 (m). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 21 (s).

Results and Discussion

Synthesis. Mono-(diphenylphosphino) and bis-(diphenylphosphino)-substituted oligothiophenes were synthesized by lithiation of the corresponding oligothiophene, followed by quenching with chlorodiphenylphosphine. In our hands, pure **PT$_2$** and **PT$_3$**
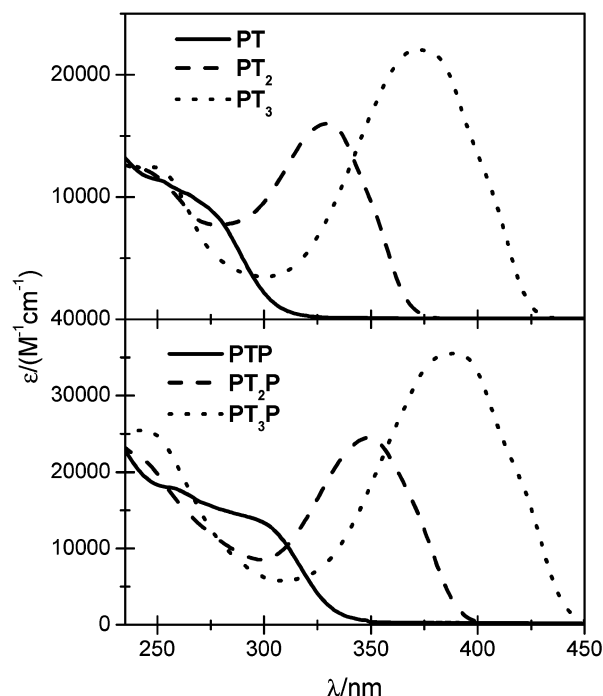

Figure 1. Solution UV−visible spectra.

were obtained by this synthetic approach, despite difficulties with this route previously reported by Field et al.[21] The compounds were isolated in low yields by column chromatography; degassing the eluent and the silica slurry did little to improve the yields. The compounds oxidize slowly in the solid state and in solution, as evidenced by the appearance of phosphine oxides by thin layer chromatography (TLC) and in the NMR spectra. Oxidation of **PTP** was achieved by reaction with an excess of H_2O_2 to give the bis(phosphine oxide), **OPTPO**.

Absorption Spectra. The absorption spectra of all the phosphines show a band between 275 nm and 400 nm, which undergoes a bathochromic shift as the oligothienyl length increases (Figure 1). In addition, a shoulder is observed at ∼250 nm, which is analogous to the n→π* transition in triphenylphosphine at 263 nm.[24−26] The data are collected in Table 1. The presence of the phosphine group results in red-shifting of the absorbance bands, relative to the unsubstituted thiophene oligomers (**T** (231 nm), **T$_2$** (303 nm), and **T$_3$** (354 nm)).[27] This is also observed in the spectra of other phosphines that contain aromatic substituents,[24] and in the amino analogues of **PTP**, **PT$_2$P**, and **PT$_3$P**.[19] Here, the shift may be understood by consideration of the frontier orbitals of these compounds. DFT calculations performed at the B3LYP/6-31G* level show that, for the phosphine-substituted oligothiophenes, the lowest unoccupied molecular orbital (LUMO) is stabilized by a bonding interaction between the thienyl π-system and the phosphorus (Figure 2). Similar effects have previously been observed in
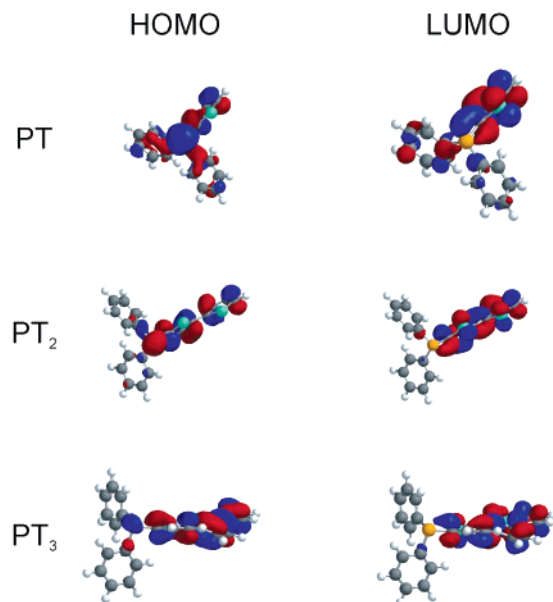
Figure 2. Frontier orbitals of **PT**, **PT$_2$**, and **PT$_3$**.

silylene-substituted oligothiophenes and are partly attributed to $\pi \rightarrow d$ back-bonding.[28] The DFT calculations also reveal that the degree of P lone-pair character in the HOMO diminishes significantly as the oligomer length increases (from **PT** to **PT$_3$**, and from **PTP** to **PT$_3$P**). With two phosphine substituents (**PTP**, **PT$_2$P**, and **PT$_3$P**), the bathochromic shift, relative to the unsubstituted analogues, is larger than that observed for the corresponding monophosphines (for example, the λ_{max} value for **PT** is red-shifted by 34 nm, relative to **T**, whereas for **PTP**, it is shifted 69 nm). This is also supported by the calculations, which show smaller HOMO−LUMO energy differences for the disubstituted compounds than for the monosubstituted analogues (see Supporting Information).

As the length of the oligothienyl group increases, the relative change in absorption maximum with each additional ring is reduced. Typically, in an oligomeric series, red shifts decrease as the oligomer length increases, until a saturation point is reached.[20,27] The major transition bands of the terthienyl compounds (**PT$_3$** and **PT$_3$P**) have low-energy shoulders and the peak for **PT$_3$P** is broad, which may be due to the presence of multiple conformations in solution, a common effect in oligo-thiophenes.[29,30] Generally, as the length of the oligomer increases, the molar absorptivity of the transition increases, which is consistent with the greater overlap between HOMO and LUMO shown in the calculations.

The solid-state absorption data (see Supporting Information) generally show the same trends that are observed in the solution spectra: A red shift in the $\pi \rightarrow \pi^*$ transition occurs with increasing chain length, and the relative red shift decreases as the oligomer length increases.

Emission Spectra. The emission data for the mono- and bisphosphines are collected in Table 1, and spectra are shown in Figures 3 and 4. Initially, emission spectra were collected in CH$_2$Cl$_2$ solution; however, some spectra (**PT$_2$** and **PT$_2$P**) showed two emission bands in this solvent. The corresponding excitation spectra for these two bands were different, strongly suggesting the presence of two compounds in solution. It was postulated that some oxidation of these phosphines was occur-ring, as has been previously observed for similar compounds,[24] and this was verified by direct oxidation of **PT$_2$P** with H$_2$O$_2$ in solution. The resulting spectrum showed only a single emission band, which was identical to the higher-energy band observed
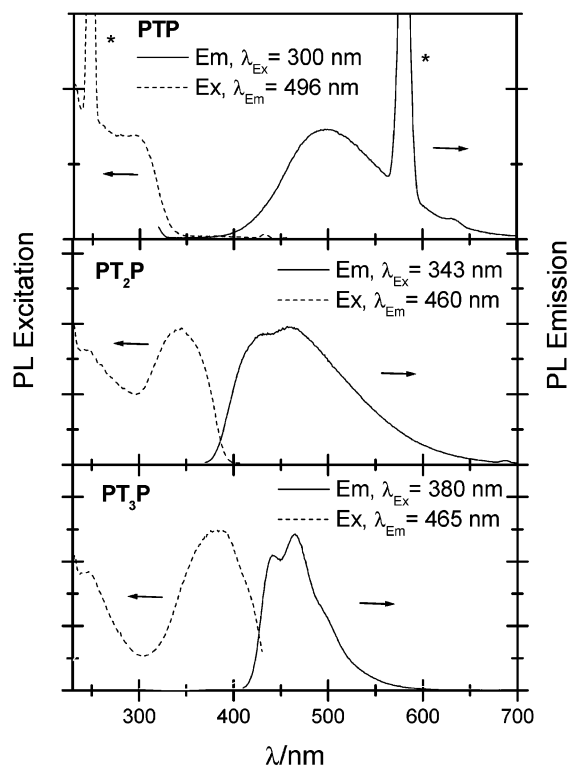

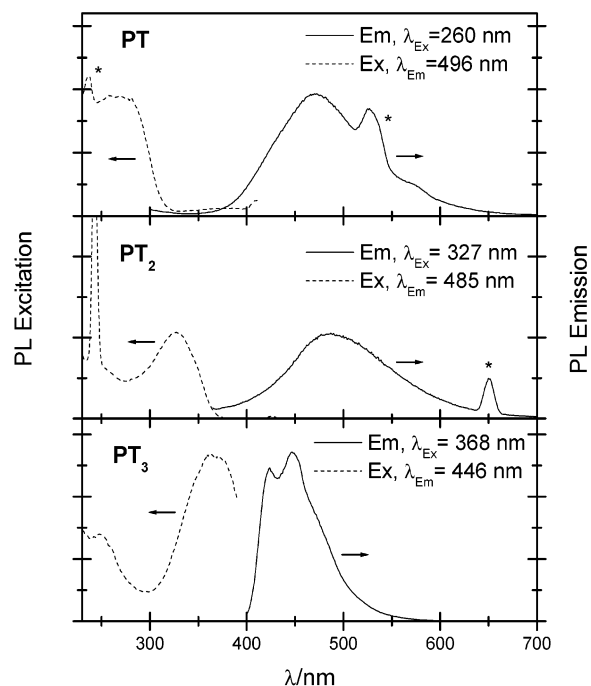**Figure 3.** Solution excitation and emission spectra of **PTP**, **PT$_2$P**, and **PT$_3$P**.

Figure 4. Solution excitation and emission spectra of **PT**, **PT$_2$**, and **PT$_3$**.

in the spectrum of **PT$_2$P**. To eliminate oxidation, the solvent for these experiments was subjected to three freeze−pump−thaw cycles to remove oxygen, and samples were prepared under nitrogen; however, even under these rigorously oxygen-free conditions, the emission spectra remained identical to those taken under typical conditions where only minimal efforts were made to exclude oxygen. Surprisingly, neither the thienyl (**PT** and **PTP**) nor the terthienyl compounds (**PT$_3$** and **PT$_3$P**) showed any evidence for oxidation in CH$_2$Cl$_2$. When the spectra of **PT$_2$P** and **PT$_2$** were obtained in hexanes, a single emission band was

observed, which corresponds to the lower-energy band in the spectrum obtained in CH₂Cl₂. Therefore, emission spectra for all the compounds were obtained in hexanes.

The emission of both **PTP** and **PT** is weak and exhibits a large Stokes shift (see Figures 3 and 4). Triphenylphosphine also exhibits a large Stokes shift, with emission occurring between 450 nm and 500 nm, depending on the polarity of the solvent used (450 nm in diethyl ether and 475 nm in acetonitrile).[24,31] In triphenylphosphine, this emission is assigned as a $\pi^* \rightarrow n$ transition, as triphenylphosphine oxide emits at 290 nm with a small Stokes shift. A large Stokes shift typically indicates a change in geometry from the ground state to the excited state, and for triphenylphosphine, this is believed to be a fast geometrical conversion from a pyramidal ground state to a more-planar excited state.[24] The amino analogue of **PTP** did not exhibit a Stokes shift and is more emissive, which is consistent with a $\pi^* \rightarrow \pi$ transition in this compound.[19] The emission bands from **PTP** and **PT** are consequently assigned to $\pi^* \rightarrow n$ transitions from excited states that are more planar than the ground state, analogous to the behavior of triphenylphosphine. The DFT calculations for **PTP** and **PT** support this assignment, with the HOMO having significant P lone-pair character and the LUMO localized primarily on the thienyl group. The emission spectrum of **OPTPO** is also in support of this assignment, because emission is observed at a much higher energy than that from **PTP**.

The emission spectrum for **PT₂** in hexanes (see Figure 4) is significantly red-shifted, relative to unsubstituted 2,2′-bithiophene, which has a maximum emission at 362 nm,[27] and is similar in appearance to the emission spectrum of **PT**, suggesting that this is also due to a $\pi^* \rightarrow n$ emission. **PT₂P** shows two broad emission bands in hexanes, which are also red-shifted, relative to bithiophene. This behavior is consistent with a $\pi^* \rightarrow n$ emission, as in **PT₂**; however, up to now, the presence of two emission bands is not understood. It is possible that multiple conformations are present in solution and emit at different energies.

The emission and excitation spectra of **PT₃P** and **PT₃** show small Stokes shifts, and the emission maxima for both are red-shifted, compared to 2,2′:5′,2″-terthiophene (426 nm).[27] The emission maximum for the bisphosphine **PT₃P** also occurs at a longer wavelength than for **PT₃**, consistent with the shifts observed in the respective absorption spectra. The excitation spectra for **PT₃P** and **PT₃** all closely match the absorption spectra. In the excitation spectra a second, smaller band is also observed at 250 nm. A similar band is observed in the excitation spectrum of terthiophene, which suggests that this may be due to a local thiophene $n \rightarrow \pi^*$ excitation.[30] An interesting question is why no low-energy emission from a planar excited state is observed from **PT₃P** and **PT₃**. The DFT calculations show the HOMO for these compounds to be largely terthienyl π in nature, and excitation does not seem to involve the phosphine group significantly; thus, planarization does not occur at the phosphorus and emission seems to be a typical oligothiophene $\pi^* \rightarrow \pi$ transition.

Solid-state emission spectra for **PTP**, **PT₂P**, and **PT₃P** are shown in Figure 5, and the data for all six compounds are collected in Table 1. All the spectra have an excitation band at ∼225 nm, which may be due to a local thienyl-based $n \rightarrow \pi^*$ excitation. **PT**, **PTP**, **PT₂**, and **PT₂P** exhibit spectra in the solid-state that are very similar to those observed in solution. The emission bands show Stokes shifts, larger in the monothienyl compounds than in the bithienyl compounds, which are assigned as $\pi^* \rightarrow n$ transitions, similar to solution. The terthienyl compounds **PT₃P** and **PT₃** have structured emission spectra, which
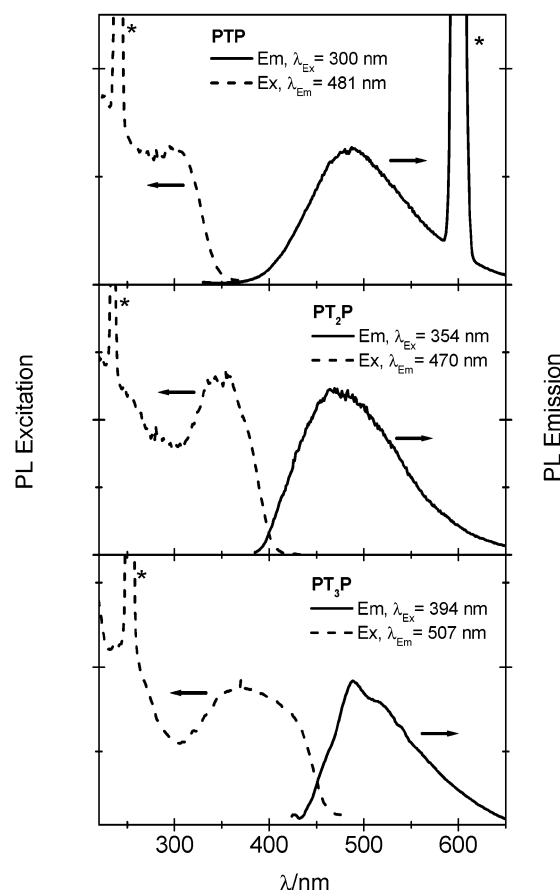

Figure 5. Solid-state excitation and emission spectra of **PTP**, **PT₂P**, and **PT₃P**.

are substantially red-shifted, compared to solution, possibly due to increased planarity of the π-system in the ground state in the solid state. Similar shifts have been previously observed in the spectra of substituted oligothiophenes.[30]

Conclusions

The absorption and emission spectra of the series of mono- and bisphosphines studied here show some interesting effects that are linked to the length of the thienyl group. Emission from the two compounds that contain a single thienyl ring (**PT** and **PTP**) show large Stokes shifts, attributed to planarization of the excited state. **PT₂** and **PT₂P** behave analogously, although **PT₂P** shows two emission bands in solution, possibly due to multiple conformations in solution. The terthienyl compounds— **PT₃** and **PT₃P**—show emission behavior similar to that observed for other terthiophenes, with a small Stokes shift. These results are significant for photophysical studies on metal complexes using these phosphines as ligands. Coordination of the phosphine occurs via the P lone pair, and, thus, the coordination can be expected to perturb the shorter (mono- and bithienyl) compounds significantly, whereas the terthienyl compounds (and presumably longer oligomers also) should be less affected by coordination. Such studies are in progress.

Supporting Information Available: Solid-state absorption and emission spectra, calculated frontier orbital energies (PDF).

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