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Three-Dimensional Nonlinear Optical Chromophores Based on Through-Space Delocalization

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Abstract: Six permutations of 4-fold donor and/or acceptor substitution of paracyclophane at the 4, 7, 12, and 15 positions were synthesized to probe the phenomenon of three-dimensional delocalization on the nonlinear optical properties of organic materials. The interplay between through-bond intramolecular charge transfer (ICT) as well as three-dimensional, or through-space, ICT processes gives rise to large quadratic hyperpolarizability values. The determination of dipolar ($\beta_{J=1}$) and octupolar ($\beta_{J=3}$) irreducible tensor contributions to the overall β tensor value is made possible by the polarized harmonic light scattering technique at 1.32 μm. The electric field-induced second-harmonic generation technique was also used at 1.91 μm for comparison. Significant experimental β values for members of the series made of two centrosymmetric benzene-like units are a clear signature of a purely through-space ICT between two aryl subunits. The two configurational isomers that pair two dipolar donor−acceptor chromophores also exhibit octupolar character. Analysis of these two with an additive model for $\beta_{J=1}$ and $\beta_{J=3}$ reveals a strong three-dimensional inter-ring charge transfer.

Introduction

Nonlinear optics (NLO) has been successfully exploited toward a variety of applications for optical signal processing.[1] Among such phenomena, second-order or quadratic NLO effects provide the means for frequency addition, electrooptic (EO) modulation, and parametric amplification or oscillation. Third-order polarization allows for self-focusing, third harmonic generation, and two-photon absorption. These effects demand that highly efficient materials be engineered so as to amplify perturbations that are weak in linear optics.[2]

In this perspective, considerable efforts have been focused on the optimization of organic molecules in view of such favorable starting assets as their large π-electron-mediated nonlinear optical polarizabilities and the potential for broad design flexibility through chemical functionalization.[3] Literature reports are replete with examples based on the donor-conjugated bridge-acceptor design that displays intramolecular charge transfer (ICT) upon excitation.[3,4] Optical polarizabilities change considerably when increasing the length of the π-electron bridge and the strength of the donor and acceptor groups.[3−5] Despite this control, the dipolar character of D-π-A structures retains considerable drawbacks. Dipole−dipole electrostatic interactions often result in an antiparallel molecular arrangement and a subsequent cancellation of the nonlinear response at bulk materials. Additionally, the highly anisotropic structure of an optimized EO material, containing aligned polar rodlike molecules, is not compatible with the polarization independent NLO response (e.g., EO modulation) required for devices to be inserted in an optical telecommunication system.[6]

Combined group theory[7,8] and quantum mechanical principles[9] provide novel guidelines for nondipolar, molecular

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structures, which have become known as *octupolar* molecules. Several examples of such octupolar organic molecules have been shown to display large molecular hyperpolarizabilities. Threefold symmetry organic planar molecules[10,11] with triaminotrinitrobenzene (TATB) as a natural template extension of the earlier *p*-nitroaniline (pNA) paradigm; or ruthenium trisbipyridine derivatives[12,13] and their supramolecular dendritic assemblies providing multiple chirality features;[12c] as well as tetrahedral molecules based on copper complexes,[14] tin organometallics,[15] and phosphorus[16] or biphenyl templates[17] have been investigated.

To take full advantage of the extended two- and three-dimensional dimensionality for molecules bearing octupolar charge distributions, one would ideally design a three-dimensional conjugated core based on the (eventually distorted) cubic template, as proposed previously in ref 19 and displayed in Figure 1. Electron donor and acceptor groups must be attached to this core, using a regiochemically precise synthetic methodology in keeping with the desired symmetry of the target molecule. The [2.2]*p*-cyclophane (pCp) framework provides a suitably flexible backbone in the form of an original polarizable transmitting unit that allows for subsequent functionalization. The two aromatic units are held in close proximity, at a distance shorter than the van der Waals distance.[18] Substitution at the 4, 7, 12, and 15 positions leads to an elongated cubic molecular structure with orthorhombic symmetry features allowing for three-dimensional multipolar spatial arrangements, including the boundary case of octupoles, as shown in the upper part of Figure 1.

An original feature of this pCp building block, in contrast with previously investigated structures, is the eventual possibility of through-space charge transfer, whereby the more traditional fully or partially conjugated subunits are separated by a gap that enables subtle electromagnetic or tunneling interactions. Efficient ICT has been shown in a model dipolar chromophore 4-(4-dihexylaminostyryl)-16-(4-nitrostyryl)[2.2]paracyclophane[19] (molecule **1** in Figure 2). A simplified analogy to a semiconductor structure would picture **1** as a one-dimensional biased heterojunction where two electron-rich potential wells are joined via a junction acting as a tunneling barrier. Moreover, molecules based on pCp may be considered as a preliminary building block toward the study of interchromophore delocalization in the solid state.[20]

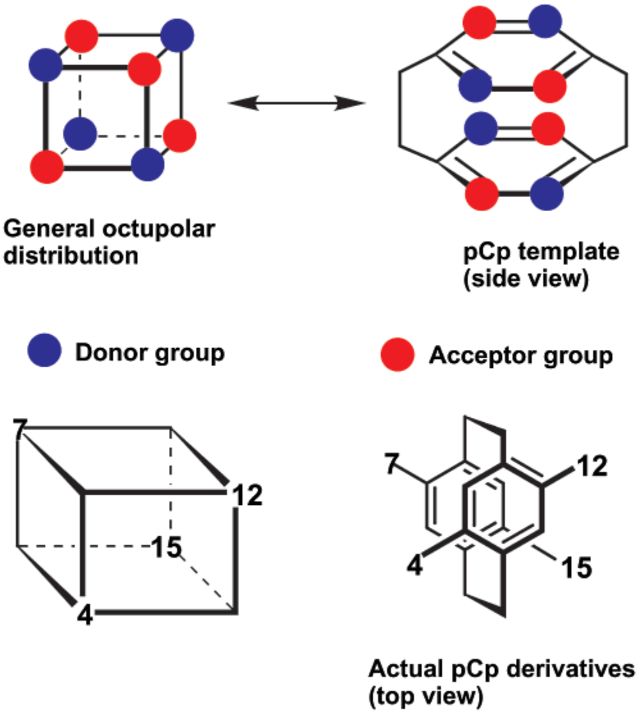

Figure 1. The (4,7,12,15)tetra-substitution pattern for [2.2]*p*-cyclophane (pCp) as a point-charge template for an octupole.

On the basis of these observations, we targeted pCp molecules with the 4,7,12,15-substitution pattern shown in Figure 1. Introduction of donor and acceptor groups generates molecules in which ICT takes advantage of the three-dimensional delocalization within the pCp core. This results in various multipolar structures where the second-order hyperpolarizability tensor β is comprised of both dipolar ($\beta_{J=1}$) and octupolar ($\beta_{J=3}$) contributions, according to the general tensorial relation for rank-3 symmetrical tensors:

$$\beta = \beta_{J=1} \oplus \beta_{J=3} \qquad (1)$$

We represent the disposition of donor and acceptor groups in the form of a distorted cube to highlight the geometric relationships between pCp substituents. Figure 2 shows the molecular structure of the chromophores prepared for this study together with the representation of donor−acceptor groups on a distorted cube.[21] Substitution consisting of four donor groups provides (4,7,12,15)-tetrakis(4′-dihexylaminostyryl)[2.2]paracyclophane (**2**) with the highest symmetry of the series. If rotational and cis/trans isomers are ignored, there are three C_2 axes leading to D_2 octupolar symmetry. This molecule can also be thought of as a relatively nonfluxional dimer of symmetrical

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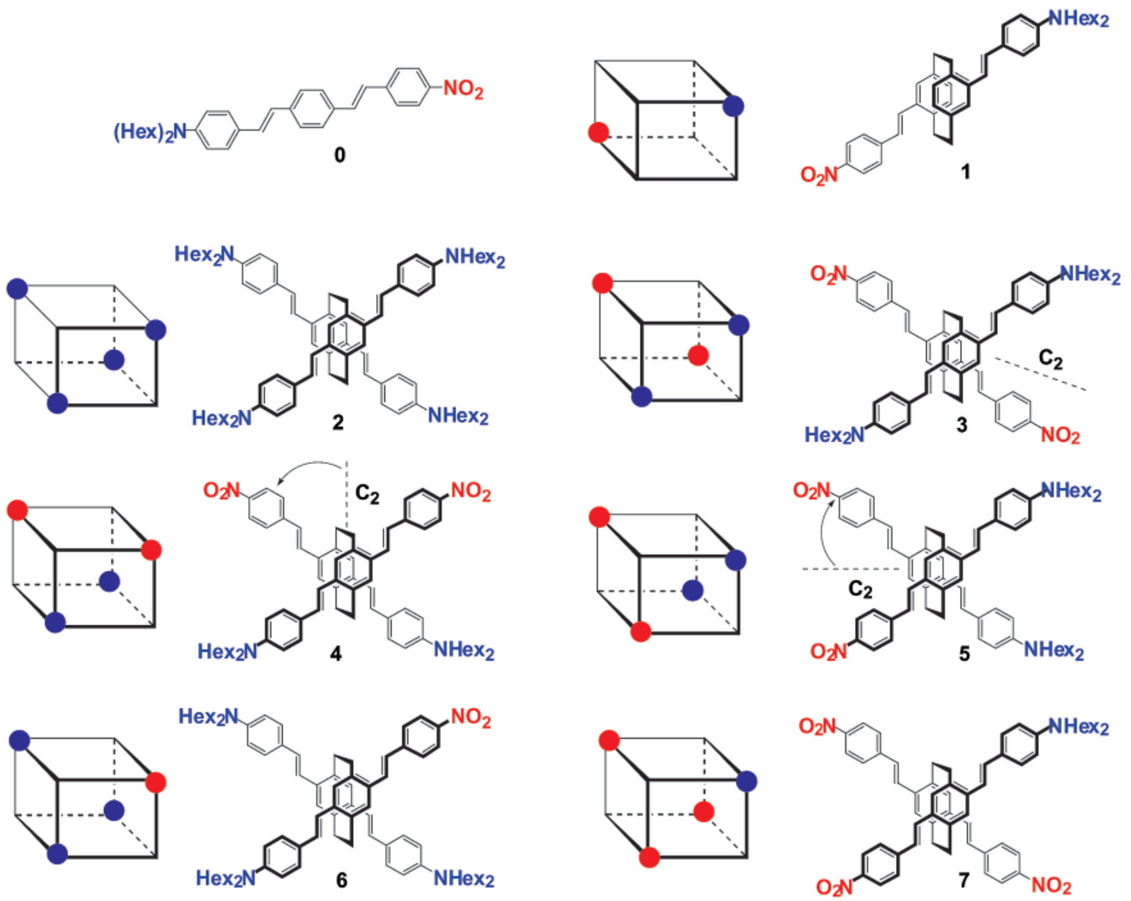

Figure 2. Tetra-donor−acceptor pCp molecules for this study with their respective cubic point-charge pattern.

D-π-D chromophores with enforced cofacial overlap at the central rings.

Compounds (4,15)-bis(4′-dihexylaminostyryl)-(7,12)-bis(4″-nitrostyryl)[2.2] paracyclophane (**3**), (4,7)-bis(4′-dihexylaminostyryl)-(12,15)-bis(4″-nitrostyryl)[2.2]paracyclophane (**4**), and (4,12)-bis(4′-dihexylaminostyryl)-(7,15)-bis(4″-nitrostyryl)-[2.2] paracyclophane (**5**) consist of substitution with two donor groups and two acceptors but differ in their regiochemistry. All three contain one C_2 axis but are distinguished by the orientation of that unique axis with respect to the paracyclophane core. Within the point-charge model, the basis for differentiation lies in the distortion of the cube. Compounds **4** and **5** can be thought of as contact pairs of D-π-A chromophores. The difference between the two lies in the relative orientation of the linear D-π-A fragments, the half-angle θ between the two D-A axes being 60° for compound **4** and 30° for compound **5**. Given the dipolar nature of the subunits, compound **5** should allow for a larger net dipole relative to **4**. In more descriptive terms, the scissorlike structure in **5** is more closed than in **4**. Compound **3** stands out as it brings together two centrosymmetric subunits, one a paradisubstituted donor and the other a paradisubstituted acceptor. This arrangement allows for a dipole that is oriented ring-to-ring in the paracyclophane subunit. A striking difference between **4** and **5** on one hand and **3** on the other hand is that the former are made up of the assembly of two strongly dipolar aromatic subunits, whereas the latter consists of two nonpolar centrosymmetric subunits, albeit leading to a polar overall system. For all three, the resulting dipoles fall along the unique C_2 axis.

With replacement of a single donor group with an acceptor in molecule **2**, all symmetry elements other than identity are lost, as in (4,7,12)-tris(4′-dihexylaminostyryl)-15-(4″-nitrostyryl)-[2.2]paracyclophane (**6**). Conceptually, this member of the series can be viewed as a D-π-A distyrylbenzene molecule brought into contact with a symmetric D-π-D chromophore. The molecule 4-(4′-dihexylaminostyryl)-(7,12,15)-tris(4″-nitrostyryl)-[2.2]paracyclophane (**7**) is analogous with **6** but with a substitutional transposition of donor and acceptor groups. This interchange leads to a molecule that, in the contact pair view, brings a D-π-A chromophore into contact with a symmetric A-π-A acceptor-type fragment.

Results and Discussion

The polarized harmonic light scattering (HLS) experiment[22] (also named hyper-Rayleigh scattering)[23] operating at 1.32 μm in chloroform solutions is used to sort out independently the norm of both dipolar ($||\beta_{J=1}||$) and octupolar ($||\beta_{J=3}||$) components,[24] using the nonlinear anisotropy $\rho = ||\beta_{J=3}||/||\beta_{J=1}||$ as inferred from depolarization ratio measurements and the total $<\beta^2{}_{\mathrm{HLS}}>$ value as measured by nonpolarized HLS:

$$<\beta^2{}_{\mathrm{HLS}}> = \frac{2}{9}||\beta_{J=1}||^2 + \frac{2}{21}||\beta_{J=3}||^2 \qquad (2)$$

The fundamental frequency ω is chosen far away from the

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Table 1. Values of the Maximum Absorption Wavelength λ_{max}, Dipole Moment μ, $\sqrt{\langle\beta_{ms}{}^2\rangle}$, ρ^2, and the Norms of $\beta_{J=1}$ and $\beta_{J=3}$ as Inferred from HLS, EFISH, and the Additive Model[a]

molecule	λ_{max} (nm)	μ (D)	$\sqrt{\langle\beta_{HLS}{}^2\rangle}$	ρ^2	$\|\|\beta_{J=1}\|\|$ (from β_{EFISH})	$\|\|\beta_{J=1}\|\|$ (from HLS)	$\|\|\beta_{J=3}\|\|$	$\|\|\beta_{J=1}\|\|_{add}$	$\|\|\beta_{J=3}\|\|_{add}$
0	416	7	126	3.2	150	170	310		
2	446		46	6.5		50	130		
3	433	3.4	50	6.3	155	55	140		
4	479	7	160	5.2	194	190	430	170	620
5	491	13.8	220	5.2	280	260	580	290	0
6	441	6.6	170	6.1	186	190	470	170	310
7	444	5.7	220	5.0	310	260	580	170	310

[a] Hyperpolarizability values are given at 1.32 μm (in 10^{-30} esu).

maximum absorption wavelength to avoid any two-photon fluorescence contribution to the scattered signal at 2ω.[25] Complementary electric field-induced second harmonic generation (EFISH) measurements at 1.91 and 1.32 μm have also been performed on nonoctupolar molecules **3**−**7** for comparison with the dipolar value $||\beta_{J=1}||$ as inferred from HLS. Dipole moments are determined using a WTW dipolemeter and an Abbe refractometer according to the Guggenheim model.[26] Experimental results are gathered in Table 1.

A first confirmation of the through-space ICT is evidenced by the significant nonzero β value of compounds **2** and **3**, although these pCp molecules are made of two centrosymmetric subunits. As expected from the D_2 symmetry of molecule **2**, the related three-dimensional charge transfer displays a strong octupolar character. The relatively weaker but nonzero dipolar contribution ($||\beta_{J=1}|| = 50 \times 10^{-30}$ esu vs $||\beta_{J=3}|| = 130 \times 10^{-30}$ esu) may arise from the fluctuations of the molecular geometry and the dipolar vibronic and rotational states contributing to the incoherent hyper-Rayleigh signal;[27] on the contrary, coherent EFISH measurements do not involve such fluctuations. From $||\beta_{J=3}||$ we infer the value of the unique nonzero Cartesian component of the β tensor:[14]

$$\beta_{XYZ} = 1/\sqrt{6}||\beta_{J=3}|| = 53 \times 10^{-30} \text{ esu at } 1.32\ \mu\text{m}$$

The β tensor of molecule **3** exhibits similar properties despite the apparently more dipolar features of its charge distribution. The significant β value of this molecule is strictly a signature of through-space interaction, as both constituent aromatic subunits are centrosymmetric and thus do not individually contribute to the overall β. The resulting β value is thus purely related to an interaction between the subunits as in the case of molecule **2** where the two subunits are identical. The main difference between **2** and **3** is the emergence, for the latter, of dipolar features along the single C_2 axis that are precluded in the former. The strong three-dimensional character of the charge transfer is related to a relatively high octupolar contribution to the β tensor, similar in magnitude to that observed in molecule **2**. The discrepancy between $\beta_{J=1}$ inferred from direct EFISH measurements and $||\beta_{J=1}||$ from HLS is not so surprising, as vibrational and rotational contributions might significantly modify the HLS signal, as pointed out before.[27]

Molecules **4** and **5** are made of two one-dimensional donor−acceptor subunits (molecule **0**) linked by two -CH$_2$-CH$_2$- bridges; they differ from each other by the value of the angle θ between the ICT axis of any of the two subunits with the C_2 symmetry axis (see Figure 2). Molecule **5** shows the largest dipole moment of the series, consistent with the angular relationship between the top and bottom D-π-A subunits. From the values of the dipolar ($\beta_{J=1}°$) and octupolar ($\beta_{J=3}°$) contributions to the β tensor of compound **0**, it is possible to evaluate the $||\beta_{J=1}||_{add}$ and $||\beta_{J=3}||_{add}$ values of these molecules on the basis of a two-dimensional additive tensorial model, assuming negligible through-space interaction between the two benzene-like subunits of the pCp molecules:[28]

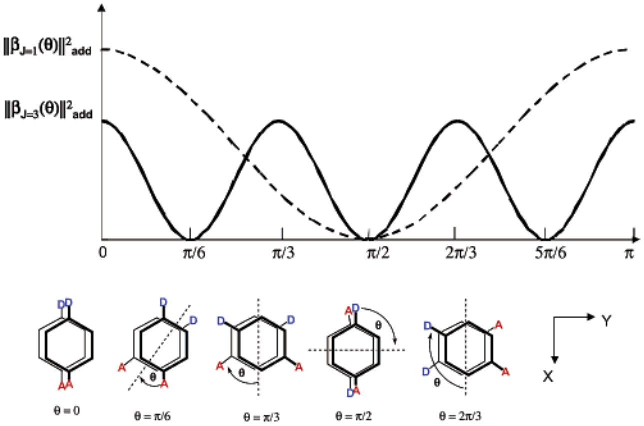

Figure 3. Progression of the additivity of $||\beta_{J=1}||^2$ (dashed) and $||\beta_{J=3}||^2$ (continuous) for molecules **4** and **5** as a function of θ, the half-angle between the dipole moment of the two D-π-A subunits of the pCp-based compounds.

$$||\beta_{J=1}||_{add} = 2 \cos\theta\ ||\beta_{J=1}°|| \tag{3}$$

$$||\beta_{J=3}||_{add} = 2 \cos 3\theta\ ||\beta_{J=3}°|| \tag{4}$$

The θ dependence of $||\beta_{J=1}||^2_{add}$ and $||\beta_{J=3}||^2_{add}$ is illustrated in Figure 3. It must be pointed out that such bimolecular stacking allows for a complete cancellation of the octupolar contribution to the β tensor when $\theta = 30°$, a configuration that cannot be met even in purely one-dimensional molecules where only one Cartesian component β_{xxx} differs from zero. Departure of the experimental $||\beta_{J=1}||$ and $||\beta_{J=3}||$ values from this model will be the signature of a significant through-space charge transfer.

From the results in Table 1, the experimental dipolar $||\beta_{J=1}||$ values of molecules **4** and **5** are satisfactorily accounted for by this additive model. This is consistent with the C_2 symmetry of the molecules, which precludes any vector-type contribution in a plane perpendicular to the C_2 axis. However, the additive model does not describe properly the experimental $||\beta_{J=3}||$ values. We suspect that these discrepancies may be accounted

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for by molecular distortions in solution, yielding to θ values that might significantly differ from those inferred from purely geometrical considerations (i.e., $\theta = 60°$ for **4** and $\theta = 30°$ for **5**). However, the large octupolar $||\beta_{J=3}|| = 580 \times 10^{-30}$ value reported for compound **5** is clearly not compatible with the $||\beta_{J=3}|| = 0$ as expected from the additive model, in the absence of any through-space ICT.

A similar behavior is also observed for molecules **6** and **7**. However, the departure from the additive model is more important for the $||\beta_{J=1}||$ of compound **7**. In such low-symmetry structures, some through-space contributions to the dipolar component of the β tensor may take place. The failure from the additive model for $||\beta_{J=3}||$ is large, especially in the case of compound **7**, and $||\beta_{J=3}||$ values come close to those reported for compounds **4** and **5**. This confirms the three-dimensional, multidirectional through-space character of the octupolar contribution for all pCp molecules reported in this work.

This nonlinear polarization behavior involving the whole molecular structure has been confirmed for the first-order hyperpolarizability β in the case of molecule **1**, using the collective electron oscillation (CEO) approach, which indicates a significant role of a through-space electronic delocalization in the second-order nonlinear response.[19] More recently, two-photon absorption spectra of compounds **2**−**7** have been computed using the third-order polarizability γ obtained from the same CEO method. Through-space charge-transfer interactions are found to play a crucial role in the two-photon absorption frequencies and cross-sections.[29]

Conclusion

In conclusion, we have reported a clear experimental evidence of large, if not dominant, through-space octupolar contributions to the second-order hyperpolarizability β tensor of various multipolar donor−acceptor pCp derivatives. As a result, there is a failure of simple tensorial additivity models that focus only on the properties of the constituent units in the paracyclophane pair, as in the case of molecule **5**. A more sophisticated treatment that incorporates through-space polarization effects must be developed. On another hand, the observed $||\beta_{J=1}||$ value in **3** shows that, even under circumstances where molecular design incorporates no dipolar features, a dipolar component may be generated from vibrational and rotational fluctuations away from the ideal molecular geometry. In a more general perspective, the availability of three-dimensional organic nonlinear octupolar molecules is a preliminary but important milestone toward the elaboration of polarization-independent materials for optical signal processing.

Experimental Details

Dipole Moment Measurements. The dipole moment μ is determined using the standard method of Guggenheim,[26] where μ is related to the refractive index n (respectively n_0) and to the dielectric constant ϵ (respectively ϵ_0) of a chloroform solution (respectively of pure chloroform) at a molecular concentration c:

$$\mu^2 = \frac{9kT}{4\pi N}\frac{3}{(\epsilon_0 + 2)(n_0^{\,2} + 2)}\left(\frac{(\epsilon - n^2) - (\epsilon_0 - n_1^{\,2})}{c}\right) \qquad (5)$$

where μ^2 is taken as the limit when c becomes vanishingly small. Refractive indices are measured with an Abbe prism refractometer (Carl Zeiss), and dielectric constants are obtained from capacitance measurements of a cylindrical condensator at 1 MHz (WTW), calibrated with a set of pure liquids of known dielectric constants. The temperature is maintained constant at 25 °C, and the relative experimental error does not exceed 2% on μ.

EFISH. The EFISH[30] is performed in chloroform solutions, with increasing concentrations ranging from 2.6×10^{-3} to 1.3×10^{-2} M. Most of EFISH experiments were performed at 1.91 μm, and a few measurements were done at 1.32 μm to check the validity of the two-level dispersion model for β. According to this model, static $\beta_{\mathrm{EFISH}}(0)$ values can be inferred from the experimental $\beta_{\mathrm{EFISH}}(\omega)$ data according to the following classical off-resonance expression:[29b]

$$\beta_{\mathrm{EFISH}}(\omega) = \beta_{\mathrm{EFISH}}(0)\,\frac{W^4}{(W^2 - (\hbar\omega)^2)(W^2 - (2\hbar\omega)^2)} \qquad (6)$$

where W is the energy of the ICT transition, and ω is the fundamental frequency. Using this expression, β_{EFISH} (1.32 μm) can be easily inferred from β_{EFISH} (1.91 μm). EFISH data reported in Table 1 are given at 1.32 μm to allow for adequate comparison with HLS results.

The 1.91 μm fundamental laser beam was obtained by Raman shifting of the 1.064 μm Nd^{3+}/YAG laser frequency by focusing the 1.06 μm beam in a high-pressure hydrogen cell (30 bar). A liquid cell with thick windows in the wedge configuration was used to determine the Maker fringes pattern. The incident beam was synchronized with a DC field (4×10^6 V m^{-1}) to induce the breaking of centrosymmetry via dipole−DC field coupling. Calibrations are made with respect to the pure solvent. Relative experimental errors do not exceed 3%.

Harmonic Light (or Hyper-Rayleigh) Scattering. The approach followed here relies on HLS as initially proposed and developed by Terhune et al.[22] A transverse single mode Nd^{3+}:YAG laser is used as the fundamental source, consisting of 10 mW peak power, 90 ns duration IR pulses at 1.32 μm, and a 10 Hz repetition rate. The incident IR intensity can be continuously monitored by a half-wave plate rotated between two crossed Glan polarizers. A small part of the incident beam is removed at a low reflection angle by a glass plate and sent onto a highly nonlinear NPP (*N*-4-nitrophenyl-prolinol)[31] powder used as a reference frequency doubler. The emitted second harmonic signal is detected by a photomultiplier. The main fundamental beam is focused into the sample using an 8 cm focal length converging lens. The sample cell is a rectangular spectrophotometric cuvette with four polished windows to allow for simultaneous longitudinal illumination and transverse collection of the scattered emission. Solutions of increasing concentrations (ranging from 10^{-3} to 10^{-2} M) of the molecules to be measured in chloroform are preliminary cleaned through 0.5 μm Millipore filters to remove most microscopic particles that could otherwise induce breakdowns in the presence of the focused laser beam. Collection of the HLS photons at 660 nm is performed in the transverse off-axis 90° direction, using a large (diameter: 50 mm) and a short focal distance ($f = 50$ mm) spherical lens to focus the light onto the photocathode of a photomultiplier tube. The numerical aperture of the optical collection system is low so as to avoid the depolarizing contribution of the off-axis beams. The detected reference and scattered harmonic signals, after spectral selection through an interference filter with 5 nm spectral resolution, are then sampled and averaged using a Stanford Research System Boxcar and processed by a computer. Variation of the scattered second harmonic intensity from the solution is recorded on the computer as a function of the reference second harmonic signal provided by the NPP powder, which scales like the square of the incoming fundamental intensity. Then $<\beta^2>$ and β

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(defined as $\sqrt{\langle\beta^2\rangle}$) values are inferred from the slopes of the resulting lines. Calibrations are made with respect to the pure chloroform solvent.

The norms $||\beta_{J=1}||$ and $||\beta_{J=3}||$ of the respective dipolar and octupolar contributions to the whole β tensor are measured using HLS depolarization measurements.[24] Variation of the angle ϕ of the linearly polarized beam is obtained by rotation of a second half-wave plate set after the glass plate to keep its reflectivity from being polarization dependent. In the absence of an analyzer, the overall scattering intensity exhibits a simple oscillatory pattern:

$$I^{2\omega} \propto [N_1(\langle\beta^2_{1,XXX}\rangle + \langle\beta^2_{1,ZXX}\rangle) + N_2(\langle\beta^2_{2,XXX}\rangle + \langle\beta^2_{2,ZXX}\rangle)]\cos^2\phi + 2[N_1\langle\beta^2_{1,ZXX}\rangle + N_2\langle\beta^2_{2,ZXX}\rangle]\sin^2\phi \quad (7)$$

where the subscript 1 (respectively 2) refers to the solvent (respectively the solute). The fundamental beam propagates along Z and is polarized in the $(X-Y)$ plane, $\phi = 0$ for a fundamental polarization parallel to the vertical X axis. From the macroscopic depolarization factor

$$D_2 = \frac{\langle\beta^2_{2,ZXX}\rangle}{\langle\beta^2_{2,XXX}\rangle} = \frac{1}{9}\frac{7 + 12\rho^2}{7 + 2\rho^2} \quad (8)$$

of the molecule to be analyzed, we can infer the nonlinear anisotropy factor $\rho = ||\beta_{J=3}||/||\beta_{J=1}||$ and henceforth the norms $||\beta_{J=1}||$ and $||\beta_{J=3}||$.

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