Metalloorganic Compounds for Nonlinear Optics: Molecular Hyperpolarizabilities of M(diimine)(dithiolate) Complexes (M = Pt, Pd, Ni)

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A series of mixed-ligand transition-metal diimine dithiolate complexes have been prepared, and their nonlinear optical properties have been investigated. Molecular hyperpolarizabilities have been obtained from electric field induced second harmonic generation experiments at 1.9 μm and range in magnitude from 0 to -39×10^{-30} esu. Variation in molecular design of the complexes, through changes in the metal ion and diimine and dithiolate ligands, can be used to affect changes in the charge-transfer-to-diimine absorption band frequency and oscillator strength. Correlation between the optical charge-transfer transition and the nonlinear optical properties appears to agree with the two-state model.

Introduction

Research in the field of nonlinear optics has concentrated on the design of new chromophores and their incorporation in suitable materials.[1] The further development of organic and metalloorganic compounds for second harmonic generation (SHG) and related second-order effects relies on determining what factors control the molecular hyperpolarizability, β. An understanding of how molecular design is related to β may provide guidelines for designing chromophores that have desired optical and nonlinear optical (NLO) properties. The focus of this relationship has been the two-state model,[2] which is based on a single excited state and which can be used to express the molecular hyperpolarizability as a function of the frequency of the absorption band maximum ($\omega_{\max}$), frequency of the applied electric field (ω), the transition dipole moment between the ground and lowest-frequency excited state (μ_{ge}), and the difference in dipole moment between the ground and excited state ($\Delta\mu$):

$$\beta_{\mathrm{CT}} = \frac{12\pi^2}{\mathrm{h}^2}\frac{{\omega_{\max}}^2}{({\omega_{\max}}^2 - 4\omega^2)({\omega_{\max}}^2 - \omega^2)}{\mu_{\mathrm{ge}}}^2\Delta\mu \quad (1)$$

This model predicts that compounds having an intense, low-frequency charge-transfer absorption band may possess a large molecular hyperpolarizability. Although the two-state model is an oversimplification for organic chromophores, the basic relationship between optical and nonlinear optical properties has been observed for numerous organic compounds.[1]

The charge-transfer (CT) properties of excited states, and therefore the nonlinear optical properties of compounds, can be altered by changes in molecular design. The optical frequency, transition dipole moment, and $\Delta\mu$ that are associated with intramolecular charge transfer in organic compounds can be tuned by changes in donor/acceptor groups, conjugation length, and the degree of aromaticity, as well as by the incorporation of metal atoms in the electronic structure.[3] As a result of the involvement of metal d orbitals in the optical charge-transfer process, the CT excited states of metalloorganic complexes have many interesting attributes that CT excited states of purely organic compounds do not have. An understanding of how the excited states of metalloorganic complexes contribute to their molecular hyperpolarizability is only beginning to emerge. Although numerous metalloorganic compounds have been examined for their nonlinear optical properties, few studies have explored the structure−property relationship for a large set of related complexes. Review articles covering nonlinear optical properties of metalloorganic compounds have appeared recently.[3−5]

Our laboratory has focused on studying the excited-state properties of mixed-ligand Pt(II) diimine dithiolate complexes.[6−11] In addition to a rich amount of photo-

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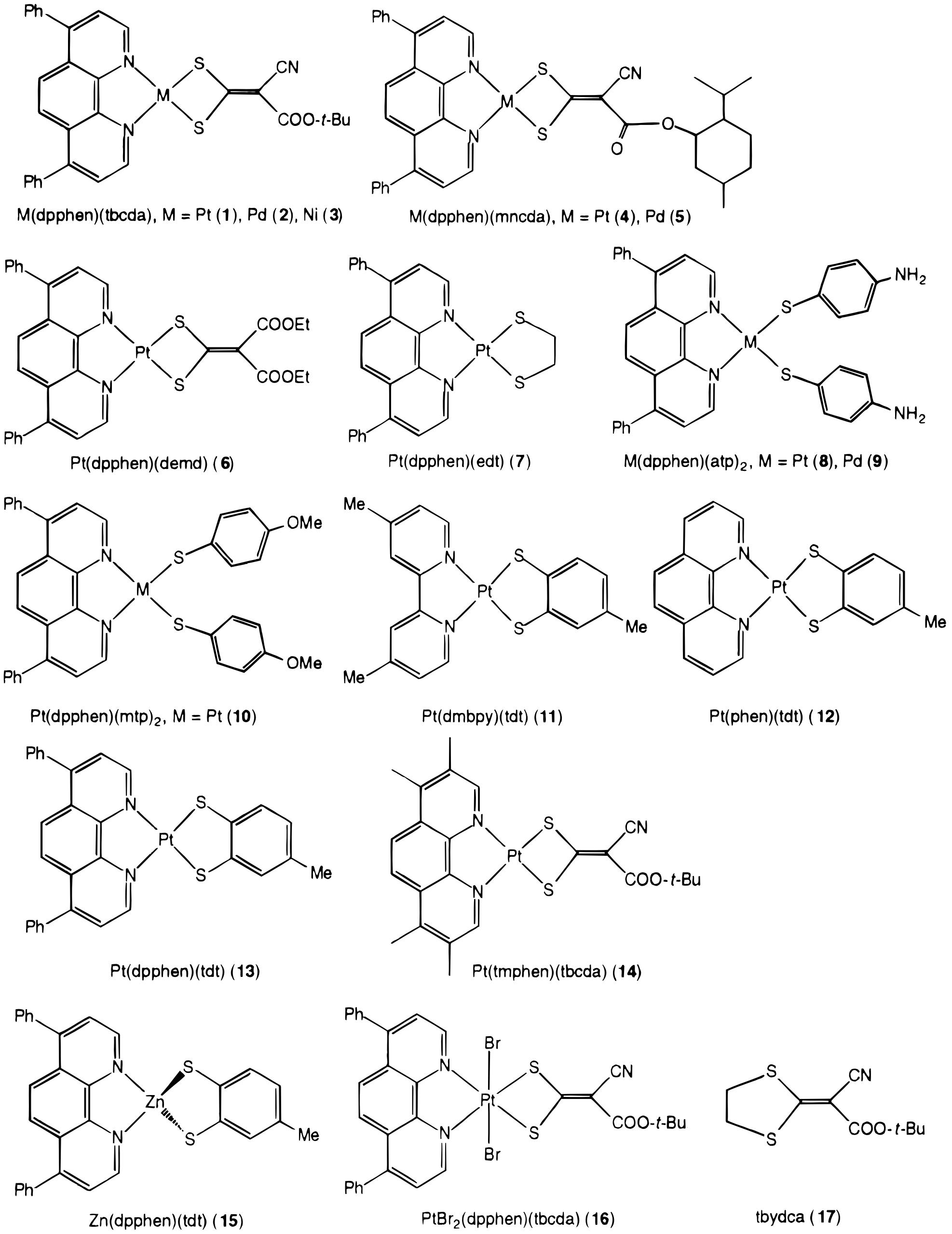
Scheme 1


M(dpphen)(tbcda), M = Pt (**1**), Pd (**2**), Ni (**3**)
M(dpphen)(mncda), M = Pt (**4**), Pd (**5**)
Pt(dpphen)(demd) (**6**)
Pt(dpphen)(edt) (**7**)
M(dpphen)(atp)$_2$, M = Pt (**8**), Pd (**9**)
Pt(dpphen)(mtp)$_2$, M = Pt (**10**)
Pt(dmbpy)(tdt) (**11**)
Pt(phen)(tdt) (**12**)
Pt(dpphen)(tdt) (**13**)
Pt(tmphen)(tbcda) (**14**)
Zn(dpphen)(tdt) (**15**)
PtBr$_2$(dpphen)(tbcda) (**16**)
tbydca (**17**)

luminescent properties, these complexes possess optical CT features that are indicative of nonlinear optical activity,[9] specifically, an intense, low-frequency, solvatochromic transition that has been assigned as a charge-transfer-to-diimine absorption. Studies of the Pt(diimine)(dithiolate) complexes thus far have focused on photoluminescence and bimolecular electron-transfer reactions associated with the long-lived triplet excited state, and the goal of the work has been to develop photocatalysts for solar-energy storage.

In this study, we report the molecular hyperpolarizabilities of M(diimine)(dithiolate) complexes. The strategy involves a systematic variation in the molecular design of the M(diimine)(dithiolate) chromophore, and the compounds prepared for this study are shown in Scheme 1. Variation in the metal ion, dithiolate donor ligand and diimine acceptor ligand have been used to tune the CT and NLO properties. This approach is intended to provide a rational basis for the design of compounds having systematically altered molecular hyperpolarizabilities.

Results

Synthesis and Characterization of Compounds 1−17. The preparation of compounds for this study followed established methods presented in the literature. The synthesis of mixed-ligand Pt(diimine)(dithiolate) complexes has been addressed in previous reports,[6−12] and new Ni(II) and Pd(II) complexes presented here were prepared by analogous procedures. The compounds have been characterized by ^{1}H NMR, infrared, and UV−vis spectroscopies, and the characterization of several representative samples has been

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Table 1. Optical and EFISH Results for Compounds 1−17

compound	no.	λ_{max}[a]	ϵ[b]	$\Delta\nu$[c]	μ[d]	β_μ[e]	β_0
Pt(dpphen)(tbcda)	**1**	457	14700	2.4	9	−15	−11
Pd(dpphen)(tbcda)	**2**	390	9800	2.6	8	−4	−3
Ni(dpphen)(tbcda)	**3**	465	11300	1.5	8	−12	−9
Pt(dpphen)(mncda)	**4**	454	14500	2.5	7	−7	−5
Pd(dpphen)(mncda)	**5**	375	10600	3.6	8	−1	−1
Pt(dpphen)(demd)	**6**	465	14500	2.1	10	−18	−13
Pt(dpphen)(edt)	**7**	476	10000	3.1	9	−17	−12
Pt(dpphen)$(atp)_2$	**8**	517		2.5	10	−39	−26
Pd(dpphen)$(atp)_2$	**9**	460		5.5	9	−10	−7
Pt(dpphen)$(mtp)_2$	**10**	503	3000	2.9	9	−31	−21
Pt(dmbpy)(tdt)	**11**	563	7000	4.0	9	−25	−15
Pt(phen)(tdt)	**12**	583	7000	3.9	9	−28	−16
Pd(dpphen)(tdt)	**13**	538	4500	4.1	9	−6	−4
Pt(tmphen)(tbcda)	**14**	421		2.7	10	0	0
Zn(dpphen)(tdt)	**15**	440	~80		8	−6	−4
Pt(dpphen)(tbcda)Br_2	**16**				6	−10	
tbdyca	**17**	316	~30000	0	2	0	0

[a] In nm. [b] In L mol^{-1} cm^{-1}. [c] Slope of solvatochromic plots. [d] In debye ± 10%. [e] In 10^{-30} esu ± 20%.

confirmed by elemental analyses. The complexes are generally stable in solution to air and light, with the notable exception of compound **7**, which decomposes in the presence of air and room light within several minutes.[13]

Molecular Hyperpolarizabilities. Electric field induced second harmonic generation (EFISH) experiments were used to obtain values for β_μ, the projection of β along the molecular dipole axis. Many of the details of the EFISH experiment have been published previously.[14] The 1.91 μm fundamental radiation (ω) used in the experiment and 954 nm second harmonic that was produced are far from absorption in order to minimize resonant enhancement. The third harmonic at 636 nm is near or within the absorption features of many of the compounds in this study, but this is not uncommon for molecules with larger hyperpolarizabilities and is taken into account upon data workup. In addition to the SHG measurements, several other solution measurements were made in order to determine β_μ, including measurements of solution third harmonic generation, refractive index, conductivity and density. The values of β_μ and μ obtained for compounds **1**−**17** from these experiments are presented in Table 1. The values of β_μ are negative for all of the compounds, except those that are zero within experimental error, and range from 0 to −39 × 10^{-30} esu. Frequency-independent β_0 values were calculated using eq 2 based on the two-state model, where ω_{max} is the peak absorption frequency.[15]

$$\beta_0 = \beta(\omega)\frac{({\omega_{max}}^2 - \omega^2)({\omega_{max}}^2 - 4\omega^2)}{{\omega_{max}}^4} \qquad (2)$$

Optical Spectroscopy. The absorption spectrum of each compound was measured in dichloromethane, and the absorption maxima and associated molar extinction coefficients are summarized in Table 1. The absorption spectra of compounds **1**−**3** are presented in Figure 1. Solvatochromic measurements were performed for each compound, using between 7 and 10 solvents. To determine the relative degree of solvatochromism, the data were fit to an empirical Pt(NN)(SS) solvent parameter[16] using a linear least-squares analysis, and the results for several compounds are presented in Figure 2. Because distinct CT bands are not observed for compounds **15** and **16**, these compounds were not included in this analysis. The data for the other compounds correlate well to the Pt(NN)(SS) solvent scale, except for compound **9**.

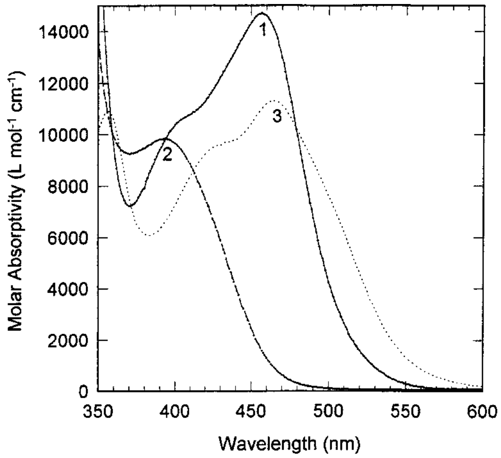

Figure 1. Absorption spectra for Pt(dpphen)(tbcda) (**1**), Pd(dpphen)(tbcda) (**2**), and Ni(dpphen)(tbcda) (**3**) in dichloromethane.

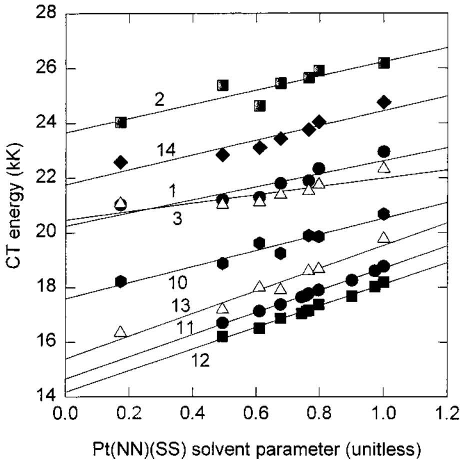

Figure 2. Plot of charge-transfer-to-diimine absorption band maximum vs Pt(NN)(SS) solvent parameter for complexes **2**, **14**, **1**, **3**, **10**, **13**, **11**, and **12** (top to bottom).

Discussion

Synthesis, Structure, and Physical Properties. The goal of this study is to understand the relationship between the charge-transfer and nonlinear optical properties of M(diimine)(dithiolate) complexes and to elucidate the role of the metal ion, dithiolate, and diimine ligands in tuning these properties. The compounds **1**−**17** were prepared to test this relationship by providing a large series of compounds having charge-transfer properties that change with electronic structure. The compounds **1**−**14** comprise a series of square-planar mixed-ligand complexes having a charge-transfer-

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to-diimine excited state that is systematically tuned through variation in the metal ion, dithiolate, or diimine ligands. Three other compounds are included in this study that represent a more significant variation in the electronic structure. The complex Zn(dpphen)(tdt) (**15**) is a representative example from a large set of Zn(diimine)(SS) complexes (SS = dithiolate or bis(thiolate)) for which electronic structure and photoluminescence have been investigated by several research groups.[17-19] The ligand-to-ligand charge-transfer (LLCT) excited state of complexes of this type is closely related to the charge-transfer-to-diimine excited state under investigation here. Important differences in electronic and structural factors between complex **15** and the others in this study are discussed below. The octahedral Pt(IV) complex, $PtBr_2$(dpphen)(tbcda) (**16**), is included in this study in order to determine how changes in the oxidation state and coordination environment affect CT and NLO properties. Finally, the organic compound *tert*-butyl-1,3-dithiolan-2-ylidenecyanoacetate (tbdyca, **17**) was prepared in order to investigate the role of intraligand charge transfer that is localized on the tbcda ligand.

Numerous other complexes were prepared for this study but were not able to be used due to (1) poor solubility in dichloromethane or other common organic solvents, (2) instability in solution at ambient conditions, or (3) absorption at the second harmonic wavelength of 954 nm. The first problem can be overcome through the use of aliphatic substituents on the ligands, such as for the ligands 1-(*tert*-butylcarboxy)-1-cyanoethylene-2,2-dithiolate (tbcda) or 4,4′-di-*tert*-butyl-2,2′-bipyridine (dbbpy). However, these substituents also contribute to the electronic factors associated with the ligands, and therefore affect the charge-transfer properties in addition to solubility.

The characterization of complexes **1**−**14** by ^{1}H NMR spectroscopy indicates a square-planar geometry for the M(diimine)(dithiolate) complexes. The complexes having unsymmetrical dithiolate ligands, such as tbcda and mncda, display a splitting of the diimine protons that are adjacent to the N atoms (6 and 6′ protons in 2,2′-bipyridyl ligands and 2 and 9 protons in 1,10-phenanthroline ligands). The tdt ligand induces a smaller splitting than the tbcda and mncda ligands, although the inequivalence of the diimine protons is clearly resolved for Pd(dpphen)(tdt) (**13**). The complexes having the symmetric dithiolate edt or two equivalent thiophenolate ligands do not display this inequivalence in the diimine protons, but a square-planar geometry is assumed for them as well. The structures of two Pt(diimine)(dithiolate) complexes that are closely related to those in this study have been determined by X-ray crystallography and possess a geometry that is a slightly distorted square-planar coordination around the Pt(II) center.[20,21] The structure of Zn(dpphen)(tdt) (**15**) is assumed to be tetrahedral, in accordance with the structures of other Zn(II) diimine bis(thiolate) complexes.[22] The complex Pt(dpphen)(tbcda)Br_2 (**16**) formed through the *trans* oxidative addition of Br_2 to Pt(dpphen)(tbcda) (**1**), is octahedral, as supported by ^{1}H NMR spectroscopy.

The M(diimine)(dithiolate) complexes possess some important structural considerations that relate to charge-transfer and NLO properties. The combination of a dithiolate electron−donor and a diimine electron-acceptor ligand coordinated to a M(II) center leads to a large ground-state dipole moment and optical charge transfer. The dipole moments of these complexes, which are in the range 8−10 D for most of them (Table 1), lie in the direction of the electron-rich dithiolate ligand along an axis that bisects the diimine and dithiolate ligands.[23] The square-planar geometry and the pseudo mirror plane bisecting the molecules require that the molecular charge-transfer axis coincides with the molecular dipole axis. This property makes complexes of this type well-suited for EFISH measurements, because the EFISH experiment samples the vector projection of the β tensor along the molecular dipole axis, μ. For some other complexes, the charge-transfer and dipole axes are not coincident, resulting in experimentally determined β_μ values that are smaller than the contribution of β along the CT axis.[24,25]

Molecular Hyperpolarizabilities. The molecular hyperpolarizabilities of compounds **1**−**17** are presented in Table 1. The results show that the compounds in this study possess optical nonlinearities in the range 0 to -40×10^{-30} esu. The negative values of β_μ indicate that values of $\Delta\mu$ are negative (eq 1), which result from the combination of a polar ground state and nonpolar CT excited state.[26] The reduction in dipole moment that accompanies CT excitation is also manifested in negative solvatochromism. Negative β values are uncommon for organic compounds. A few examples have been reported, including merocyanine dyes, dicyanoquinoidal compounds, and squaraine dyes.[1,27] For comparison, the values of β are in the range -41 to 94×10^{-30} esu for the squaraine dyes having absorption maxima in the 518−572 nm range.[28c] However, the CT excited states of organic compounds usually have larger dipole moments than the ground states, resulting in positive values of $\Delta\mu$ and, therefore, positive values of β. Several metalloorganic compounds possess negative values of β, including Ni(salen), arenechromium tricarbonyl, and $W(CO)_5$(pyridine) compounds.[28-30]

Comparison of the magnitudes of β for the compounds in this study with those reported in the literature requires some points of caution. The values of β_μ

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extracted from the EFISH experiment are sensitive to the frequency of the laser fundamental, the solvent used and other experimental considerations. The first of these factors reflects the effect of resonant enhancement of β that occurs when the second harmonic frequency approaches the frequency of the CT absorption band. The β_μ results from EFISH experiments using a 1.064 μm or 1.34 μm fundamental radiation may have substantial resonant enhancement, especially for compounds with long-wavelength CT absorption bands. Zero-frequency values (β_0) are often reported as a way to correct for resonant enhancement and to compensate for differences in the fundamental frequency used in separate experiments. Comparison of the values of β for different compounds is strongest when the same EFISH experimental methods have been used. Therefore, comparison will focus on the molecular hyperpolarizabilities of compounds **1**−**17** and hundreds of other organic and metalloorganic compounds investigated at the DuPont Laboratories.[14,27,31−41] The magnitudes of β for some of the compounds in this study are among the largest observed for metalloorganic compounds using this EFISH setup. The values of β for Pt(dpphen)(atp)$_2$ and Pt(dpphen)(mtp)$_2$ are similar in magnitude to those for 4-nitro-4′-methoxystilbene (34 $\times 10^{-30}$ esu) and 4-nitro-4′-aminostilbene (40 $\times 10^{-30}$ esu), although the latter compounds have absorption maxima of 370 and 402 nm, respectively, in chloroform.

The purpose of this study, however, is not simply to generate compounds with large values of β. Rather, it is to understand the relationship between the charge-transfer and nonlinear optical properties for the Pt(diimine)(dithiolate) chromophore. Therefore, the comparison of β values *within* the series of compounds **1**−**17** is important. The values of β range from 0 to -39×10^{-30} esu and reflect a variation in molecular design and electronic structure. The metal ion and the dithiolate and diimine ligands each affect the optical charge-transfer and nonlinear-optical properties in ways that can be understood in terms of their orbital contributions.

Optical Charge-Transfer Properties. Charge-transfer excited states are the origin of optical nonlinearity. Complexes belonging to the M(diimine)(dithiolate) family possess charge-transfer-to-diimine and charge-transfer-to-dithiolate excited states.[7,42] Metal-centered d−d states and ligand-centered $\pi-\pi^*$ states that involve little or no radial charge transfer do not contribute to optical nonlinearities, and discussion will therefore focus on charge-transfer excited states.

The lowest energy excited state for Pt(diimine)(dithiolate) complexes studied previously was assigned as charge-transfer-to-diimine in nature.[16] Excitation to a state of this type involves a transition from a HOMO that is a mixture of metal d and dithiolate orbital character to a LUMO that is a diimine π^* orbital. The transition is characterized by an intense absorption band lying at lower frequency than the ligand $\pi-\pi^*$ bands. The polar ground state of mixed-ligand complexes and the change in dipole moment that accompanies charge-transfer-to-diimine excitation give rise to large solvatochromic effects, in which the CT absorption band shifts to higher frequency in solvents of greater polarity. Systematic tuning of the electron-donating or electron-accepting ability of the dithiolate and diimine ligands leads to large changes in the CT band frequency and has provided strong support for the charge-transfer-to-diimine assignment.[16] Additional support for the orbital nature of the HOMO and LUMO has come from molecular orbital calculations.[6,43]

The CT absorption spectra of compounds **1**−**14** support an assignment of a charge-transfer-to-diimine excited state for these complexes. For each complex, the lowest-frequency absorption band lies red-shifted from the ligand $\pi-\pi^*$ bands, and has a molar extinction coefficient in the range of 4000−15 000 L mol^{-1} cm^{-1}. For compounds **1**−**14**, negative solvatochromism (hypsochromism) of the CT absorption band is observed, which is consistent with the charge-transfer-to-diimine transition and is not observed for the charge-transfer-to-dithiolate transition. The magnitude of solvatochromism for the charge-transfer-to-diimine transition is also much greater than is seen in related systems with dπ−π^*(diimine) metal-to-ligand charge-transfer (MLCT) transitions.[44]

Compounds **15**−**17** require special consideration, because their optical charge-transfer properties are different than those of **1**−**14** in important ways. The absorption and emission spectra of Zn(dpphen)(tdt) (**15**) are very similar to the Zn(diimine)(SPh)$_2$ and Zn(diimine)(tdt) complexes reported in the literature.[19,45] The CT absorption spectrum of Zn(bpy)(tdt) was assigned to an "interligand transmetallic charge transfer" by Koester, and was subsequently termed a ligand-to-ligand charge-transfer by Benedix et al.[17] Tetrahedral mixed-ligand Zn(diimine)(SPh)$_2$ complexes have been the topic of extensive research by Crosby and co-workers, and the charge-transfer and photoluminescent properties of complexes of this type involve a LLCT excited state.[18,19] The role of the Zn(II) ion in LLCT excitation is proposed to be minimal, with the HOMO being dithiolate-localized and the LUMO being diimine-localized. Although there are several important differences between the tetrahedral Zn(II) and d^8 square-planar complexes (vide supra), the relevant CT excited state for both types of complexes appears to involve similar orbitals.

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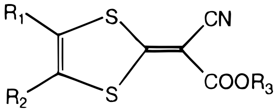
The lowest-energy excited state for Pt(dpphen)(tbcda)-Br_2 (**16**) has not been unambiguously assigned. The excited-state manifold of complex **16** is proposed to contain a charge-transfer-to-diimine excited state that involves similar orbitals as the Pt(dpphen)(tbcda) (**1**) precursor. The CT absorption band is shifted to higher frequency as a result of the metal oxidation and lies at approximately the same energy as dithiolate- and diimine-localized intraligand $\pi-\pi^*$ states. A more detailed discussion of the CT properties of complex **16** is presented elsewhere.[13]

The absorption spectra of tbdyca (**17**) and the uncoordinated K_2(tbcda) ligand were investigated in order to probe the relation of the intraligand charge-transfer excited state to the charge-transfer-to-diimine excited state in the metal complexes having tbcda or similar 1,1-dithiolates. Closely related [cyano(alkoxycarbonyl)-methylene]-2-ylidene-1,3-dithiol compounds (**18**) were studied by Shimizu, Nogami, and co-workers for their CT and NLO properties.[46] The absorption band maxima for compounds **17** (316 nm), **18** (368−378 nm), and K_2(tbcda) (341 nm) are shifted to higher frequencies relative to the lowest frequency maxima of complexes **1**−**14**, are insensitive to solvent and have molar extinction coefficients in the range of 30 000 L mol^{-1} cm^{-1}. A value of β for compound **18** (having $R_1 = R_2 = H$, $R_3 =$ Et) was found to be -13×10^{-30} esu using EFISH methods.



18

R_1 = H, Me
R_2 = H, Me
R_3 = Me, Et, n-Pr, n-Bu, -Pr

The combination of thio donor group and cyano and alkoxycarbonyl acceptor groups on the methylene bridge facilitates intramolecular charge-transfer. Molecular orbital calculations using the Pariser−Parr−Pople method for compound **18** (with $R_1 = R_2 = H$) were published and confirm that excitation leads to charge transfer from the dithiovinylene group to the electron-accepting cyano and ester groups.[46]

Application of the Two-State Model. The two-state model has been effective in relating molecular hyperpolarizability to optical charge-transfer parameters for organic compounds. When $\omega \ll \omega_{max}$, eq 1 can be simplified to an expression for the zero-frequency term β_0,[15] which is the intrinsic hyperpolarizability and does not involve resonant enhancement:

$$\beta_0 = 1.617\,\lambda_{max}{}^3 f\Delta\mu \tag{3}$$

According to eq 3, β_0 should be most strongly influenced by λ_{max}. A correlation is found between the CT absorption band maxima and the experimentally determined values of β_0 for the compounds in this study. Figure 3 is a plot of β_0 vs $\lambda_{max}{}^3$, which shows that there is a reasonably good agreement to the prediction of the two-state model in terms of the dependence of β_0 on wavelength. It is interesting to note that the data for the complexes having tdt ligands (**11**−**13**) appear offset from the nearly linear correlation of the data for the other compounds. Although the trend of an increasing magnitude of β_0 with $\lambda_{max}{}^3$ appears to hold for the tdt complexes, their β_0 values are smaller in magnitude than would be predicted on the basis of wavelength alone.

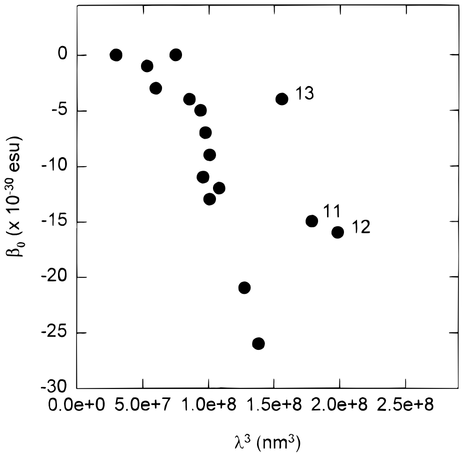


Figure 3. Plot of β_0 vs cubed wavelength of the charge-transfer-to-diimine absorption band maximum for complexes **1**−**14**.

Equation 3 also predicts a dependence of β_0 on the oscillator strength, *f*. Unfortunately, a detailed analysis of oscillator strengths for the complete series is not possible due to CT absorption features of some compounds that are partially obscured by other features. However, some general observations can be made regarding molar extinction coefficients. For square-planar M(diimine)(dithiolate) complexes, molar extinction coefficients range from 3000 to 15 000 L mol^{-1} cm^{-1}. Pd(II) complexes possess smaller ϵ values than similar Pt(II) complexes, which, along with the small λ_{max} values, may contribute to the smaller values of β for the Pd(II) complexes. The only other apparent trend is that the complexes having tbcda possess larger ϵ values than complexes having other dithiolates.

An analysis of the solvatochromic data was used to attempt to extract values of $\Delta\mu$ for the compounds **1**−**17**. According to theories of solvatochromism, the solvent-induced shifts in frequency ($\Delta\nu$) are a function of the ground-state dipole (μ_g), the difference in dipole moment between the ground and the excited state ($\Delta\mu$), the solvent−solute interaction radius (α), and the solvent refractive index (η).[47] Although many different expressions appear in the literature for this function, most take the form of expression 4:

$$\Delta\nu \approx \frac{\mu_g}{\alpha^3}\,\Delta\mu\Delta\,\frac{(2\eta^2-2)}{(2\eta^2+1)} \tag{4}$$

This relation implies that for compounds having the same interaction radius and ground-state dipole moment, a correlation should exist between absorption band frequency and the solvent refractive index function (third term in eq 4). This correlation is *not* observed

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for the M(diimine)(dithiolate) complexes, suggesting that the solvatochromism observed for these complexes is not a simple function of only the solvent refractive index and that other factors contribute to $\Delta\nu$. Therefore, values of $\Delta\mu$ cannot be extracted from solvatochromic data. The correlation of the solvatochromic data to the empirical Pt(NN)(SS) solvent scale was used to determine if any trends in the *degree* of solvatochromism could be found. Most of the compounds displayed solvatochromic shifts of similar magnitude (Figure 2). In general, the radial separation between the metal/dithiolate HOMO and the diimine LUMO, and therefore $\Delta\mu$, is not expected to change significantly through the series, based on the structures of the complexes and the orbital model that has developed. The only trend that emerged from the analysis was that the complexes having tdt ligands (**11**−**13**) appear to have slightly greater solvatochromic shifts than the other compounds. Because they have the same ground-state dipole moment as the other complexes and because there is no reason to assume that they have a different interaction radius, the solvatochromic data suggest that they possess a larger value of $\Delta\mu$.

The values of β for the series of compounds **1**−**17** appear to depend on optical charge-transfer properties, as predicted by the two-state model. The role of the metal ion, dithiolate, and diimine ligands in tuning the optical and nonlinear optical properties are considered below.

Role of the Metal. A primary interest in studying metalloorganic complexes for nonlinear optics is to explore how the inclusion of metal atoms in organic frameworks changes NLO properties. In certain NLO chromophores, transition-metal centers act as electron-donating or electron-accepting groups.[3] In other examples, the role of the metal is less clear, with electronic and structural effects proposed.[3]

The results in Table 1 indicate that Pt(II) complexes have enhanced β_μ values over Pd(II) analogues. The results for complexes **1**−**3** provide an opportunity for comparison of three complexes whose structures differ only in the metal ion. The metal has an effect of increasing both the wavelength and molar absorptivity of the charge-transfer-to-diimine absorption band following the order Pd(II) < Pt(II) < Ni(II) (Figure 1). This observation strongly supports metal orbital involvement in the charge-transfer-to-diimine excited state. This trend in wavelength, which has also been observed for the CT absorption band of $M(bpy)R_2$ complexes (with M = Ni, Pd, Pt), follows the trend in second ionization potentials of the metals.[48] Comparison of the CT absorption properties of the complex Pd(dpphen)(tdt) (**13**) (λ_{max} = 538 nm, ϵ = 4500 L mol^{-1} cm^{-1}) with those of the analogous Pt(dpphen)(tdt) complex (λ_{max} = 594 nm $\epsilon \sim$ 7000 L mol^{-1} cm^{-1}) further support the trend. The latter complex was prepared for EFISH measurements but was not able to be used due to absorption interference. It is interesting to note that Vogler and co-workers reported that, for the series of complexes M(BABA)(dithiolate) where M = Pt(II), Pd(II) and Ni(II), BABA = biacetylbis(anil) and dithiolate = mnt and tdt, the CT absorption maximum depends only slightly on the metal ion, although the molar extinction coefficients follow the same trend that is observed for complexes **1**−**3**. [49]

The greater SHG efficiency of platinum complexes relative to palladium analogues has been reported in the literature for other metalloorganic systems. For a series of complexes of the type $M(PEt_3)_2$(X)(4-Y-phenyl) where M = Pd(II), Pt(II), X = Br$^-$, I$^-$ and Y = NO_2, CHO, the platinum complexes show slightly higher SHG intensities from powder samples in each case.[50] Similarly, powder SHG signals were greater for $Pt(bpy)Cl_4$ than for $Pd(bpy)Cl_4$, in which the metal ions are in the M(IV) oxidation state.[51] Although the results of these powder tests indicate that Pt compounds possess greater optical nonlinearities than Pd analogues, the influence of bulk properties of the solids (crystal lattice space group, particle size, etc.) on the measured SHG intensity limits the value of such comparisons. EFISH measurements of complexes having a ferrocene donor group and metal halide acceptor group were reported by Balavoine and indicate that β increases along the series Ni(II) < Pd(II) < Pt(II).[52,53] Other complexes of third-row metal ions do not show enhancements over those of second-row metal ions. For example, EFISH results for the series $M(CO)_4$(1,10-phenanthroline) show no difference in the value of β_μ for M = Cr, Mo, and W, even though the relevant CT excited state is MLCT in nature.[30] In the case of $(Cp)_2$M(4-nitrostyrylpyridine) systems, iron-containing complexes have greater β_μ values than ruthenocene derivatives. This difference was attributed to lower lying d-orbitals of Ru(II), which results in a higher frequency MLCT transition.[29] These different trends indicate that an understanding of how metal d orbitals affect molecular hyperpolarizabilities requires an understanding of the influence of metal orbitals on the optical charge-transfer properties.

The ground-state dipole moment does not change appreciably between complexes having different metal ions, and this result reflects the placement of the metal ion in the center of the molecule. The solvatochromic shifts also do not change significantly between Ni, Pd, and Pt analogues. This supports the idea that $\Delta\mu$ is insensitive to the metal ion, because $\Delta\nu$ depends on the product of μ and $\Delta\mu$.

Replacing the group VIIIB metal ion in the M(diimine)(dithiolate) chromophore with Zn(II) has a profound influence on the optical CT properties. The LLCT absorption band of Zn(dpphen)(tdt) (**15**) ($\lambda_{max} \cong$ 440 nm, $\epsilon \cong$ 40 L mol^{-1} cm^{-1}) is shifted to shorter wavelength and decreases greatly in intensity relative to the charge-transfer-to-diimine absorption band of Pd(dpphen)(tdt) (**13**) (λ_{max} = 538 nm, ϵ = 4500 L mol^{-1} cm^{-1}) or Pt(dpphen)(tdt) (λ_{max} = 594 nm, ϵ = 7000 L mol^{-1} cm^{-1}). These changes are attributed to the influence that the Zn(II) ion has, relative to the group VIIIB metal ions, on both the energy of the HOMO and the orbital overlap

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between the HOMO and LUMO. The closed-shell d^{10} Zn(II) ion is proposed to have only a small orbital contribution to the HOMO, which is consistent with the high oxidation potential for Zn(II). The tetrahedral geometry also leads to poor orbital overlap between the HOMO and LUMO, as supported by calculations of the dependence of the molar extinction coefficient on the torsion angle between the ligands.[17] The small value of β_μ for complex **15** coincides with a short-wavelength and low-intensity CT absorption band. The results indicate that large values of β are not anticipated for Zn(diimine)(SS) compounds, where S = thiolate or SS = dithiolate, in accordance with the two-state model (eq 1).

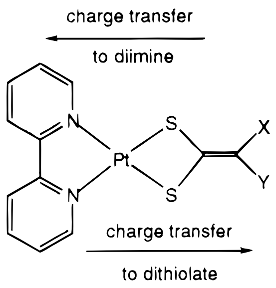
The complex $PtBr_2$(dpphen)(tbcda) (**16**) is an analogue to the Pt(diimine)(dithiolate) system, in which the oxidation state and coordination number of the metal ion has been changed. Oxidation from Pt(II) to Pt(IV) leads to a decrease in the electron-donating ability of the metal center, which is reflected in a decrease in the CT band wavelength and a decrease in β_μ. Unfortunately, information regarding the effect of either oxidation to Pt(IV) or the occupation of axial sites by Br^- on ϵ or $\Delta\mu$ could not be obtained from the absorption spectra.

Role of the Dithiolate. The dithiolate ligand acts as an electron donor in the M(diimine)(dithiolate) chromophore, and therefore contributes to the orbital composition of the HOMO. A wide variety of thiolates and dithiolates are known to coordinate to transition metals,[54−57] and several have been utilized for square-planar mixed-ligand systems. Seven (di)thiolate ligands having differing electron-donating strengths are included in this study. In addition, structural variation is achieved in using dithiolates that form four- or five-member chelate rings as well as in using monodentate thiolates.

Several of the complexes contain 1,1-dithiolates of the type $S_2C{=}C(X)(Y)$, where X = cyano and Y = *tert*-butylcarboxy or menthylcarboxy, or X = Y = ethylcarboxy. Comparison of the absorption spectra for compounds that differ only in the groups X and Y indicates that these groups have small effects on the electronic structure of the dithiolate ligands. For example, the CT absorption maxima for the compounds Pt(dpphen)(dithiolate) with dithiolate = tbcda (**1**), mncda (**4**), and demd (**6**) differ by only 11 nm, and molar absorptivity is insensitive to changes in the X and Y groups. The EFISH results for these three compounds, as well as for the two Pd(dpphen)(Rcda) compounds, where R = *tert*-butyl (**2**) or menthyl (**5**), are less clearly interpreted. Although the similar values of β_μ for compounds **1** and **6** agree with the similarity in their CT properties, the lower values for the mncda complexes **3** and **4** relative to the tbcda analogues presently is not understood.

The tbcda, mncda, and demd donor ligands contain electron-withdrawing groups in conjugation with the dithiolate unit, which may result in two effects that reduce the magnitude of β in complexes having these ligands. The first effect is that the electron-withdrawing cyano and ester groups decrease the electron-donating strength of the dithiolate. The tdt, edt and thiophenolate ligands lack these electron-withdrawing groups, and the λ_{max} and β values are increased in complexes having these stronger dithiolate donors. The second effect relates to the presence of low-energy charge-transfer-to-dithiolate excited states. A low-energy π^* orbital of some dithiolates is capable of acting as an acceptor orbital in a charge-transfer-to-dithiolate transition. Charge-transfer-to-dithiolate excited states have been characterized for complexes of the type $[Ir(L\text{-}L)(Rcda)]^-$, $[Pt(Rcda)_2]^{2-}$, and Pt(L-L)(Rcda) systems where L-L = chelating phosphines or 1,5-cyclooctadiene.[58−60] In mixed-ligand Pt(diimine)(Rcda) complexes, assignment of a charge-transfer-to-dithiolate transition in the absorption spectra has not been made, but molecular orbital calculations suggest that it lies at higher energy than the charge-transfer-to-diimine transition.[6]

Scheme 2



Two vectorially opposed charge-transfer axes, one involving charge-transfer-to-diimine and the other involving charge-transfer-to-dithiolate, are expected to limit the molecular hyperpolarizability (Scheme 2). The effect of opposing charge-transfer axes in compounds having multiple donor and acceptor groups has been studied for several organic and at least one coordination compound.[61,62] The results demonstrate that, unless the two charge-transfer axes can add vectorially to give a substantial sum, the molecule will have diminished optical nonlinearity. The effect increases as the two transitions become closer in energy.

It was mentioned above that the tbcda ligand possesses an intraligand charge-transfer excited state. To probe if dithiolate-localized ILCT contributes to the optical nonlinearity of complexes having tbcda, the compound tbdyca was investigated. Although compounds similar to **18** were reported to have β_μ values of 13×10^{-30} esu as measured by EFISH,[14] the negligible value of β_μ for compound **17** found in this study indicates that an ILCT excited state localized on the tbcda ligand does not appear to significantly influence the value of β_μ for the tbcda complexes.

The results in Table 1 demonstrate that complexes having dithiolate or thiolate ligands that do not possess electron-withdrawing substituents exhibit enhanced

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values of β_μ. The ethanedithiolate (edt) ligand in compound **7** serves to increase $\lambda_{\max}$ by a small amount over the Rcda and demd analogues, but ϵ is coincidentally decreased, and the values of β_μ for complexes **1**, **6**, and **7** are very close in magnitude. It is interesting to note that the ethanedithiolate moiety has also served as an electron-donor group in push−pull polyenes, and a study by Zyss and co-workers indicated that the electron-donating strength of a dithio group can be as large as that for a dimethylamino group in these polyenes.[63] The toluenedithiolate (tdt) ligand lowers the CT absorption band energy a significant amount from analogous Rcda, demd, or edt complexes, as can be seen from the absorption band maxima for Pt(dpphen)(tdt) (594 nm) vs Pt(dpphen)(tbcda) (457 nm) or for Pd(dpphen)(tdt) (538 nm) vs Pd(dpphen)(tbcda) (390 nm). The molar extinction coefficient is also lowered by approximately 50% for the complexes having tdt. The solvatochromic data suggest that the tdt complexes may involve a greater degree of change in dipole moment upon excitation, as reflected by their greater solvatochromic shifts relative to other dithiolate complexes. The EFISH results show that the tdt complexes possess larger values of β_μ than analogues having Rcda, demd, or edt donor ligands. For example, Pt(dmbpy)(tdt) ($\beta_\mu = -25 \times 10^{-30}$ esu) and Pt(phen)(tdt) ($\beta_\mu = -28 \times 10^{-30}$ esu) have larger molecular hyperpolarizabilities than the similar Pt(dpphen)(tbcda) ($\beta_\mu = -15 \times 10^{-30}$ esu) complex. The differences between the analogous Pd(dpphen)(dithiolate) complexes **2** and **13**, with dithiolate = tbcda and tdt, are less significant.

Among the compounds having the largest optical nonlinearities are the complexes **9** and **10**, which have para-substituted thiophenolate ligands. Although, the *p*-aminothiophenolate and *p*-methoxythiophenolate donor ligands do not lower the CT absorption band energy as much as the tdt chelating dithiolate does, they significantly increase the magnitude of β. The amino groups of complex **9** serve to increase $\lambda_{\max}$ and the magnitude of β_μ from the values for complex **10**, which has methoxy substituents. These results agree with the relative donor strengths of these groups in organic compounds. Complexes having thiophenolate derivatives with H and NO_2 in the para position continue the trend of decreasing $\lambda_{\max}$ as the thiolate becomes a weaker electron donor.

Role of the Diimine. A low-energy empty π^* orbital of the diimine serves as the electron-accepting orbital in the M(diimine)(dithiolate) chromophore. A full study of how electron-donating and electron-withdrawing substituents on 2,2′-bipyridine and 1,10-phenanthroline affect the charge-transfer-to-diimine excited-state properties has been presented recently.[16] Unfortunately, only a few compounds in which the diimine alone was varied were able to be studied by EFISH. Compounds Pt(dmbpy)(tdt) (**11**) and Pt(phen)(tdt) (**12**) have β_μ values that are too close in magnitude to distinguish, but the molecular hyperpolarizability for Pt(dpphen)(tbcda) (**1**, $\beta_\mu = -15 \times 10^{-30}$ esu) is significantly larger than that for Pt(tmphen)(tbcda) (**14**, $\beta_\mu = 0$ esu). The longer-wavelength charge-transfer-to-diimine absorption band for compound **1**, relative to that for compound **14**, arises from a lower LUMO for dpphen than for tmphen, and supports the increase in the magnitude of β_μ.

Conclusions

The relationship between the optical charge-transfer properties and molecular hyperpolarizabilities for a series of M(diimine)(dithiolate) and related compounds has been investigated. The magnitude of β can be varied substantially with changes in molecular structure and substituents. The factors that are important to the two-state model can be used as guidelines for the design of this chromophore. The most important factor is the CT absorption band wavelength, which appears to influence β most strongly. The results of this study, as well as the results from previous work, provide methods for tuning $\lambda_{\max}$ by changes in the metal ion, dithiolate and diimine ligands in a predictive manner.

The oscillator strength and $\Delta\mu$ are two other factors that are important to the two-state model, but their values are less easy to tune and less easy to predict. In agreement with the results of previous studies, the Pt(II) metal ion serves to increase the oscillator strength to a greater degree than Pd(II) or Ni(II) in square-planar M(diimine)(dithiolate) complexes. Dithiolate ligands also play a role in tuning f, but no dependence on the diimines studied was observed. The difference in dipole moment between the ground and CT excited states is a factor that appears to be insensitive to variation in the M(diimine)(dithiolate) complexes studied.

The results of this study indicate strategies for increasing the molecular hyperpolarizability of M(diimine)(dithiolate) complexes. Pt(II) metal centers provide the largest benefits to optical nonlinearity on the basis of the shift to longer wavelength and greater oscillator strength of the CT absorption bands that they affect. Because the HOMO is comprised of orbital contribution mainly from the dithiolate chelate ring, increasing the length of conjugation of the dithiolate is not expected to influence $\Delta\mu$ and β. However, the electronic properties of the dithiolate are important to the energy of the HOMO, and new dithiolate ligands having electron-donating substituents would be effective in increasing the donor strength of the dithiolate. Because the LUMO is localized on the diimine, $\Delta\mu$ may be increased by extending the conjugation length and by placing electron-withdrawing substituents further from the metal center.

Future work is directed at studying the effect of the diimine on tuning the NLO properties and the incorporation of these compounds into polymer hosts in order to develop bulk materials for nonlinear optics. The degree of understanding as to how optical properties of metalloorganic compounds relate to their nonlinear optical properties is not nearly as developed as that for organic compounds. The study of additional compounds related to those presented here may help to identify unique properties or advantages of metalloorganic chromophores.

Experimental Section

Synthesis and Characterization of Compounds. The compounds 4,7-diphenyl-1,10-phenanthroline (dpphen), 3,4-toluenedithiol (H_2tdt), 1,2-ethanedithiol (H_2edt), 4-aminothiophenol (Hatp), 4-methoxythiophenol (Hmtp), 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen) and (−)-menthol were

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purchased from Aldrich Chemicals and used as received. $PdCl_2$ was used as received from Johnson Matthey Alfa/Aesar.

The compounds Pt(dpphen)Cl_2, Pt(tmphen)Cl_2, 1-(*tert*-butylcarboxy)-1-cyanoethylene-2,2-dithiolate (K_2tbcda), 1,1-bis(ethylcarboxy)ethylene-2,2-dithiolate (K_2demd), Pt(dpphen)(tbcda) (**1**), and Pt(dpphen)(edt) (7) were prepared according to literature methods,[6,8,64,65] and the syntheses of Pt(dmbpy)(tdt) (**11**), Pt(phen)(tdt) (**12**), and Pt(dpphen)(tbcda)Br_2 (**16**) are presented elsewhere.[13,16]

Pd(dpphen)(tbcda) (2). Samples of $PdCl_2$ (177 mg) and dpphen (336 mg) were heated in 75 mL of H_2O with 1 drop of HCl for 15 h. The resulting yellow precipitate was filtered, washed with water, and dried under vacuum. The 478 mg of Pd(dpphen)Cl_2 isolated was suspended in 25 mL acetone, and a solution of 300 mg K_2tbcda dissolved in 30 mL MeOH was added. The mixture turned a bright yellow-orange color within a few minutes and was allowed to stir at room temperature for 3 h. The precipitate was filtered, washed with water, methanol, and diethyl ether and dried under vacuum. The yield was 550 mg (90% based on Pd). ^{1}H NMR ($CDCl_3$) δ 8.45 (1 H, d, $J = 4$ Hz), 8.40 (1 H, d, $J = 5$ Hz), 8.05 (2 H, s), 7.70 (2 H, dd) 7.60 (10 H, m), 1.33 (9 H, s). Anal. Calcd for $C_{32}H_{25}N_3O_2PdS_2$: C, 58.76; H 3.85. Found: C, 58.13; H, 3.87.

Ni(dpphen)(tbcda) (3). This compound was prepared following the procedure for Pd(dpphen)(tbcda), using $NiCl_2$ in place of $PdCl_2$. The resulting orange-brown solid was determined to be a mixture of products, presumably Ni(dpphen)(tbcda) and [Ni(dpphen)$_2$][Ni(tbcda)$_2$], as indicated by electronic spectroscopy. The desired product was separated using preparatory thin layer chromatography on silica plates. A yield was not determined. ^{1}H NMR ($CDCl_3$) δ 8.38 (1 H, d, $J = 8$ Hz), 8.31 (1 H, d, $J = 4$ Hz), 8.01 (2 H, s), 7.69 (2 H, dd,) 7.58 (10 H, s) 1.46 (9 H, s).

K_2(mncda). Cyanoacetic acid (10.8 g) was dissolved in 40 mL of CH_2Cl_2 and 4 mL of DMSO and cooled to 0 °C. A solution of 12 mL oxalyl chloride in CH_2Cl_2 was slowly added, liberating much gas. The resulting yellow solution was stirred until gas evolution ceased (1 h). After reducing the volume under vacuum to approximately 5 mL, the acid chloride was redissolved in fresh CH_2Cl_2. A solution of 19.844 g of (−)-menthol in 50 mL of CH_2Cl_2 was added slowly and allowed to stir for 8 h, equilibrating to room temperature. Water (250 mL) was added, and the organic layer was extracted and washed with another 250 mL aliquot of water. The CH_2Cl_2 solution was reduced to 75 mL under vacuum and cooled to −2 °C overnight. Further reduction of the solvent yielded a tan precipitate, which was filtered and characterized as menthylcyanoacetate. ^{1}H NMR ($CDCl_3$) δ 4.75 dt (C*H*O), 3.41 (CH_2), 2.01−0.74 multiplets shifted from (−)menthol. IR (KBr, cm^{-1}) 2263 (CN), 1738 (CO). The dithiolate was prepared by a modification of the method of Jensen and Henricksen.[65] A 0.9955 g sample of menthylcyanoacetate, 0.6077 g of KOH, and 0.35 mL of CS_2 were reacted in dioxane at 10 °C for 1.5 h. The solvent was then removed under vacuum, and the addition of acetone caused the precipitation of a yellow powder, which was filtered and washed once with acetone. The crude product was used without further purification, although it most likely contained a small amount of KOH impurity. ^{1}H NMR ($CDCl_3$) δ 4.63 dt (C*H*O), 2.00−0.75 multiplets.

Pt(dpphen)(mncda) (4). The complex was prepared using the same procedure as for Pt(dpphen)(tbcda), except using K_2(mncda). ^{1}H NMR ($CDCl_3$) δ 8.81 (1 H, d), 8.75 (1 H, d), 8.07 (2 H, s), 7.79 (2 H, m), 7.67−7.60 (10 H, m), 4.76 (1 H, dt), 1.94−0.72 multiplets. IR (KBr, cm^{-1}) 2202 (CN), 1678 (CO), 1451 (C═C).

Pd(dpphen)(mncda) (5). The complex was prepared using the same procedure as for Pt(dpphen)(mncda), except using Pd(dpphen)Cl_2. ^{1}H NMR ($CDCl_3$) δ 8.58 (1 H, d, $J = 5$ Hz), 8.52 (1 H, d, $J = 5$ Hz), 8.04 (2 H, s), 7.76 (2 H, d, $J = 5$ Hz), 7.67−7.58 (10 H, m), 4.58 (1 H, dt), 1.86−0.67 multiplets. IR (KBr, cm^{-1}) 2202 (CN), 1683 (CO), 1457 (C═C).

Pt(dpphen)(demd) (6). This compound was prepared following the procedure for Pt(dpphen)(mncda), using 273.8 mg of Pt(dpphen)Cl_2 and 165.5 mg of K_2(demd) (demd = 1,1-bis(diethylcarboxy)ethylene-2,2-dithiolate). The product was recrystallized from $CHCl_3$ to give a bright orange powder. A synthetic yield was not determined. ^{1}H NMR ($CDCl_3$) δ 8.72 (2 H, dd), 8.09 (2 H, s), 7.76 (2 H, dd), 7.60 (10 H, m), 4.09 (4 H, q), 1.21 (6 H, t). IR (KBr, cm^{-1}) 1678 (CO), 1423 (C═C).

Pt(dpphen)(atp)$_2$ (8). A solution of 43 mg of aminothiophenol (Hatp) and 1.5 equiv of NaOH in MeOH was added to a suspension of 103.0 mg of Pt(dpphen)Cl_2 in 50 mL of acetone, turning the solution dark purple. After being stirred for 1 h, the solution was filtered via cannula into another flask to separate out unreacted Pt(dpphen)Cl_2. The volume was reduced under vacuum to 10 mL, and ether was added to precipitate a purple product. ^{1}H NMR ($CDCl_3$) δ 10.10 (2 H, d, 4 Hz), 7.98 (2 H, s), 7.72 (2 H, d, 8 Hz), 7.53 (14 H, m), 6.40 (4 H, d, 8 Hz), 3.36 (br). Anal. Calcd for $C_{36}H_{28}N_4PtS_2$: C, 55.73; H, 3.64. Found: C, 55.75; H, 3.60.

Pd(dpphen)(atp)$_2$ (9). The complex was prepared using the same procedure as for Pt(dpphen)(atp)$_2$, except using Pd(dpphen)Cl_2. ^{1}H NMR ($CDCl_3$) δ 9.17 (2 H, d, $J = 4.5$ Hz), 8.04 (2 H, m), 7.85 (2 H, s), 7.72 (2 H, d, $J = 4.5$ Hz), 7.64−7.59 (10 H, m), 7.28 (4 H, d, $J = 8$ Hz), 6.27 (4 H, d, 7 Hz).

Pt(dpphen)(mtp)$_2$ (10). This compound was prepared following the procedure for Pt(dpphen)(atp)$_2$, using 136.5 mg of Pt(dpphen)Cl_2 and 0.06 mL of 4-methoxythiophenol (Hmtp) and 40 mg of KOH. A yield of 203.5 mg of purple product was obtained (100% yield based on Pt). ^{1}H NMR ($CDCl_3$) δ 10.13 (2 H, d), 8.00 (2 H, s), 7.75 (2 H, d), 7.57 (14 H, m), 6.56 (4H d), 3.60 (6 H, s). Anal. Calcd for $C_{38}H_{30}N_2O_2PtS_2$: C, 56.64; H, 3.75. Found: C, 56.79; H, 3.70.

Pd(dpphen)(tdt) (13). A 270 mg sample of Pd(dpphen)Cl_2 was placed in a round-bottom flask under N_2, and 50 mL of degassed acetone was added to form a suspension. To this was added a solution of 0.08 mL of H_2tdt and excess NaOH in 30 mL of MeOH and 30 mL of CH_2Cl_2. The mixture, which turned red-purple, was stirred for several hours. The solvent was removed under vacuum, and the resulting purple residue was redissolved in ca. 5 mL of CH_2Cl_2 and filtered. This solution was poured into hexanes to precipitate a red-purple solid, which was filtered, washed with hexanes and ether and dried under vacuum. The yield was 246.7 mg (79% based on Pd). ^{1}H NMR ($CDCl_3$) δ 9.11 (2 H, dd, $J = 4$ Hz, 5 Hz), 7.93 (2 H, s), 7.74 (2 H, dd, $J = 5$ Hz), 7.57 (10 H, m), 7.05 (1 H, d, $J = 8$ Hz), 6.98 (1 H, s), 6.65 (1 H, d, $J = 8$ Hz), 2.15 (3 H, s).

Pt(tmphen)(tbcda) (14). This complex was prepared following the procedure for Pt(dpphen)(tbcda), using 220.0 mg of Pt(tmphen)Cl_2 and 206.0 mg of K_2(tbcda). A yield of 132.0 mg of a bright yellow solid was obtained (46% based on Pt). ^{1}H NMR (DMSO-d_6) δ 9.29 (2 H, s), 8.29 (2 H, s), 2.73 (6 H, s), 2.60 (6 H, s), 1.37 (9 H, s). Anal. Calcd for $C_{24}H_{25}N_3O_2PtS_2$: C, 44.58; H, 3.90. Found C, 44.58; H, 3.64.

Zn(dpphen)(tdt) (15). This complex was prepared following the general procedure outlined by Koester.[45] A 208.5 mg sample of Zn(tdt)$\cdot$2H_2O was partially dissolved in warm EtOH in a round-bottom flask. A solution of 316.0 mg of dpphen dissolved in warm EtOH was added, and an orange precipitate formed. The mixture was stirred for an hour, and the product filtered and washed with EtOH and diethyl ether. A synthetic yield was not determined. ^{1}H NMR ($CDCl_3$) δ 9.26 (2 H, d), 8.03 (2 H, s), 7.90 (2 H, d), 7.58−7.53 (10 H, m), 7.33 (1 H, d), 7.20 (1 H, s), 7.12 (1 H, d), 2.36 (3 H, s).

tbdyca (17). The compound *tert*-butyl-1,3-dithiolan-2-ylidenecyanoacetate (tbdyca) was prepared following the method of Jensen and Henricksen for analogous dithiolanes.[64] A sample of 1.00 g of K_2(tbcda) was dissolved in 70% EtOH in a round-bottom flask under N_2. A large excess of 1,2-dibromoethane was added, and the mixture was stirred and gently heated for ~3 h. The resulting bright yellow solution was reduced to 40 mL under vacuum and then poured into cold hexanes. A white solid precipitated from solution and was filtered, washed with water, and recrystallized from diethyl ether/water. A yield of 525 mg (63%) was obtained. ^{1}H NMR ($CDCl_3$) δ 3.54 (4 H, dd, $J = 8$ Hz, 16 Hz), 1.50 (9 H, s).

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Spectroscopic Characterization. ^{1}H NMR spectra were recorded on a Bruker AMX-400 spectrometer operating at 400 MHz. Chemical shifts are reported relative to TMS but were measured based on internal solvent peaks ($CDCl_3$, δ 7.24; DMSO-d_6, δ 2.49). Infrared spectra were recorded on a Mattson Galaxy 6020 FT-IR spectrophotometer, and samples were in KBr pellets.

Optical Spectroscopy. Absorption spectra were recorded on a Hitachi U-2000 UV−visible spectrophotometer having a wavelength range of 190−1100 nm, wavelength accuracy of ±0.4 nm, and a photometric accuracy of ±0.002 absorbance units. Only spectroscopic grade solvents were used for absorption measurements, and solvent backgrounds were subtracted from the sample absorption spectra.

Electric Field Induced Second Harmonic Generation and Related Experiments. The experimental details of the EFISH experiment have been described elsewhere.[14] All compounds were measured in dichloromethane solution using 1.91 μm radiation for both second harmonic and third harmonic measurements. The harmonic amplitudes and coherence lengths were measured separately. Measurements of solution density, refractive index, and dielectric constant for each sample were used to calculate β_μ.

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