On the Second-Order Nonlinear Optical Structure−Property Relationships of Metal Chromophores

Karel Base,[†] Mark T. Tierney,[†] Alain Fort,[‡] Jacques Muller,[‡] and Mark W. Grinstaff*,[†,§]

Department of Chemistry, P. M. Gross Chemical Laboratory, Duke University,
Durham, North Carolina 27708, and Institut de Physique et de Chimie des Materiaux de Strasbourg,
CNRS 67037 Strasbourg, France

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The synthesis and solvent-dependent second-order polarizability, β, responses of three new platinum(II) chromophores are reported. A strong correlation between the metal chromophore electronic structure and the second-order polarizability is observed that substantiates the use of the two-state model to design, optimize, and study new NLO chromophores.

Introduction

A current challenge in materials chemistry and engineering is to afford a specific macromolecular property by tuning a molecular structure through deliberate chemical changes. Materials that display nonlinear optical (NLO) activity are of fundamental interest and technological use for a number of photonic applications, including optical switching, communications, and data storage and retrieval.[1−8] The rational design of organic chromophores with specific NLO activity is possible since the development of structure−property relationships (SPRs).[9−13] In comparison, the relationship between structure and nonlinear optical activity for inorganic chromophores is not as well defined or understood.[14,15] To date, few metal chromophores approach the NLO responses of current organic chromophores, and we attribute this to the lack of NLO SPRs to guide the research and to the limited number of studies conducted.[16] Our approach for developing NLO SPRs relies on synthesizing and characterizing highly solvatochromic metallochromophores and measuring the second-order polarizability, β, in solvents of varying polarity.[17] Herein, we report the solvent-dependent β responses of three new platinum(II) chromophores and insights into the relationship between electronic structure and second-order polarizability.

NLO SPRs for organic compounds are developed by synthesizing donor−acceptor chromophores with a particular electronic structure and measuring the molecular polarizabilities. These data combined with computational studies provide a clearer picture of the factors that affect NLO responses and the interrelationships between the molecular structure and first-, second-, and third-order polarizabilities.[9−13,18−21] The relationship between the second-order polarizability, β, and the degree of charge-separated character (i.e., polarization, or bond-length alternation, BLA, MIX in polymethines) in the ground-state structure of an organic chromophore can be understood within the confines of a two-state model,

$$\beta \propto \frac{{\mu_{ge}}^2 \Delta\mu}{{E_{ge}}^2}$$

where β is proportional to the square of the transition dipole moment (μ_{ge}) and to the dipole difference between the first excited and ground states ($\Delta\mu$) and inversely proportional to the square of the transition energy (E_{ge}) between the ground

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[†] Duke University.

[‡] Institut de Physique et de Chimie des Materiaux de Strasbourg.

[§] http://www.chem.duke.edu/~mwg.

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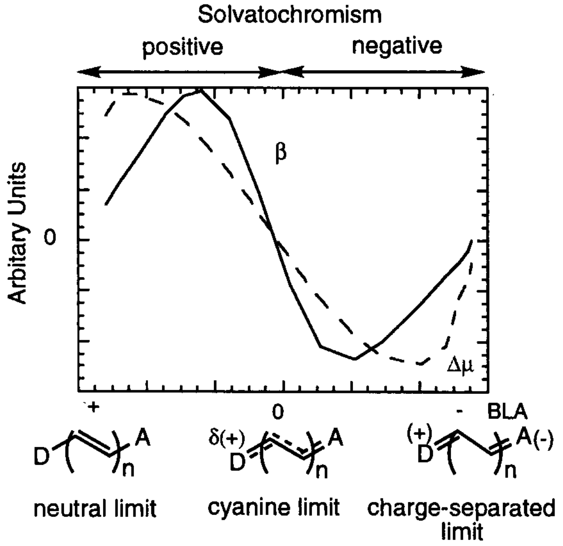

Figure 1. Structure–property relationship for linear polymethines where D = donor and A = acceptor.

and first excited states.[22–24] As shown in Figure 1, the second-order polarizability, β, for linear polymethines varies dramatically as the ground-state structure becomes more charge-separated, going from left to right along the x-axis. The second-order polarizability first increases going from the neutral polyene limit to the cyanine limit, and then reaches a maximum for an intermediate structure. Next, β decreases and passes through 0 at the cyanine limit. Moving from the cyanine limit to the charge-separated limit, β continues to decrease, becoming negative, and then reaches a minimum for an intermediate charge-separated structure. Finally, β increases and returns to 0 at the charge-separated limit. The regions of positive β values ($\Delta\mu > 0$) and negative β values ($\Delta\mu < 0$) are associated with positive and negative solvatochromism, respectively.

Results and Discussion

Square-planar d^8 platinum(II) compounds possess several favorable structural and physical properties[25,26] amenable to NLO study[15] and SPR development, including (i) rigid planar structures, (ii) high thermal stability, (iii) polarizable metal, (iv) solvatochromic transitions, (v) significant metal–ligand orbital overlap, and (vi) charge-transfer transitions. The ground-state dipole moment (≈10 D) of these donor (thiolate)–platinum–acceptor (diimine) complexes is aligned in the direction of the donor.[15] Importantly, the electronic structure (e.g., sulfur to oxygen) of these complexes can be varied dramatically while not substantially altering the metal coordination and geometry.

To ensure sufficient solubility for physical characterization and solvent-dependent β measurements, three new Pt(II) diimine dithiolate complexes containing sterically demanding groups were synthesized.[27,28] Reaction of 4,7-diphenylphenanthroline platinum(II) dichloride with the corresponding dithiolates or catecholate yielded **I**, **II**, and **III**. The molecular structures are shown in Chart 1.

Chart 1

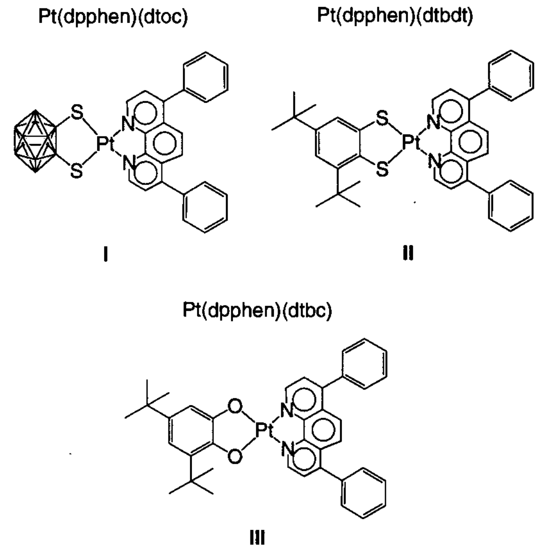

Table 1. Values of $\mu^*\beta(0)$ and λ_{max} for **I–III** in Various Solvents[a]

	$\mu^*\beta$ (0) (10^{-48} esu)/λ_{max} (nm)			
	C_7H_8 (0.099)[b]	$CHCl_3$ (0.259)	CH_2Cl_2 (0.309)	DMSO (0.444)
I	+118/483	−166/460		
II	−212/689	−412/634	−433/612	−480/590
III	−523/717	−635/657	−669/621	−597/601

[a] Top entries are $\mu^*\beta(0)$ values (in units of 10^{-48} esu) with an estimated error of ±10%. Bottom entries are the corresponding λ_{max} (nm) of the chromophore in a particular solvent. [b] Solvent polarities increase from left to right, and the normalized $E^N{}_T$ values of the solvent are denoted within parentheses.[29]

Solutions of **I**, **II**, or **III** exhibit an intense absorption at 290 nm for the $\pi-\pi^*$ transition of diphenylphenanthroline, and a second charge-transfer absorption at lower energy that is strongly solvatochromic (Table 1). All three chromophores display a hypsochromic (or blue) shift with increasing solvent polarity (i.e., negative solvatochromism),[29] and this effect is more pronounced in complexes **II** and **III**. For example, **III** is soluble in solvents ranging from toluene to methanol ($\Delta E \approx 4000$ cm^{-1}). Cyclic voltammograms of **I**, **II**, and **III** in CH_2Cl_2 (0.1 M $TBA^+PF_6^-$ vs Ag/AgCl) reveal a quasireversible reduction at approximately −1.2 V for the diimine reduction. Complexes **I** and **II** possess a quasireversible oxidation at 0.6 V, whereas **III** possesses a reversible oxidation wave at 0.4 V. Photoluminescence from **I** and **II** is observed at 298 and 77 K. **I** and **II** lie upon the line defined by the energy of emission vs the difference between the ground-state oxidation and reduction potentials of other previously characterized Pt(diimine)(1,2-dithiolate) complexes.[25,26] These data support a charge-transfer transition assignment from a mixed platinum–thiolate HOMO to a π^* diimine LUMO.

With regard to the SPR as presented in Figure 1, the negative solvatochromism (i.e., the ground state is more charge-separated than the excited state) of **I**, **II**, and **III** indicates that these Pt chromophores lie somewhere between the cyanine and charge-separated limits. Chromophore **I** possesses the largest oscillator strength of these three similar metal complexes, suggesting that it may lie nearest to the cyanine limit. The large solvatochromic

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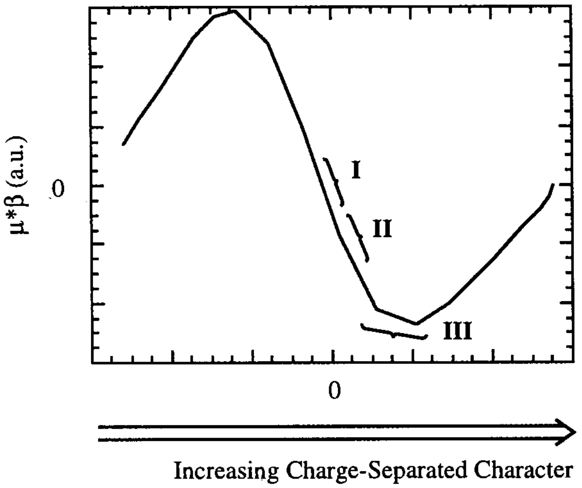

Figure 2. Second-order polarizability curve for **I**−**III**.

effect observed for these Pt(II) complexes also indicates that the magnitude of $\Delta\mu$ (the dipole difference between the first excited and ground states) is significant, and moreover $\Delta\mu$ increases from **I** to **III**. Chromophore **III**, the oxygen analogue, possesses the greatest charge-separated character and should be at the far right on the charge-separated axis. Qualitatively, the ground-state structures of **I**, **II**, and **III** display a gradual increase in charge-separated character and should represent specific regions between the cyanine and charge-separated limits in a SPR graph.

Electric-field-induced second-harmonic generation (EFISH) measurements of $\mu^*\beta(0)$ for **I**, **II**, and **III** were performed in solvents of increasing polarity using a fundamental wavelength of 1.907 μm.[30] A systematic tuning of the ground-state charge-separated character in these Pt chromophores was achieved by varying the solvent. The $\mu^*\beta(0)$ responses and absorption maxima as a function of solvent are presented in Table 1. Importantly, the second-order NLO responses vary with solvent polarity and span a wide range. As shown in Table 1, **I** possesses a positive signal in toluene and a negative one in chloroform. This change in $\mu^*\beta(0)$ sign on going to more polar solutions indicates that **I** lies near the cyanine limit. The $\mu^*\beta(0)$ responses of **II** are negative and decrease from toluene to DMSO. However, the negative $\mu^*\beta(0)$ responses for **III** first decrease and then increase as the solvent polarity increases, identifying the negative peak of the β curve. These results lead to the interpretation sketched in Figure 2 and allow us to assess the shape of the β curve for an inorganic chromophore.

Conclusions

A number of important conclusions can be drawn from these data, given the strong correlation between the metal chromophore electronic structure and the second-order polarizability. First, these platinum(II) chromophores possess solvent-dependent second-order polarizability responses, underlying the importance of both molecular structure and the influence of the solvent medium. Second, β for inorganic chromophores can be optimized and platinum chromophore **III** exhibits one of the largest negative second-order polarizabilities measured for a metal complex. Third, these data for inorganic chromophores conform to the two-state model which relates the molecular structure and the second-order polarizability. Fourth, as suggested previously for organic chromophores, this present study also proposes that NLO spectroscopy may be a new analytical tool for characterizing the electronic structure of inorganic complexes. Finally, these results further substantiate the use of the two-state model and its concepts for the design, optimization, and study of new NLO chromophores.

Experimental Section

All solvents were dried and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 400 MHz NMR. Elemental analyses were performed by E+R Microanalytical Labs. Absorption spectra were measured on a Hewlett-Packard 8452 diode array spectrometer. Emission spectra were recorded on a Perkin Elmer LS50B.

Pt(dpphen)(dtoc) (I). Pt(dpphen)(dtoc) was synthesized by reacting 1,2-dithiolato-*closo*-1,2-dicarbadodecaborane(12) with Pt(dpphen)Cl_2 and Proton Sponge in CH_2Cl_2 for 3.5 h (yield 82%). Anal. Calcd: C, 45.07; H, 3.78; N, 3.62. Found: C, 44.94; H, 3.93; N, 3.84.

Pt(dpphen)(dtbdt) (II). Pt(dpphen)(dtbdt) was synthesized by reacting 3,5-di-*t*-butylbenzenedithiol with Proton Sponge and Pt(dpphen)Cl_2 in CH_2Cl_2 for 5 h (yield 25%). Anal. Calcd: C, 58.52; H, 4.65; N, 3.59. Found: C, 58.65; H, 4.70; N, 3.51.

[Pt(dpphen)(dtbc) III. Pt(dpphen)(dtbc) was synthesized by reacting di-*tert*-butyl catechol with KOH and Pt(dpphen)Cl_2 in refluxing CH_2Cl_2 for 24 h (yield 74%). Anal. Calcd: C, 61.03; H, 4.85; N, 3.75. Found: C, 60.78; H, 4.91; N, 3.68.

EFISH Measurements. The conventional EFISH (electric-field-induced second harmonic) technique was used to measure the quadratic hyperpolarizability of the compounds.[30,31] The initial wavelength 1.064 μm of a Nd:YAG laser was shifted to 1.907 μm by stimulated Raman scattering in a high-pressure hydrogen cell. DC electric field pulses with amplitude up to 30 kV/cm were applied to the solutions placed in a wedge cell. The second-harmonic signals were calibrated to a quartz wedge (quadratic hyperpolarizability taken equal to 1.1 10^{-19} esu at 1.907 μm). Experimental details and analytical expressions for the mean microscopic hyperpolarizability γ are given in ref 31. Neglecting the purely electronic contribution (appropriate for medium-sized conjugated molecules) leads to the expression

$$\gamma = \frac{\mu\beta(2\omega)}{5kT}$$

where kT is the Boltzmann factor, μ_g is the dipole moment of the molecular ground state, and β stands for the vector part of tensor $\beta_{ijk}(2\omega)$. In the two-level approximation the dispersion dependence of the quadratic hyperpolarizability $\beta(\omega)$ is described by the simple dispersion factor

$$\beta(\omega) = \frac{\omega_{\max}^4}{(\omega_{\max}^2 - \omega^2)(\omega_{\max}^2 - 4\omega^2)}\beta(0)$$

where the ω's are the pulsations corresponding respectively to the fundamental laser wavelength λ and $\lambda_{\max}$ and $\beta(0)$ is the intrinsic static hyperpolarizability.

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