Chromophores

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Molecular Symmetry and Solution-Phase Structure Interrogated by Hyper-Rayleigh Depolarization Measurements: Elaborating Highly Hyperpolarizable D_2-Symmetric Chromophores**

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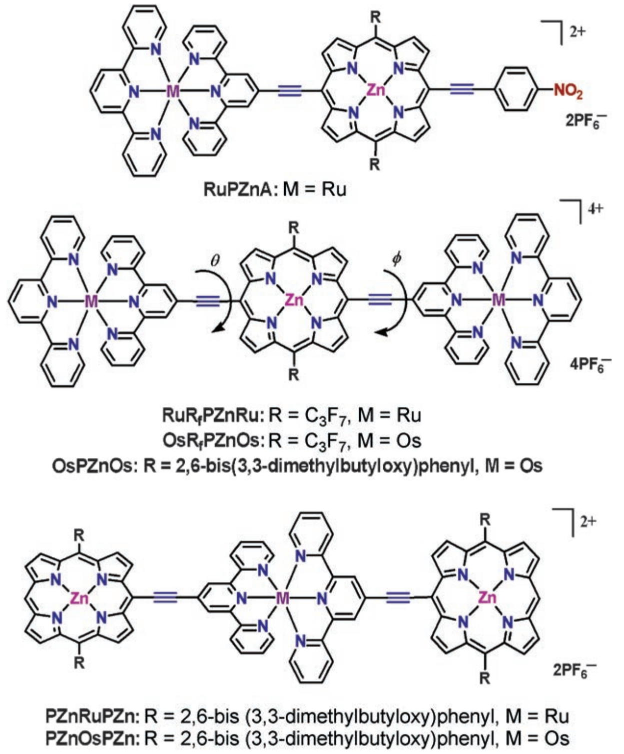
It has long been recognized that the measured magnitudes of dynamic hyperpolarizabilities (β_λ values) can depend sensitively on molecular structure.[1] Whether a chromophore with nonlinear optical properties (NLO chromophore) is an electronically asymmetric, dipolar, donor–linker–acceptor (D–L–A) molecule, or an electronically symmetric, yet noncentrosymmetric, D–L–D or A–L–A octopolar structure, oscillator strength and the extent to which charge is redistributed in electronic transitions depend on the degree of coupling of D and A to the conjugated L. In virtually all known NLO chromophores studied to date, the orientations of D, L, and A are not rigidly fixed; hence, the experimentally determined electronic coupling between these units is generally established by the distribution of condensed-phase conformeric populations set by the nature of D–L and L–A connectivity.[2] Further, if one considers octopolar chromophores, the requirement of noncentrosymmetry places further restrictions on important spatial relationships between D, L, and A: nearly all known NLO octopoles have either D_{3h} or T_d symmetry.[3] It has been recognized that D_2 and D_{2d} symmetries could be exploited in the design of single-oscillator octopolar NLO chromophores,[4] or octopolar compounds that exhibit metal-to-ligand charge-transfer transitions;[5] however, it has been stated that no interesting chromophoric benchmarks yet have such symmetries.[6] The few established NLO octopoles with D_2 symmetry are characterized by weakly coupled oscillators in which 3D charge redistribution occurs by a through-space delocalization mechanism.[7] We report here that strongly coupled D_2-symmetric oscillators provide an important motif for potent octopolar NLO chromophores and demonstrate the utility of hyper-Rayleigh light scattering (HRS) measurements[8] to interrogate conformeric populations of chromophores having D_2 and D_{2d} symmetries at ambient temperature in solution.

The utility of HRS in probing structure derives from the fact that it is intrinsically sensitive to symmetry; at the molecular level, a hyperpolarizable molecule must be noncentrosymmetric. When a substantial HRS signal is observed from an isotropic solution of molecules, at least a fraction of them must have noncentrosymmetric structures. This property of even-order nonlinear optical probes of electronic structure has been utilized to characterize the electrooptic characteristics of nondipolar chromophores **RuR$_f$PZnRu**, **OsR$_f$PZnOs**, **OsPZnOs**, **PZnRuPZn**, and **PZnOsPZn** (Scheme 1).



Scheme 1. Structures of investigated compounds.

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These nonemissive species belong to a class of supermolecules in which (porphinato)zinc(II) (**PZn**) and metal(II)polypyridyl (**M**) units are connected by an ethynyl linker that mixes effectively PZn-based and metal polypyridyl charge-resonance absorption oscillator strength, and aligns the respective charge-transfer transition dipoles of these chromophoric building blocks along the highly conjugated molecular axis.[9] These structures exhibit extensive excited-state interpigment electronic interactions, and are notable for having high oscillator strength excited-state absorptions over broad spectral windows of the near-infrared;[9b] related electronically asymmetric chromophores such as **RuPZn** and **RuPZnA** are known to manifest extraordinarily large β_λ values at telecommunication-relevant wavelengths.[9a] Interestingly, HRS measurements indicate that **RuR$_f$PZnRu**, **OsR$_f$PZnOs**, and **OsPZnOs**[9b] have nonzero dynamic hyperpolarizabilities; Table 1 lists NLO responses observed for these compounds at an incident irradiation wavelength λ_{inc} of 800 nm. Note that frequency-resolved femtosecond HRS measurements show neither demodulation nor an increase in phase delay with increasing amplitude modulation frequency, and this indicates the absence of any multiphoton fluorescence contribution to these observed HRS signals (Supporting Information).[8c] Moreover, the magnitudes of these hyperpolarizabilities greatly exceed the values that one could expect from local time-dependent solvent electric-field fluctuations at a centrosymmetric molecule.[10]

Table 1: Dynamic hyperpolarizabilities β [10^{-30} esu] and depolarization ratios ρ determined via hyper-Rayleigh light-scattering experiments at $\lambda_{\text{inc}} = 800$ nm.[a]

Compound[b]	β_{HRS}[c]	β_λ[d]	ρ
CV	208	340	1.4 ± 0.1
DR1	22[e]	54[e]	3.4 ± 0.3[e]
RuPZnA[9a]	90 ± 10	220 ± 20	2.9 ± 0.3
RuR$_f$PZnRu	165 ± 20	90 ± 10	1.7 ± 0.5
OsR$_f$PZnOs	200 ± 20	110 ± 10	1.9 ± 0.4
OsPZnOs[9b]	240 ± 20	130 ± 10	1.8 ± 0.4
PZnRuPZn	230 ± 35	123 ± 18	1.3 ± 0.2
PZnOsPZn	66 ± 4	36 ± 3	1.4 ± 0.2

[a] Conditions: $T = 20\,°\text{C}$, solvent = CH_3CN. β_λ values are independent of frequency modulation of the fundamental beam. [b] **CV** = crystal violet (purely octopolar); **DR1** = disperse red 1 (largely dipolar). [c] Defined as $[\langle\beta^2_{zzz}\rangle + \langle\beta^2_{yzz}\rangle]^{1/2}$. [d] Defined as β_{yyy} for **CV**, as β_{zzz} for $\rho > 2.5$, and as $\beta_{xyz} = \beta_{xzy} = \beta_{yxz} = \beta_{yzx} = \beta_{zxy} = \beta_{zyx}$ for $\rho < 2.5$. The relations between β_{HRS} and β_λ are $\beta^2_{\text{HRS}} = [\langle\beta^2_{zzz}\rangle + \langle\beta^2_{yzz}\rangle] = 8/21\,\beta^2_{yyy}$ for **CV** (D_{3h}), $\beta^2_{\text{HRS}} = [\langle\beta^2_{zzz}\rangle + \langle\beta^2_{yzz}\rangle] = 6/35\,\beta_2^{zzz}$ for dipolar compounds, and $\beta^2_{\text{HRS}} = [\langle\beta^2_{zzz}\rangle + \langle\beta^2_{yzz}\rangle] = 120/35\,\beta^2_{xyz}$ for octopolar (T_d, D_2, or D_{2d}) compounds. [e] Reference values for HRS experiments at 1300 nm, as **DR1** shows multiphoton fluorescence at $\lambda_{\text{inc}} = 800$ nm.[11]

Therefore, the conformeric populations of these compounds must have dipolar or octopolar symmetry in solution. To ascertain which of these possibilities is correct, HRS depolarization ratios ρ were determined.[12] The magnitude of ρ indicates the nature of the contribution to the NLO response: for a purely octopolar chromophore, a lower limit of 1.5 is found, while for an ideal dipolar ($C_{\infty v}$) molecule, ρ is 5.[13] This latter ρ value is attained only in the limit of an HRS experiment with an infinitely small numerical aperture for a hypothetical chromophore that has no finite off-diagonal tensor contributions to β_λ for the experimental molecular symmetry. The HRS depolarization ratios for classic octopolar chromophores, such as the tricyanomethanide anion crystal violet, **CV**, and 1,3,5-trihydroxy-2,4,6-trinitrobenzene have been determined to be 1.5;[14] in contrast, disperse red 1 (**DR1**), a benchmark dipolar chromophore, has a ρ value of 3.4 under identical experimental conditions (Table 1).

Compounds **RuR$_f$PZnRu**, **OsR$_f$PZnOs**, and **OsPZnOs** have depolarization ratios of about 1.5. The chemical topologies of these structures (see Scheme 1) exclude the possibilities of dipolar (i.e., C_{2v} symmetry with $\beta_{zxx} = -\beta_{zzz}$) or octopolar solution-phase symmetries of T_d or D_{3h}, and therefore suggest that the HRS response derives from structural conformers that have octopolar D_2 and D_{2d} symmetries. Such symmetries require **MPZnM** conformers having $\theta \approx -\phi$ and $\theta = -\phi = |45°|$, respectively, where these angles correspond to the torsional relationships between the terpyridyl (trpy) units and the PZn least-squares plane (see Scheme 1). As a D_{2h} structure is centrosymmetric ($\theta = \phi = 0°$), and the experimentally determined ρ values indicate that dipolar conformers ($\theta \neq -\phi$) contribute little to the measured HRS signal, the HRS depolarization experiments have a number of important consequences. While the barrier to rotation of unencumbered aromatics about a ≡ bond is low,[15a–c] conjugative interactions reduce the extent of condensed-phase conformational heterogeneity. If a Boltzmann-weighted distribution of torsional angles similar to that manifested by closely related conjugated structures is assumed, where $|\theta|$ and $|\phi|$ are predominantly less than 50°,[15c] only a few percent of the **MPZnM** conformers in solution will have structures in which $\theta \approx -\phi$. We therefore propose that the nonzero nonlinear optical response observed for **MPZnM** structures derives predominantly from a small population of conformers which have octopolar D_2 and/or D_{2d} structures at ambient temperature.

To test this hypothesis, additional control compounds **PZnRuPZn** and **PZnOsPZn** were synthesized (Scheme 1); these species are required to exhibit nearly homogeneous conformeric populations manifesting D_{2d} pseudosymmetry because the central terpyridyl units are fixed in an orthogonal configuration. Due to this structural feature, electronic coupling between the terminal PZn units of **PZnRuPZn** and **PZnOsPZn** is necessarily diminished with respect to that which exists between the terminal M units of their **MPZnM** analogues (Supporting Information). The analogous dynamic hyperpolarizabilities and depolarization ratios for **PZnRuPZn** and **PZnOsPZn** are compiled in Table 1. The nonzero hyperpolarizabilities of these species indicate noncentrosymmetry, and the corresponding depolarization ratios confirm that these NLO responses derive almost exclusively from octopolar structures.

While these data are consistent with the hypothesis that the substantial hyperpolarizabilities determined for nominally nonpolar **RuR$_f$PZnRu**, **OsR$_f$PZnOs**, and **OsPZnOs** derive from D_2/D_{2d} conformeric subpopulations present in solution, we emphasize that the β_{HRS} values measured for pseudo-D_{2d}-symmetric **PZnRuPZn** and **PZnOsPZn** stem

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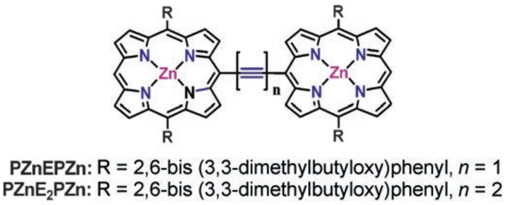
from essentially all of the chromophores probed in the HRS experiment. Given the differences in the solution-phase HRS-active conformeric populations between the **MR$_f$PZnM/MPZnM** and **PZnMPZn** chromophore families, it is important to stress other key factors that control the relative magnitudes of the measured β_{HRS} values. Note that, in addition to the disparate degrees of electronic communication between the terminal chromophoric components noted above, which influence the extent of charge redistribution in the key electronic states that contribute to β, resonance enhancement effects at $\lambda_{\mathrm{inc}} = 800$ nm for **PZnRuPZn** and **PZnOsPZn** are significantly less than those apparent for **RuR$_f$PZnRu**, **OsR$_f$PZnOs**, and **OsPZnOs** (see electronic absorption spectra in the Supporting Information).

The impact that an octopolar D_2/D_{2d} conformeric subpopulation has on measured solution-phase β_{HRS} values can be seen also in the related chromophores **PZnEPZn** and **PZnE$_2$PZn** (Scheme 2). Compounds **PZnEPZn** and **PZnE$_2$PZn** lack the oscillator strength and excited-state charge-redistribution contributions driven by the central M unit of the **PZnMPZn** structures, but feature strong PZn–PZn electronic coupling.[15] Previous studies on *meso*-to-*meso* ethynyl-linked (porphinato)metal compounds demonstrated that ethynyl-linked **PZnEPZn** has a modest distribution of PZn–PZn torsional angles in solution.[15a–d] In contrast, **PZnE$_2$PZn**,[15e–g] which has diminished electronic coupling between its PZn units relative to that of the **PZnEPZn** benchmark,[15a–c,16] necessarily has a larger distribution of torsional angles in the condensed phase. Because both **PZnEPZn** and **PZnE$_2$PZn** conformeric distributions are centered about a coplanar geometry, the more extensive torsional-angle distribution of **PZnE$_2$PZn** would be expected to feature larger Boltzmann-weighted populations of HRS active D_2- and D_{2d}-symmetric conformers.



Scheme 2. Structures of **PZnEPZn** and **PZnE$_2$PZn**.

Multiphoton fluorescence-free (Supporting Information) dynamic hyperpolarizabilities and depolarization ratios determined for **PZnEPZn** and **PZnE$_2$PZn** are listed in Table 2. Like **MR$_f$PZnM/MPZnM** and **PZnMPZn** chromophores, these two compounds are nondipolar. The data in Table 2 show clearly that both **PZnEPZn** and **PZnE$_2$PZn** have nonzero HRS responses, and dictate that HRS-active, noncentrosymmetric conformeric populations must be present in solution; determinations of depolarization ratios indicate that the HRS response must be derived from conformeric subpopulations with octopolar D_2/D_{2d} symmetry. It is important to compare these HRS responses to that observed for a dipolar **PZnE** benchmark compound (Table 2), which has a modest β_{HRS} value. Note that, while **PZnEPZn** and **PZnE$_2$PZn** HRS responses determined at $\lambda_{\mathrm{inc}} = 1300$ nm exhibit similar depolarization ratios, the dynamic hyperpolarizability measured for **PZnE$_2$PZn** is nearly twice that observed for **PZnEPZn**. Because **PZnEPZn** and **PZnE$_2$PZn** have closely related electronic absorption spectra (see ref. [15] and the Supporting Information), the difference between the measured β_{HRS} values for these two compounds cannot be ascribed to two-photon resonance-enhancement effects. Rather, the twofold greater HRS response of **PZnE$_2$PZn** reflects the greater degree of structural inhomogeneity of this species in solution relative to that of **PZnEPZn**, and a larger concentration of HRS-active D_2 or D_{2d} conformers in solution. These data for **PZnEPZn** and **PZnE$_2$PZn** define an archetypal example for which measurements of HRS hyperpolarizability and depolarization ratio can be used in tandem to probe the relative degrees of structural inhomogeneity of related chromophores in solution.

Table 2: Dynamic hyperpolarizabilities β [10^{-30} esu] and depolarization ratios ρ determined by means of hyper-Rayleigh light-scattering experiments at $\lambda_{\mathrm{inc}} = 1300$ nm[a] for **PZnEPZn** and **PZnE$_2$PZn**.

Compound	β_{HRS}[b]	β_{λ}[c]	ρ
PZnE	40 ± 20	100 ± 50	3.1 ± 1.0
PZnEPZn	410 ± 60	220 ± 30	1.3 ± 0.1
PZnE$_2$PZn	830 ± 100	440 ± 50	1.5 ± 0.1

[a] Conditions: $T = 20$ °C, solvent $=$ CH$_3$CN. β_{λ} values are multiphoton fluorescence-free high-frequency limits. [b] Defined as $[\langle \beta_{zzz}^2 \rangle + \langle \beta_{yzz}^2 \rangle]^{1/2}$. [c] Defined as β_{zzz} for $\rho > 2.5$, and as $\beta_{xyz} = \beta_{xzy} = \beta_{yxz} = \beta_{yzx} = \beta_{zxy} = \beta_{zyx}$ for $\rho < 2.5$. The relations between β_{HRS} and β_{λ} are $\beta_{\mathrm{HRS}}^2 = [\langle \beta_{zzz}^2 \rangle + \langle \beta_{yzz}^2 \rangle] = 6/35\,\beta_{zzz}^2$ for dipolar compounds, and $\beta_{\mathrm{HRS}}^2 = [\langle \beta_{zzz}^2 \rangle + \langle \beta_{yzz}^2 \rangle] = 120/35\,\beta_{xyz}^2$ for octopolar (T_d, D_2 or D_{2d}) compounds.

In summary: 1) Strongly coupled D_2-symmetric oscillators can act as potent octopolar NLO chromophores; 2) HRS depolarization experiments show that the measured hyperpolarizability in **MPZnM** structures derives predominantly from **MPZnM** conformers in which the torsional angles between the trpy units and the PZn plane are approximately equivalent in magnitude and opposite in sign, that is, this small solution-phase structural subpopulation has exceptional hyperpolarizabilities; 3) Analogous studies on **PZnMPZn** chromophores confirm that the substantial measured hyperpolarizabilities for these species derive from their pseudo-D_{2d}-symmetric structure; and 4) The NLO responses of ethynyl- and butadiynyl-linked bis(porphinato)zinc(II) chromophores **PZnEPZn** and **PZnE2 PZn** underscore that HRS signal intensity is correlated with the relative population of D_2/D_{2d}-symmetric conformers present in solution. Finally, the data reported herein not only demonstrate that molecular symmetry and solution-phase structure can be interrogated by means of measurements of HRS depolarization ratio; because D_2-symmetric octopolar chromophores provide the opportunity for biaxial alignment (e.g., by coordination of a binucleating ligand to the central metal ion of the porphyrin), **MPZnM** species may be hyperpolarizable building blocks for new classes of nonpolar chiral electrooptic materials.[15]

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Experimental Section

Synthetic procedures, characterization data, and NMR spectra of new compounds, as well as a description of the HRS instrumentation, are provided in the Supporting Information.

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[16] That solution-phase **$PZnE_2PZn$** has a greater number of D_2 and D_{2d} conformers, and hence diminished electronic coupling, is also confirmed by ultrafast spectroscopic experiments, which will be detailed elsewhere.

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