Synthesis and Characterization of Transition Metal Systems Containing Phosphino-Oligothiophene Ligands for Nonlinear Optical Materials

R. Dustan Myrex and Gary M. Gray*

Department of Chemistry, University of Alabama−Birmingham, 201 Chemistry Building, 901 14th Street South, Birmingham, Alabama 35294-1240

Amelia G. VanEngen Spivey[†] and Christopher M. Lawson

Department of Physics, University of Alabama−Birmingham, CH 310, 1530 Third Avenue South, Birmingham, Alabama 35294-1170

Polythiophenes exhibit interesting third-order nonlinear optical properties but poor solubilities. Incorporating polythiophenes into transition metal complexes should yield readily soluble materials, and the transition metal substituent may alter third-order nonlinear optical properties of the polythiophene. In this paper, we report the synthesis and characterization of 2-diphenylphosphinothianaphthene, **A**, and its *trans*-PdCl$_2$L$_2$, **B**, and *cis*-PtCl$_2$L$_2$, **C**, analogues. Additionally 2-diphenylphoshino-5:2′,5′:2″-terthiophene, **D**, its *trans*-PdCl$_2$L$_2$ complex, **E**, both first prepared by Wolf,[25] the previously unprepared *cis*-PtCl$_2$L$_2$ analogue, **F**, and the oxide of **A**, **G**, were prepared and investigated for nonlinear optical (NLO) behavior. No appreciable third-order NLO behavior was observed for **A**, **D**, or **G**. However both **E** and **F** exhibited nonlinear refraction, as shown by Z-scan measurements, and nonlinear absorption. The nonlinear absorption was significantly stronger for **E**, indicating that the metal center has a significant affect on nonlinear absorption. This is the first reported observation of this type of nonlinear behavior in metal−phosphinothiophene systems.

Introduction

There has been strong interest in conjugated polymers over the last two decades because of their optoelectronic properties. The extended π-conjugated networks and large concentration of easily polarizable electrons possessed by such polymers can lead to nonresonant third-order nonlinear optical properties in these materials. Polythiophene systems are one type of such polymers and have already seen use as antistatic coatings, hole-injection materials for polymeric light-emitting diodes, and field-effect transistors.[1,2] One major limitation of the use of polythiophenes as optoelectronic materials is that polythiophenes with five or more repeat units exhibit very low solubilities that make processing difficult. One popular method for improving the solubilities of these materials is to substitute thiophene rings at the β-position with alkyl groups, with butyl to octyl being common choices.

Incorporation of the polythiophene groups into transition metal complexes is an alternate and less studied approach for improving the solubilities of polythiophenes. This approach has the added advantage that substitution of the polythiophene by a metal complex may modify the optoelectronic properties of polythiophene. We and others have demonstrated that polythiophene groups may be incorporated into transition metal complexes via functionalization of the polythiophenes with phosphines followed by coordination of the phosphine groups

to the transition metals.[3−6,26−28] We have recently used this approach to prepare both oligomeric complexes with phosphine-substituted bithiophenes and monomeric complexes with similar ligands that were models for the corners and edges in the oligomers.[13] The complexes exhibited high solubilities, but the bithiophene groups contained too few thiophenes to exhibit interesting optoelectronic properties.

To determine if complexes of phosphine-substitued oligothiophenes with greater degrees of conjugation will exhibit interesting optoelectronic properties, we have carried out a study of the third-order nonlinear optical properties of two such ligands, diphenylphosphinothianaphthene, **A**, and 2-diphenylphoshino-5:2′,5′:2″-terthiophene, **D**, their *trans*-PdCl$_2$L$_2$ and *cis*-PtCl$_2$L$_2$ complexes, and 2-diphenyloxophosphino-5:2′,5′:2″-terthiophene using Z-scan and nonlinear absorption intensity-dependent transmission measurements. The results of these studies are reported in this paper. Syntheses and complete multinuclear NMR spectroscopic characterizations for ligands and complexes that have not been previously reported have also been carried out and are summarized in this paper.

† Present address: Department of Physics, University of Puget Sound, 1500 N. Warner St. #1031, Tacoma, WA 98416-1031.

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Experimental Section

Materials. THF was first dried by allowing it to stand over $MgSO_4$ for at least 12 h, followed by distillation from CaH_2, and finally by distillation from Na/benzophenone onto molecular sieves. The dry THF was used within a few hours of collection. Other solvents were reagent-grade and were degassed using high-purity (99.998%) nitrogen before use. Terthiophene, palladium chloride, chlorodiphenylphosphine, and 1.6 M *n*-butyllithium were of sufficient purity from suppliers for immediate use. Literature methods were used for the dichloro(1,4-cyclooctadiene)platinum(II) chloride precursor.[7]

NMR Spectroscopic Characterization. Multinuclear ${}^{31}P\{{}^{1}H\}$ and ${}^{1}H$ NMR spectra were run on a Bruker ARX-300 NMR spectrometer. Chloroform-*d* solutions of the ligands and complexes were prepared under nitrogen. The ${}^{31}P\{{}^{1}H\}$ spectra were referenced to external 85% phosphoric acid in a coaxial tube that also contained chloroform-*d*, while the ${}^{1}H$ spectra were referenced to internal tetramethylsilane.

2-Diphenylphosphino-5:2′,5′:2″-terthiophene, $C_{24}H_{17}PS_3$ (D). A modification of Wolf's method[25] was used to prepare 2-diphenylphosphino-5:2′,5′:2″-terthiophene in much higher yield. A mixture of 2.5 mL (4.0 mmol) of a solution of 1.6 M *n*-butyllithium in hexanes and 20 mL of THF was added to a solution of 0.99 g (4.0 mmol) of 2:2′,5′:2″-terthiophene in 100 mL of THF. The reaction mixture was cooled in an acetone/dry ice bath during the reaction, and the addition took place over 30 min. When the addition was completed, the reaction mixture was allowed to warm at room temperature and stirred for 30 min. Next, 0.718 mL (4.0 mmol) of neat chlorodiphenylphosphine was added to the reaction mixture from a gastight syringe, and the resultant solution was stirred an additional 15 min. A few drops of degassed, deionized water were then added to quench any residual butyllithium or chlorodiphe-

nylphosphine, and the solvent was removed on a rotary evaporator. The residue was extracted with degassed ethyl ether to separate the product from the LiCl byproduct, and the extracts were combined and evaporated to dryness to yield 1.29 g (74.7%) of crude **D**. ${}^{1}H$ NMR (chloroform-*d*): δ 6.87−6.96 (3H, m), 7.07−7.09 (2H, m), 7.12−7.15 (2H, m), 7.27−7.37 (10H, m). ${}^{31}P\{{}^{1}H\}$ NMR (chloroform-*d*): δ −18.30 (s).

2-Diphenylphosphinothianaphthene, $C_{20}H_{15}PS$ (A). Following the procedure for **D**, 1.000 g (7.45 mmol) of thianaphthene, 4.66 mL (7.45 mmol) of *n*-butyllithium, and 1.34 mL (7.45 mmol) of chlorodiphenylphosphine yielded 1.53 g (64.6%) of crude **A** as a white solid. ${}^{1}H$ NMR (chloroform-*d*): δ 7.25−7.47 (12H, m), 7.51−7.53 (1H, m) 7.74−7.83 (2H, m). ${}^{31}P\{{}^{1}H\}$ NMR (chloroform-*d*): δ −16.56 (s).

Dichlorobis(2-diphenylphosphino-5:2′,5:2′-terthiophene)palladium(II) Chloride, $PdCl_2(C_{24}H_{17}PS_3)_2 \cdot CH_2Cl_2$ (E·CH₂Cl₂). A mixture of 0.113 g (0.639 mmol) of palladium chloride powder and 0.553 g (1.278 mmol) of **E** in 75 mL of degassed acetonitrile was stirred for 18 h at ambient temperature under nitrogen. Then, the solid that had precipitated from solution was collected by filtration and recrystallized from a dichloromethane/hexanes mixture to yield 2.91 g (43.7%) of analytically pure **E·CH₂Cl₂** as a red, crystalline solid. ${}^{1}H$ NMR (chloroform-*d*): δ 7.00−7.24 (6H, m), 7.35−7.47 (6H, m), 7.65−7.75 (5H, m). ${}^{31}P\{{}^{1}H\}$ NMR (chloroform-*d*): δ 13.19 (s). Anal. Calcd: C, 51.90; H, 3.10. Found: C, 51.60; H, 3.23.

Dichlorobis(2-diphenylphosphinothianaphthene)palladium(II) Chloride, $PdCl_2(C_{20}H_{15}PS)_2$ (B). Using the procedure for **E**, 0.177 g (0.100 mmol) of palladium chloride and 0.637 g (0.200 mmol) of **A** yielded 0.701 g (86.1%) of analytically pure **B** as large orange needles. ${}^{1}H$ NMR (chloroform-*d*): δ 7.32−7.51 (8H, m), 7.73−7.83 (6H,m), 8.14 (1H, m). ${}^{31}P\{{}^{1}H\}$ NMR (chloroform-*d*): δ 14.53 (s). Anal. Calcd: C, 59.02; H, 3.71. Found: C, 58.96; H, 3.71.

Dichlorobis(2-diphenylphosphino-5:2′,5′:2′- terthiophene)platinum(II) Chloride·CH₂Cl₂, $PtCl_2(C_{24}H_{17}PS_3)_2 \cdot CH_2Cl_2$ (F·CH₂Cl₂). To approximately 75 mL of degassed dichloromethane were added 0.748 g (2.0 mmol) of dichloro(1,4-cyclooctadiene)platinum(II) chloride and 1.730 g (4.0 mmol) of **D**. This solution was stirred at ambient temperature for 18 h, and then the solvent was removed under vacuum. Soxhlet extraction with hexanes removed the residual **D** and yielded 1.66 g (80.0%) of analytically pure **F·CH₂Cl₂** as a golden-yellow powder. ${}^{1}H$ NMR(chloroform-*d*): δ 6.90−6.97 (4H, m), 7.01 (1H, s), 7.05−7.07 (1H, m), 7.10−7.12 (1H, m), 7.14−7.17 (2H, m), 7.22 (1H, m), 7.26−7.35 (3H, m), 7.54−7.57 (3H, m). ${}^{31}P\{{}^{1}H\}$ NMR (chloroform-*d*): δ 5.33(s), ${}^{1}J({}^{31}P,{}^{195}Pt)$ 3698 Hz). Anal. Calcd: C, 49.00; H, 2.99. Found: C, 48.95; H, 3.08.

Dichlorobis(2-diphenylphosphinothianaphthene)platinum(II) Chloride·CH₂Cl₂, $PtCl_2(C_{20}H_{15}PS)_2 \cdot CH_2Cl_2$ (C·CH₂Cl₂). A solution of 0.187 g (0.500 mmol) of dichloro(1,4-cyclooctadiene)platinum(II) and 0.318 g (1.00 mmol) of **A** in 75 mL of degassed dichloromethane was stirred at ambient temperature for 18 h, and then the solvent was removed under vacuum. The resulting yellow powder was washed with several portions of degassed hexanes and then dried under high-vacuum to yield 0.320 g (70.9%) of analytically pure **C·CH₂Cl₂** as a pale yellow powder. ${}^{1}H$ NMR (chloroform-*d*): δ 7.10−7.16 (3H, m), 7.24−7.30 (3H, m), 7.32−7.36 (1H, m), 7.40−7.47 (1H, m), 7.49−7.58 (4H, m), 7.66−7.76 (3H, m). ${}^{31}P\{{}^{1}H\}$ NMR (chloroform-*d*): δ 7.62 (s and d, ${}^{1}J({}^{31}P,{}^{195}Pt)$ 3697 Hz). Anal. Calcd: C, 49.86; H, 3.16. Found: C, 49.83; H, 3.17.

2-Diphenyloxophosphino-5,2′:5′,2″-terthiophene, $C_{24}H_{17}OPS_3$ (G). A solution 0.250 g (0.578 mmol) of **D** and 1.000 g of urea-stabilized hydrogen peroxide pellet (35% peroxide by weight), from Acros Organics, in 75 mL of methanol was stirred at ambient temperature for 21 h, and then the solvent was removed under

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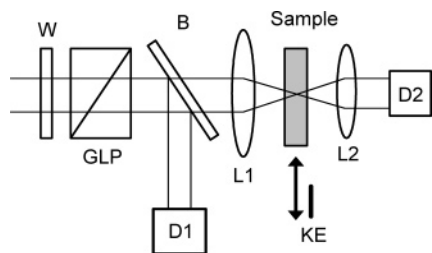
Figure 1. Experimental configuration for nonlinear absorption (NLA) measurements. W = half-wave plate, GLP = Glan-laser polarizer, B = beam splitter, L1 = 100 cm focal length lens, L2 = 20 cm focal length lens, KE = knife edge, D1, D2 = detectors.

vacuum. The residual urea was extracted from the residue with deionized water, and the insoluble **G** was dried under high vacuum overnight. ^{1}H NMR (chloroform-*d*): δ 7.01−7.22 (7H, m), 7.23−7.79 (10H, m). ^{31}P{^{1}H} NMR (chloroform-*d*): δ 21.80 (s).

Optical Characterization of the Ligands and Complexes. The linear and nonlinear optical properties of the complexes in solution were characterized by UV−visible absorption, nonlinear absorption,[8−10] and Z-scan measurements.[11] Together, this series of measurements allowed both the absorptive and refractive components of the optical nonlinearities of the complexes and the linear optical properties to be probed.

Nonlinear absorption (NLA) measurements probe the percent transmission of a sample as a function of the incident light fluence (energy per unit area) or intensity. Fluence-dependent (i.e., nonlinear) transmission through a sample can be caused by physical processes such as two-photon absorption, excited-state absorption, nonlinear scattering, or a combination of such processes.[8] Figure 1 shows the experimental configuration used for NLA measurements. The frequency-doubled Nd:YAG laser produces 7 ns pulses at 532 nm with a repetition rate of 10 Hz. After passing through a wave plate and polarizer combination, which is used to control the pulse energy, part of the 8 mm diameter beam (about 5%) is reflected by beam splitter B toward reference detector D1. The remaining portion of the beam is focused by lens L1 ($f = 1$ m) into the sample. The translation stage and knife edge, KE, are used to measure the beam radius at the focus, which is typically 100−120 μm. After passing through the sample, the transmitted light is re-collimated by L2 and sent into detector D2. During a NLA scan, the input energy is varied using the wave plate−polarizer combination, and the reference energy and transmitted signal energy are detected simultaneously. The incident energy, E_{in}, is calculated from the reference energy by measuring the ratio of energy at D2 to the energy at D1 without a sample, and the incident and transmitted fluences are calculated from the energies using $F = E/(0.5\pi w_0^2)$.

A refractive nonlinearity behaves as an intensity-dependent contribution to the index of refraction, $n = n_0 + n_2^I I$, where n_0 is the index of refraction under low-intensity illumination and n_2^I is the nonlinear refractive index. The Z-scan technique is used to isolate and probe the refractive part of the optical nonlinearity. Figure 2 shows the experimental configuration for the top-hat Z-scan measurement.[11,12] The frequency-doubled Nd:YAG laser produces 7 ns pulses at 532 nm with a repetition rate of 10 Hz. After passing through the wave plate and polarizer combination that is used to control the pulse energy, the 8 mm diameter laser beam is expanded by a 3× telescope before hitting a 3 mm aperture, A1. The light transmitted by aperture A1 is focused by the 20 cm lens to a spot of radius approximately 50 μm in the 2 mm sample. After passing through the sample, the beam is split into two portions for open-aperture and closed-aperture Z-scan detection at detectors D2 and D3, respectively. Detector D1 is used as a reference. The transmission of the closed aperture, A2, is typically between 0.02 and 0.05. The open-aperture detector records changes in transmission due to absorptive nonlinearities only, while the closed-aperture detector
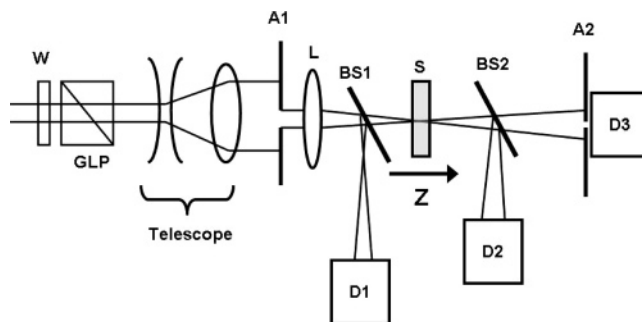
Figure 2. Experimental configuration for top-hat Z-scans. "Open" and "closed" aperture Z-scans are measured simultaneously by detectors D2 and D3, respectively, while detector D1 serves as a reference. W = half-wave plate, GLP = Glan-laser polarizer, A1, A2 = apertures, L = 20 cm focal length lens, BS1, BS2 = beam splitters, D1, D2, D3 = detectors, S = sample.

records changes in transmission caused by both absorptive and refractive nonlinearities. By taking the ratio of the closed-aperture to open-aperture signals, one can isolate the change in transmission due solely to the refractive nonlinearity quantified by n_2^I.

Results and Discussion

Ligand Syntheses. The phosphine-substituted terthiophene and thianaphthene ligands **A** and **D** were prepared as shown in Scheme 1. The reactions were run in a dry ice/acetone slush bath (−80 °C) to minimize isomeric scrambling of the lithiated thiophene and hence maximize the yield of the desired ligand. Generation of the lithiated species was rapid, and addition of the chlorodiphenylphosphine was carried out within 30 minutes of completion of the *n*-butyllithium addition. The crude ligands were used in subsequent reactions because the ^{31}P{^{1}H} NMR spectra of the **A** and **D** were singlets and the ^{1}H NMR spectra contained only the resonances for the phenyl and either the terthiophenyl or thianaphthenyl protons in the expected ratios. The procedure used to prepare **D** is a modification of that reported by Wolf.[25] This modification avoids chromatographic purification and gives **D** in a significantly higher yield (74.7% versus 29%).

Syntheses of the Complexes. The palladium(II) chloride complexes were synthesized by combining stoichiometric amounts of palladium chloride and the appropriate ligand in acetonitrile as shown in Scheme 2. The mixtures were stirred for 18 h at ambient temperature to yield the desired products as insoluble precipitates. The synthesis of complex D by Wolf and co-workers has previously been reported.[25] The platinum-(II) chloride complexes were prepared by the reaction of stoichiometric amounts of dichloro(1,4-cyclooctadiene)platinum-(II) and the appropriate ligand in dichloromethane as also shown in Scheme 2.

Oxidation of Ligand D. The oxide of ligand **D**, **G**, was prepared by the reaction of the ligands with a urea/hydrogen peroxide complex in dichloromethane. The urea byproduct was separated from **G** by washing with water to give an essentially quantitative yield of crude **G**. The ^{1}H NMR and ^{31}P{^{1}H} NMR spectra of this product contained no unexpected resonances, and it was used without further purification.

NMR Characterization of the Ligands and Complexes. The ^{31}P{^{1}H} NMR chemical shifts of ligands **D** and **A** are shown in Table 1 and are consistent with those reported for 2-diphenylphosphinothiophene (−19.43 ppm) and 5-diphenylphosphino-2,2′-bithiophene (−18.57 ppm).[13] The ^{31}P{^{1}H} NMR spectra of the palladium complexes, **B** and **E**, both exhibited a singlet,

Scheme 1

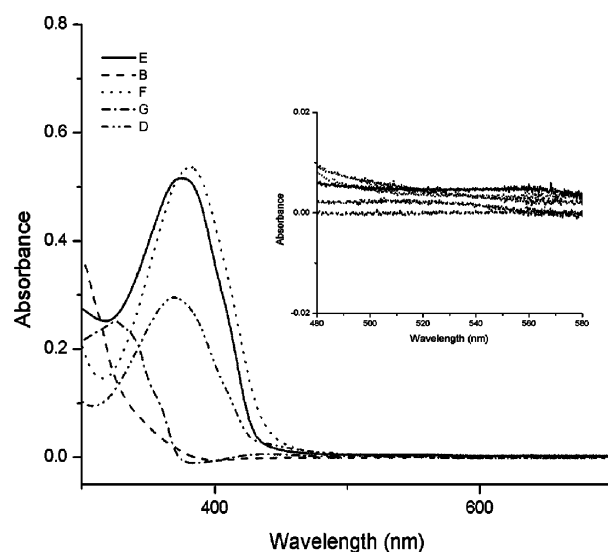1. 1 *n*-Butyllithium, THF,
   Dry Ice/Acetone

2. 1 PPh$_2$Cl

D

A

Scheme 2
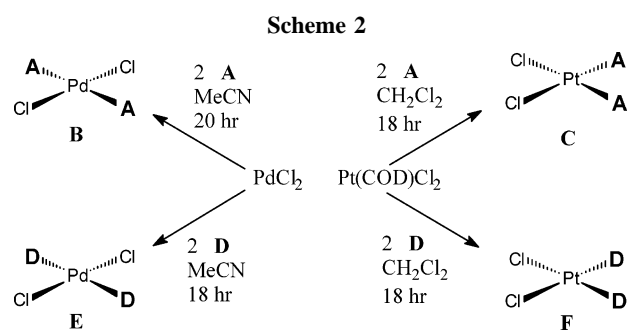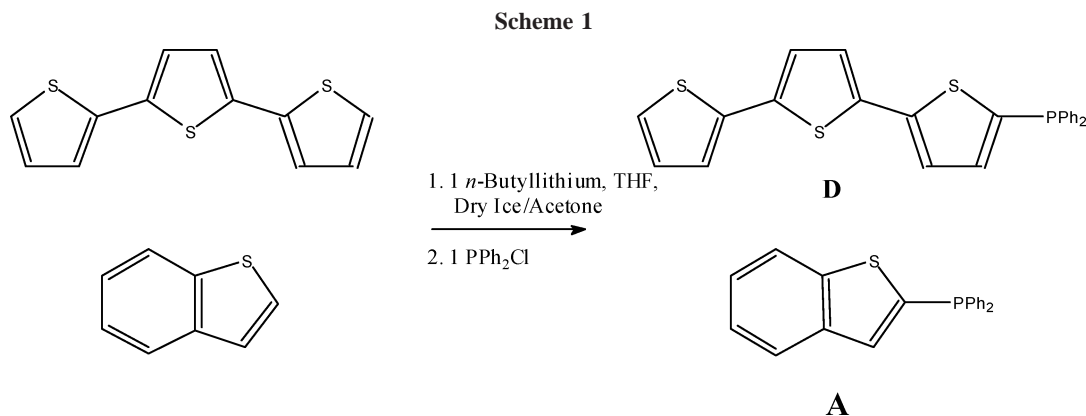
Table 1. ^{31}P{^{1}H} NMR Chemical Shifts and Coordination Chemical Shifts for Compounds A−F

compound	δ (ppm)	$\Delta\delta$ (ppm)
C$_{24}$H$_{17}$PS$_3$ (**D**)	−18.30	
C$_{20}$H$_{15}$PS (**A**)	−16.56	
trans-PdCl$_2$**D**$_2$ (**E**)	13.19	31.49
trans-PdCl$_2$**A**$_2$ (**B**)	14.53	31.09
cis-PtCl$_2$**D**$_2$ (**F**)	5.34	23.64
cis-PtCl$_2$**A**$_2$ (**C**)	7.62	24.18

Figure 3. Linear absorption spectra of the five compounds in dichloromethane. The concentration is 1.0×10^{-5} mol/L for **B**, **D**, **E**, **F**, and **G**. The inset shows the region centered around the excitation wavelength of 532 nm.

indicating that only one of the geometrical isomers had formed. The chemical shifts of the ^{31}P{^{1}H} NMR resonances of **B** and **E** do not directly indicate whether the geometrical isomer was *cis* or *trans*. However, the ^{31}P NMR coordination chemical shifts, $\Delta\delta$ ($\delta_{\text{coordinated}} - \delta_{\text{free}}$), for both complexes are similar to the ^{31}P NMR coordination chemical shifts observed for other *trans*-PdCl$_2$(phosphine)$_2$ complexes but approximately 10 ppm smaller than those observed for *cis*-PdCl$_2$(phosphine)$_2$ complexes.[14] The ^{31}P{^{1}H} NMR spectra of the platinum complexes, **C** and **F**, both exhibited a superimposed singlet and doublet, indicating that only one of the geometrical isomers had formed. The platinum complexes were assigned as *cis*-isomers based on the $^1J(^{195}$Pt,^{31}P) of approximately 3700 Hz. This is consistent with those observed for other *cis*-PtCl$_2$(phosphine)$_2$ complexes and approximately 1000 Hz higher than those observed for *trans*-PtCl$_2$(phosphine)$_2$ complexes.[15]

The ^{31}P NMR coordination chemical shift depends on two main factors: (1) a decrease in the electron density at the phosphorus nuclei due to the donation of the lone pair of phosphorus to the metal, and (2) a decrease in electron density at the phosphorus due to expansion of the substituent− phosphorus−substituent (SPS) angle upon coordination.[16] Thus comparing the ^{31}P NMR coordination shifts of ligands **A** and **D** provides a comparison of the manner in which these ligands coordinate to metal centers. The ^{31}P NMR coordination chemical shifts for the palladium complexes, **B** and **E**, were both

approximately 31 ppm, while those for the platinum complexes, **C** and **F**, were both approximately 24 ppm. This suggests that the changes in the SPS angles on going from the free to coordinated ligand are very similar for ligands **A** and **D** and, thus, that the differing substitution on the thienyl substituents of ligands does not significantly affect the SPS of either the free or coordinated ligands. This observation is consistent with previous results that indicate that the number of thiophene units in the oligothiophene substituent of Ph$_2$P(C$_4$H$_2$S)$_n$H ligands (n = 1, 2, 3) has very little effect upon the chemical shift of the free phosphine ligand.

Linear and Nonlinear Optical Properties of the Complexes in Solution. Figure 3 shows the linear absorption spectra of dichloromethane solutions of five of the compounds at equal concentrations. The dichloromethane solvent has negligible linear absorption in this spectral region. All of the compounds show an absorption band between 250 and 400 nm. These bands undergo a bathochromic shift with both phosphine functionalization and metal coordination of the phosphine. With phosphine functionalization, red shifts of 12 and 17 nm, respectively, were observed in terthiophene and thianaphthene. Another red shift occurs upon coordination to a metal. For **D** the shift is about 8 nm (368 → 376 nm) for palladium (**E**) and about 34 nm (368 → 402 nm) for platinum (**B**). This behavior is consistent with results that have been observed by other groups.[25] For example,
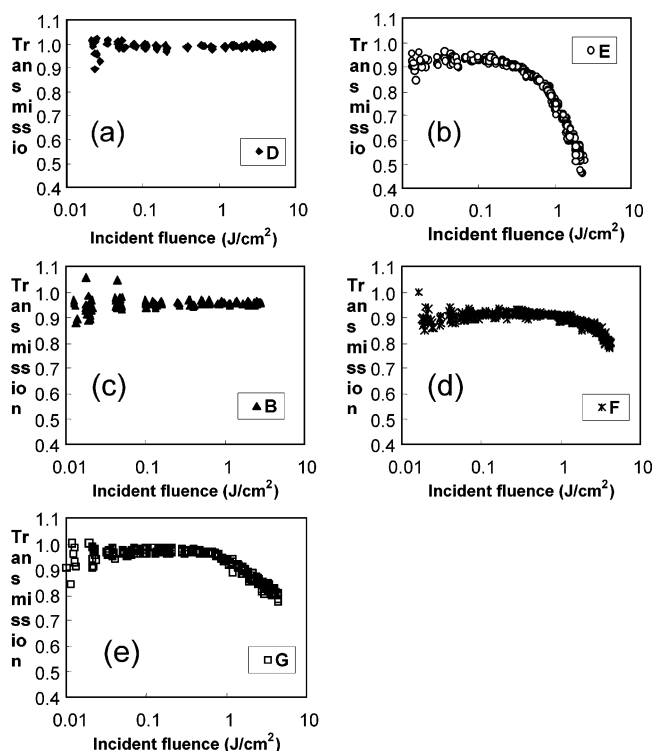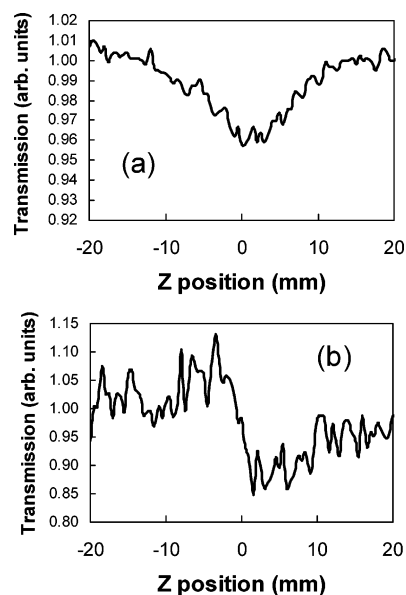
Figure 4. Nonlinear absorption scans of transmission as a function of incident fluence through 2 mm samples of the complexes in solution. The concentration is 1.1×10^{-3} mol/L in CH_2Cl_2 for **D**, **E**, **F**, and **G**. For **B**, the concentration is 2.5×10^{-3} mol/L in CH_2Cl_2. The decrease in transmission at high incident fluence is a characteristic signature of reverse saturable absorption.

density functional theory has demonstrated that the oligothiophene LUMO is stabilized via interaction with the phosphorus.[17] This is thought to be a result of $\pi-d$ back-bonding between the π-orbitals of the thienyl moiety and an empty d-orbital on the phosphorus. These shifts, although small, demonstrate the tuning ability of thienylphosphine systems, moving the absorption band deeper into the visible region.

Nonlinear absorption measurements were also performed on the same five compounds. Figure 4 shows the optical transmission through a 2 mm sample solution of each complex as a function of incident fluence. The nonlinear absorption properties of the complexes are shown to vary widely. Whereas **B** and **D** exhibit simple linear transmission, **E**, **F**, and **G** show clear reverse saturable absorption, with the transmission decreasing with increasing incident fluence. With 2.3 J/cm² incident fluence, the transmission through 2 mm of **E** (*trans*-PdCl₂(**D**)₂) drops from its linear value of approximately 90% to approximately 55%. In contrast, the nonlinear absorption behavior of **F** and **G** is much weaker. Because **B** did not exhibit nonlinear optical behavior, the nonlinear optical properties of **A** and **C** were not studied.

Figure 4 shows that the coordination of **B** to a metal (either Pd (**E**) or Pt (**F**)) or oxidation of the phosphorus in **B** (**G**) increases the reverse saturable absorption properties of the complex. Conversely, the dichloropalladium(II) complex of **A** does not exhibit reverse saturable absorption. A comparison of Figure 4 (the NLA results) to Figure 3 (the linear absorption of the complexes) shows that the complexes that exhibit reverse saturable absorption are also those in which the absorption band has shifted to the red, causing some small linear absorption at 532 nm (as shown in the inset in Figure 3). This suggests that the nonlinear absorption in Figure 4 is caused by excited-state

Figure 5. (a) Open-aperture Z-scan signal for 1.07×10^{-3} mol/L solution of *trans*-PdCl₂**D**₂ (**E**) in CH_2Cl_2 measured using the top-hat Z-scan configuration. Note the weak, but measurable, nonlinear absorption. (b) Normalized ratio of closed- to open-aperture Z-scan signals for the same sample. The peak-before-valley structure indicates that n_2^I is negative.

absorption (rather than two-photon absorption), since some ground-state absorption is required for excited-state absorption to take effect. Excited-state absorption has been studied in porphyrins,[18] expanded porphyrins,[9,10,19] and phthalocyanines,[20−22] but to our knowledge this is the first observation of nonlinear absorption of this type in polythiophene complexes.

The nonlinear absorption effect can also be observed in the open-aperture Z-scan data, as seen in Figure 5a. However, the NLA data in Figure 4 are more useful because measurements are made over a wider range of fluences, which allow the observation of the fluence at which reverse saturable absorption begins to be observed.

The refractive part of the optical nonlinearity is also probed using Z-scan measurements. Figure 5b shows the ratio of the closed-aperture to open-aperture scans as a function of position Z for a 1.07×10^{-3} mol/L solution of **E** in CH_2Cl_2. The peak−valley structure of the Z-scan signal indicates that $n_2^I < 0$. Previous work from our group has shown that this is not solely a thermal $d\eta/dT$ effect but that some electronic contribution is responsible for the observed nonlinearity.[29] For the top-hat Z-scan configuration used here, the magnitude of the nonlinear refractive index can be calculated analytically using[11,12]

$$|n_2^I| = \frac{2.7\lambda}{2\pi I_0 L_{\text{eff}}} \tanh^{-1}\left[\frac{\Delta T_{p-\nu}}{2.8(1-S)^{1.14}}\right] \qquad (1)$$

where $\Delta T_{p-\nu}$ is the difference in normalized transmission between the peak and valley of the Z-scan signal. The factor S is the transmission of the closed aperture, λ is the wavelength, and I_0 is the intensity at the beam focus. The effective sample length is given by $L_{\text{eff}} = (1 - \exp[-\alpha_s L_s])/\alpha_s$, where L_S is the sample length and α_s is the linear absorption coefficient of the sample. The intensity at the beam focus is given by $I_0 =$

(29) Floyd, J. M.; Gray, G. M.; Spivey, A. G. V.; Lawson, C. M.; Pritchett, T. M.; Ferry, M. J.; Hoffman, R. C.; Mott, A. G. *Inorg. Chim. Acta* **2005**, *358* (13), 3773−3785.

Table 2. Linear Absorption Coefficient and Nonlinear Refractive Index Values Measured at 532 nm with 7 ns Pulses in CH$_2$Cl$_2$

complex	concentration (mol L^{-1})	α (cm^{-1})	n_2^{I} (m^2 W^{-1})
trans-PdCl$_2$**A**$_2$ (**B**)	2.5×10^{-3}	0.07	$|n_2^{\mathrm{I}}| < 6 \times 10^{-19}$
trans-PdCl$_2$**D**$_2$ (**E**)	1.1×10^{-3}	0.30	-1.8×10^{-18}
C$_{24}$H$_{17}$PS$_3$ (**D**)	1.1×10^{-3}	0.07	$|n_2^{\mathrm{I}}| < 4 \times 10^{-19}$
cis-PtCl$_2$**D**$_2$ (**F**)	1.1×10^{-3}	0.15	-1.5×10^{-18}
C$_{24}$H$_{17}$OPS$_3$ (**G**)	1.1×10^{-3}	0.34	$|n_2^{\mathrm{I}}| < 4 \times 10^{-19}$

$\sqrt{\pi \ln 2}(n_0 E/w_0^2 \tau)$, where n_0 is the index of refraction of the solution, E is the pulse energy, and τ is the temporal pulse width. The beam diameter is approximately $w_0 = \lambda f/d$.[12] In this work, the index of refraction of the complexes in solution is assumed to be the index of refraction of the solvent. (We use n_0 for CH$_2$-Cl$_2$ and n_0 for CS$_2$.[23]) Experimental accuracy is verified when the n_2^{I} for CS$_2$, measured under the same conditions, is in good agreement with the literature value.[24] Table 2 shows values of n_2^{I} for solutions of five of the complexes, as well as the values of α_s in each sample at 532 nm.

The results of the Z-scan measurements provide different and complementary information to the NLA measurements in these complexes. For example, although **E**, **F**, and **G** all exhibited some nonlinear absorption in Figure 4, only **E** and **F** exhibit measurable nonlinear refractive properties at these concentrations. This suggests that although phosphine functionalization changes the nonlinear absorptive properties of the terthiophene ligand, it has a weaker effect on its nonlinear refractive properties. When metal atoms are incorporated into the ligand, the enhancement of the nonlinear absorption shown in Figure 4 depends strongly on which metal is added. However, the measured values of n_2^{I} for solutions of **E** and **F** are virtually identical, suggesting that the nonlinear refractive properties are much less dependent on the nature of the metal.

The fact that n_2^{I} is negative in these complexes indicates self-defocusing in the solutions, meaning that a laser beam would spread out spatially in the far field after transmission through the sample. By defocusing the beam in the far field, this nonlinear refractive effect could conceivably enhance any limiting of the transmitted fluence due to reverse saturable absorption in the samples.

Conclusion

Both functionalization of terthiophene with a diphenylphosphino group to form **D** and the coordination of the diphenylphosphino group of **D** to transition metals have significant effects on the linear and third-order nonlinear optical properties of the compounds. Bathochromic shifts in the $\lambda_{\max}$ were as high as 50 nm relative to the parent terthiophene molecule. Extending the conjugation length of the thiophene segment and modification of the substituents on phosphorus could allow for even better tuning of the absorption window. Of particular interest is that the palladium(II) and platinum(II) complexes of **D** are the first transition metal complexes with phosphinothiophene substituents that have been demonstrated to be active nonlinear absorbers. Furthermore the third-order property responsible for this behavior is reverse-saturable absorption rather than two-photon absorption. Our preliminary results suggest that the choosing of an appropriate metal center and increasing the conjugation of the ligand should allow for the further optimization of the NLO behavior in complexes of the type presented herein.