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Environmental and Excitonic Effects on the First Hyperpolarizability of Polar Molecules and Related Dimers

Francesca Terenziani,^{*,†} Sampa Ghosh,[‡] Anne-Claire Robin,[§] Puspendu K. Das,[‡] and Mireille Blanchard-Desce^{*,§}

Dipartimento di Chimica GIAF and INSTM UdR-Parma, Università di Parma, Parco Area delle Scienze 17/a, 43100 Parma, Italy, Department of Inorganic and Physical Chemistry, Indian Institute of Science, 560012 Bangalore, India, and Chimie et Photonique Moléculaire, Campus de Beaulieu, Université de Rennes 1, UMR CNRS 6510, Case 1003, 35042 Rennes Cedex, France

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We investigate the second-order nonlinear optical properties of a push–pull chromophore in different external and supramolecular environments, through a combined experimental and theoretical approach. In particular, we compare the first hyperpolarizability (β) of a model dipolar and polarizable chromophore with that of a charged analogue and of a molecular dimer based on the chromophore itself. We find that the β value of the model chromophore in solutions of low-polarity solvents is strongly affected by association effects, already at concentrations of 10^{-3} M. The presence of a positive charge in close proximity to the chromophore is found to lead to a 100% increase of the β response of the model push–pull chromophore. This effect is of major importance for biological applications, in particular when chromophores are used as markers in charged anisotropic environments. Finally, excitonic effects, beyond the Frenkel exciton approximation, are discussed for the dimer and found to be more important the higher the order of nonlinearity is.

Introduction

In the past 2 decades, reliable guidelines for the design of highly responsive molecules for second-order nonlinear optics (NLO) have been developed. Second-order NLO applications such as electro-optic modulation require that active molecules are processed into devices, usually based on chromophore-containing polymer films, where the NLO molecules are present at high concentration.¹ Second-order NLO phenomena are also exploited to image biological membrane dynamics using nonlinear microscopy through the second-harmonic generation (SHG) response of labeling NLO-active membrane markers.² In these conditions, active NLO chromophores interact with each other (such as in concentrated samples) or with a charged environment (membrane surface). Taking into account all of these interactions is of fundamental importance, in particular for polar and polarizable chromophores where dipole–dipole and charge–dipole interactions can significantly affect both the microscopic and macroscopic responses. For instance, it is well-recognized that intermolecular dipole–dipole interactions between push–pull chromophores play an important role in condensed phase because such interactions can trigger self-dimerization of “free” chromophores in electro-optic polymers, thus having a detrimental effect on second-order macroscopic optical nonlinearities.³ At opposite, dipolar interactions can lead to self-organization in mutichromophoric bundles resulting in higher figures of merit for electro-optic modulation.^{4–6} Whereas the effect of environment (solvent polarity) on the NLO response (in particular on the quadratic hyperpolarizability, β) of

individual push–pull chromophores has been investigated thoroughly,^{7–9} the mutual effect of intermolecular interactions on the NLO response of dipolar chromophores in close proximity is seldom considered. Some studies carried out on model systems where two or more push–pull chromophores are placed into close proximity by covalent grafting through a paracyclophane moiety¹⁰ or onto a triphenyl carbinol,¹¹ calixarene,¹² binaphthyl,^{13,14} β -cyclodextrin,⁵ or phenyl moieties⁶ indeed give different trends. Additive contributions of the individual monomers¹³ and decrease^{10,15} or increase^{10,16} of the global response with respect to the additive behavior have been reported. This suggests that dipolar interactions can indeed affect the individual nonlinear response and that this effect is strongly dependent on the geometry (i.e., relative orientation and distance between monomers, as shown by an early theoretical study on dimers of *p*-nitroanilines¹⁷) but also the nature of the push–pull chromophore whose dipole moment and polarizability determine the strength of interchromophoric interactions. Indeed more polar and polarizable push–pull chromophores are expected to show stronger modification of their NLO responses as a consequence of Coulombic interactions.^{6,18,19} In addition, stronger Coulombic interactions should also favor self-association of free chromophores, driving, in concentrated samples, the formation of dimers and multimers and controlling the relative orientation of the chromophores in the resulting multimetric nanoassemblies. Such dipole–dipole-driven supramolecular effects are expected to be of major importance in concentrated samples and/or low-polarity environments. Charge/dipole effects are also expected to strongly influence the NLO response of push–pull chromophores since charge–dipole Coulombic interactions are even stronger.

Consequently, the knowledge and ability to predict the molecular NLO responses of isolated molecules are not sufficient per se as far as real applications are concerned: more realistic model systems mimicking real conditions are needed to better

* Corresponding authors. Phone: +39 0521 905438(F.T.); +33 2 23 23 62 77(M.B.-D.). Fax: +39 0521 905556 (F.T.); +33 2 23 23 62 77(M.B.-D.). E-mail: francesca.terenziani@unipr.it (F.T.); mireille.blanchard-desce@univ-rennes1.fr (M.B.-D.).

[†] Università di Parma.

[‡] Indian Institute of Science.

[§] Université de Rennes 1.

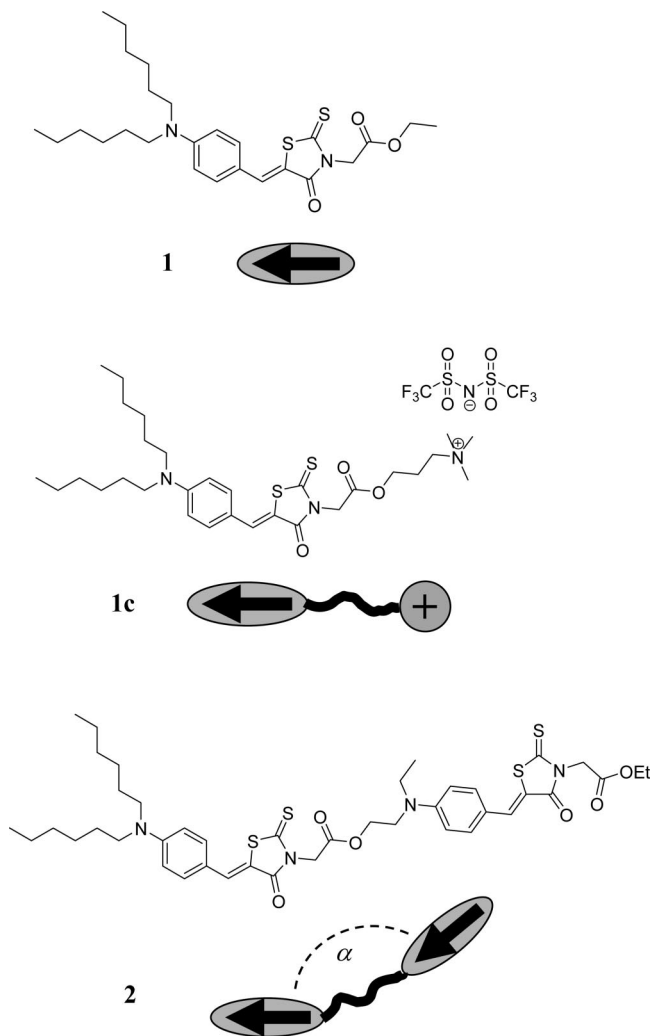


Figure 1. Structures and schematic representations of the investigated compounds.

account for interactions between NLO chromophores. This calls for studies to probe how molecules interact and self-organize and to predict the properties of chromophores in the real operating conditions. Following this line, our strategy has been to mimic concentration and charge effects in model systems: in particular, we compare the first hyperpolarizability of a single dipolar and polarizable chromophore with that of a charged analogue and of a molecular dimer based on the chromophore itself. The effects stemming from (i) the presence of a charge, (ii) concentration, and self-alignment (iii) interchromophore interactions are investigated and discussed by the aid of a few-state-based theoretical model. A previous study has shown that the third-order NLO responses of such systems are strongly affected by interchromophore interactions.¹⁹ It is thus of particular interest to investigate if second-order nonlinear responses (namely, first hyperpolarizabilities), which have important applications such as in SHG, electro-optic modulation, etc., are also affected and how such effects can be steered to achieve larger NLO responses in samples under real conditions.

Methods

Synthesis and NMR Studies. Compounds **1**, **1c**, and **2** (see Figure 1) were synthesized following the experimental protocol reported in ref 19. NMR studies were performed in C_6D_6 and $CDCl_3$. Nuclear Overhauser enhancement spectroscopy (NOE-

TABLE 1: First Column, Experimental HRS Hyperpolarizabilities ($\omega = 1.16$ eV) with Respect to the Monomeric Compound in Toluene; Columns 2 and 3, Calculated HRS Hyperpolarizabilities ($\omega = 1.16$ eV), Total Results and Results in the Heitler–London Approximation, Respectively; Column 4, Calculated Static HRS Hyperpolarizabilities^a

product (solvent)	$\langle\beta_{HRS}(2\omega)\rangle$ exptl	$\langle\beta_{HRS}(2\omega)\rangle$ calcd total	$\langle\beta_{HRS}(2\omega)\rangle$ calcd HL	$\langle\beta_{HRS}(0)\rangle$ calcd total
1 (toluene)	1.0	1.00		0.21
1 ($CHCl_3$)	2.0	1.39		0.22
1c (toluene)	2.0	1.62		0.23
2 (toluene)	0.8	1.07	1.09	0.20
2 , additive (toluene)		0.97		0.19
linear dimer (toluene)		3.43	3.03	0.49
linear dimer, additive (toluene)		2.00		0.41

^a All calculated values are reported with respect to $\langle\beta_{HRS}(2\omega)\rangle$ obtained for **1** in toluene.

SY) spectra were recorded at room temperature on a Bruker Avance 500 instrument.

Elemental Analyses. Elemental analyses were performed at the C.R.M.P.O. (Centre Régional de Mesures Physiques de l'Ouest) in Rennes. Compound **1** (490.72 g mol⁻¹): C 63.62% (calcd 63.64%), H 7.85% (calcd 7.81%), N 5.74% (calcd 5.71%), S 12.75% (calcd 13.07%). Compound **1c** (843.00 g mol⁻¹): C 45.80% (calcd 45.59%), H 5.86% (calcd 5.74%), N 6.37% (calcd 6.65%), S 14.97% (calcd 15.21%). Compound **2** (839.16 g mol⁻¹): C 60.28% (calcd 60.11%), H 6.60% (calcd 6.49%), N 6.70% (calcd 6.68%), S 15.29% (calcd 15.28%).

Hyper-Rayleigh Scattering Measurements. The first hyperpolarizability of the compounds were measured by the hyper-Rayleigh scattering (HRS) technique in solution.²⁰ The fundamental from an Nd³⁺:YAG laser (Spectra Physics, Quanta Ray, Prolab 170, 10 ns, 10 Hz) was focused loosely on a cylindrical cell. The incident laser beam power was monitored with a power meter (Scientech H410) and kept at 13–15 mJ/pulse. Second-harmonic (SH) signal at 532 nm obtained as a result of incoherent scattering from the molecules in solution at 90° was dispersed through a monochromator (Jobin Yvon Horiba, Triax 550) using a slit width of 1 mm. The output from the monochromator was incident on a photomultiplier tube (Philips Photonis XP2262B), amplified and processed in a digital storage oscilloscope. The experimental setup is described in details elsewhere.²¹ The apparatus was first calibrated with the reference *p*-nitroaniline (pNA) in dioxane (external reference method).²² By comparing the slopes of the $I_{2\omega}/I_{\omega}^2$ versus c_{solute} curves for pNA and the compounds, we obtained the $\langle\beta\rangle$ values of the compounds in toluene and chloroform using

$$\frac{\text{slope}_{\text{sample}}}{\text{slope}_{\text{ref}}} = \frac{\langle\beta_{\text{sample}}\rangle^2}{\langle\beta_{\text{ref}}\rangle^2} \quad (1)$$

Absence of two-photon induced fluorescence was checked by wavelength scan of the SH scattering signal through the monochromator. Solute concentrations were kept in the range of 10^{-4} – 10^{-7} M unless otherwise specified (i.e., investigation of effect of interchromophoric interactions in moderately concentrated solutions). The $\langle\beta\rangle$ of compound **1** in toluene has been found to be 3.1 with respect to pNA in the same solvent. In Table 1, all measured $\langle\beta\rangle$ values are given with respect to **1** in toluene.

Crystal Structure Determination. The crystallographic structure analysis was performed by the Centre de Diffraction

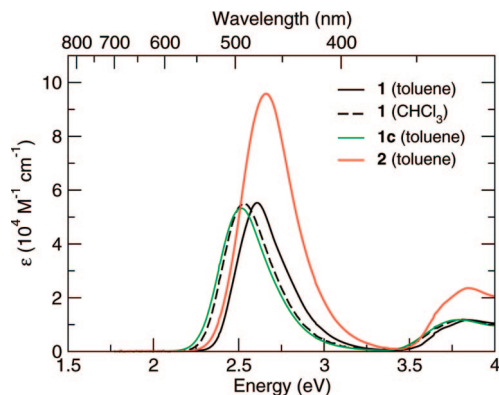


Figure 2. Absorption spectra of all compounds in toluene and of **1** in CHCl_3 .

métrie X at University of Rennes 1. Orange, stick-form crystals of dye **1** suitable for crystallographic structure analysis could be obtained by slow crystallization from an ethanol solution at room temperature. The crystal investigated by X-ray diffraction (XRD) (crystal size $0.04 \times 0.06 \times 0.59 \text{ mm}^3$) belongs to the monoclinic system, with cell dimensions $a = 10.2398(9) \text{ \AA}$, $b = 17.9078(16) \text{ \AA}$, $c = 29.697(3) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 93.853(5)^\circ$, $\gamma = 90^\circ$, and $V = 5433.3(9) \text{ \AA}^3$. The space group is P_c , and $Z = 8$. The empirical formula is $\text{C}_{26}\text{H}_{38}\text{N}_2\text{O}_3\text{S}_2$, the molar mass is 490.7, and the calculated density is 1.2 g cm^{-3} . The three-dimensional X-ray data were collected at 100(2) K on an APEXII, Bruker-AXS diffractometer, with the Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The intensity data of 57 035 reflections were collected; 23 334 unique reflections were used in the analysis [$R(\text{int}) = 0.0744$]. The structure was solved by direct methods using the SIR97 program²³ and then refined with full-matrix least-squares methods based on F^2 (SHELX-97)²⁴ with the aid of the WINGX program.²⁵ All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 23 334 unique intensities and 1190 parameters converged at $\omega R(F^2) = 0.086$ ($R(F) = 0.0548$) for 13 783 observed reflections with $I > 2\sigma(I)$.

Theoretical Model. Our approach relies on a two-state description of the dipolar reference molecule, based on its two fundamental (the neutral and the zwitterionic) resonating structures. It also accounts for molecular vibrations and for solvation interaction, fully taking into account the molecular polarizability thanks to a self-consistent treatment.²⁶ The model for the solvated chromophore is used to fit the solvatochromic behavior of the reference chromophore (**1**) and, hence, to extract the relevant model parameters. The fact that the molecular polarizability is completely accounted for allows us to export the molecular parameters in order to model the same chromophore in different environments.¹⁸ Indeed the same molecular parameters (derived in ref 19) are used to investigate not only HRS and two-photon absorption (TPA) properties of the reference chromophore but also linear and nonlinear properties of its derivatives **1c** and **2**.

The presence of a charge nearby the dipolar chromophore simply modulates the energy of the zwitterionic basis state via electrostatic interaction between the charge itself and the \pm charges on the acceptor/donor moieties. This interaction is screened by the solvent dielectric constant. The only additional parameter is the position of the charge with respect to the chromophore. This distance between the acceptor moiety and the charge is estimated to 15 \AA .¹⁹

Interacting chromophores are commonly described by the use of the Frenkel exciton model, based on the assumption that chromophores interact via their transition dipole moments and that only states having the same number of excitations can interact (Heitler–London approximation). Following ref 18 we instead consider all possible terms stemming from the electrostatic interaction between chromophores and, hence, evaluate the validity of the aforementioned approximation. The relevant Hamiltonian, detailed in refs 18 and 19, can be divided into two main parts, one conserving the exciton number (Heitler–London approximation) and one beyond this approximation:

$$H = H_{\text{HL}} + H_{n-\text{HL}} \quad (2)$$

where the single terms are given by

$$H_{\text{HL}} = \hbar\omega_{\text{CT}} \sum_i n_i + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{V_{ij}}{\eta^2} [\mu_{\text{CT}}^2 (b_i b_j^+ + b_j^+ b_i) + (\mu_{\text{E}} - \mu_{\text{G}})^2 n_i n_j] \quad (3)$$

$$H_{n-\text{HL}} = \frac{1}{2} \sum_i \sum_{j \neq i} \frac{V_{ij}}{\eta^2} [\mu_{\text{CT}}^2 (b_i b_j + b_j^+ b_i^+) + 2(\mu_{\text{E}} - \mu_{\text{G}}) \mu_{\text{CT}} (b_i + b_i^+) n_j] \quad (4)$$

In these expressions i and j indexes run over subchromophores; n_i is the operator which counts excitations (0 or 1) on the i th subunit; b_i (b_i^+) is the operator which destroys (creates) one exciton on i ; ω_{CT} is the excitation energy of the single subchromophore; μ_{CT} , μ_{G} , and μ_{E} are the transition, ground-state, and excited-state dipole moments, respectively, of the single subunit; V_{ij} is proportional to the electrostatic interaction in vacuum between two fully zwitterionic subchromophores at positions i and j . Interactions are screened by the solvent squared refractive index (η^2). All molecular properties (energies and dipole moments) in Hamiltonians 3 and 4 are relevant to the *interacting* single subchromophore, i.e., they differ from the isolated reference chromophore because the presence of other chromophores at close distance induces changes in the molecular properties as due to the molecular polarizability. This effect is again self-consistent and can be well-estimated through a mean-field calculation. This is an important difference with respect to commonly used models: parameters entering the problem are not fixed but self-consistently depend on the supramolecular arrangement, and their evolution can be followed when changing supramolecular variables. The mean-field renormalization of molecular properties depends again on the V_{ij} terms, but in this case interactions (being static in nature) are screened by the solvent dielectric constant.¹⁹

The first part of Hamiltonian 3 is the (mean-field) description of single subchromophores; the second part corresponds to the excitonic Hamiltonian in the so-called Heitler–London approximation, i.e., it conserves the number of excitons; this part is composed by the exciton migration term and by the exciton–exciton interaction contribution. Hamiltonian 4 breaks the Heitler–London approximation, mixing states differing by one and two excitations.

Results

Structures of the studied compounds are given in Figure 1. HRS results in diluted solutions are reported in Table 1, first column. Absorption spectra of the three compounds in toluene and of **1** in CHCl_3 are shown in Figure 2. Analysis of the linear spectra allowed extracting the molecular parameters needed to describe the behavior of all the compounds through a theoretical

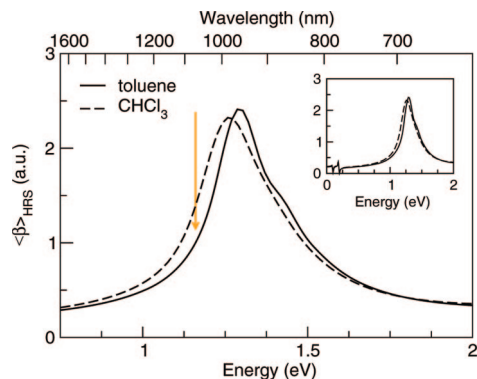


Figure 3. Frequency-dependent first hyperpolarizability calculated for chromophore **1** in toluene and CHCl_3 . The arrow marks the frequency used in the HRS experiments. The inset shows a larger frequency region, down to $\omega = 0$.

model accounting for two states per chromophoric unit.¹⁹ These parameters were also used to reproduce the TPA spectra of the species considered in this work.¹⁹ In addition, it was shown that strong excitonic contributions affect the TPA response of the dimer, with important effects stemming from interchromophore interactions beyond the standard Frenkel exciton model.¹⁹ It is thus of particular interest to test to what extent these interchromophore interactions affect the first-order hyperpolarizability. By using the same model to analyze HRS results, we show in the present paper that important conclusions can be drawn on environmental and concentration effects, self-organization, and interchromophore interactions. Calculated results (total and Frenkel exciton approximation) are reported in the last three columns of Table 1.

A strong increase of the $\langle\beta\rangle$ response of the monomer is observed when going from toluene to CHCl_3 . We interpret this as due to the red-shift of the absorption when increasing solvent polarity (see Figure 2). In fact, the SH response is in the vicinity of a two-photon resonance at the incident wavelength, and thus a steep dispersion of β is expected. This is pictured in Figure 3, where the energy dependence of the $\langle\beta\rangle$ response for **1** is calculated for toluene and CHCl_3 as solvents: the red-shift of the two-photon resonance in the $\langle\beta\rangle$ response in CHCl_3 implies a significant increase of the response itself at the investigated wavelength (marked with an arrow). This behavior is indeed typical of all push–pull chromophores having a solvatochromic absorption band, such as *p*-nitroanilines;⁹ on the contrary, for chromophores whose absorption band is barely affected by the

solvent polarity the variation of the $\langle\beta\rangle$ response when changing the solvent must be related to other phenomena, such as variations of dipole moments and/or failure of the simple two-state description.⁸

An analogous increase of the response is measured when going from the monomer (**1**) to the charged compound (**1c**). This can again be linked to the red-shift of the band: indeed **1c** in toluene has an absorption band at almost the same position than **1** in CHCl_3 (Figure 2), and the corresponding $\langle\beta\rangle$ values are similar, according to both experimental and calculated results (Table 1). This major increase (i.e., 100%) of the second-order polarizability of chromophore **1c** as compared to that of its neutral analogue **1** indicates that the presence of a charge in proximity of the NLO chromophore can significantly affect its NLO response. This is of particular importance for biological applications when the NLO-phores are used as markers in charged environments (e.g., membranes or polyelectrolytes such as DNA).

The response of the dimer (**2**) is comparable to that of the monomer, showing that the response of the dimer strongly differs from that of two *independent* chromophores. Indeed the $\langle\beta\rangle$ value measured for **2** indicates that the dimer is folded, as already estimated on the basis of absorption and TPA spectra,¹⁹ which could be reproduced by fixing an angle $\alpha = 40^\circ$ (see Figure 1). By fixing this same angle, we calculate $\langle\beta\rangle$ responses of the same order for **2** and **1** (Table 1, second column). A 10% increase is predicted (excitonic contributions) with respect to the simple vectorial sum of the responses of the two subunits. Non-Heitler–London effects are weak (2%). It is interesting to note that excitonic effects are more important for the TPA response of **2**¹⁹ than for the β response. In particular, at 1064 nm, standard excitonic effects increase the TPA response by 115% with respect to the additive behavior, and non-Heitler–London contributions are responsible for a further 8% increase.

Having proven the validity of the adopted theoretical model, we apply it to describe the properties of a hypothetical linear dimer (corresponding to $\alpha = 180^\circ$ in Figure 1) based on the same chromophore. Such a linear dimer would have a much higher $\langle\beta\rangle$ response than the monomeric compound (more than 3 times bigger). Moreover excitonic effects are expected to be very important, contributing a 70% increase of the $\langle\beta\rangle$ response with respect to the additive behavior. Also for the hypothetical linear dimer, excitonic contributions are expected to be much more important for the TPA response (200% increase at 1064 nm) than for the β response (70% increase at 1064 nm).¹⁹ Along

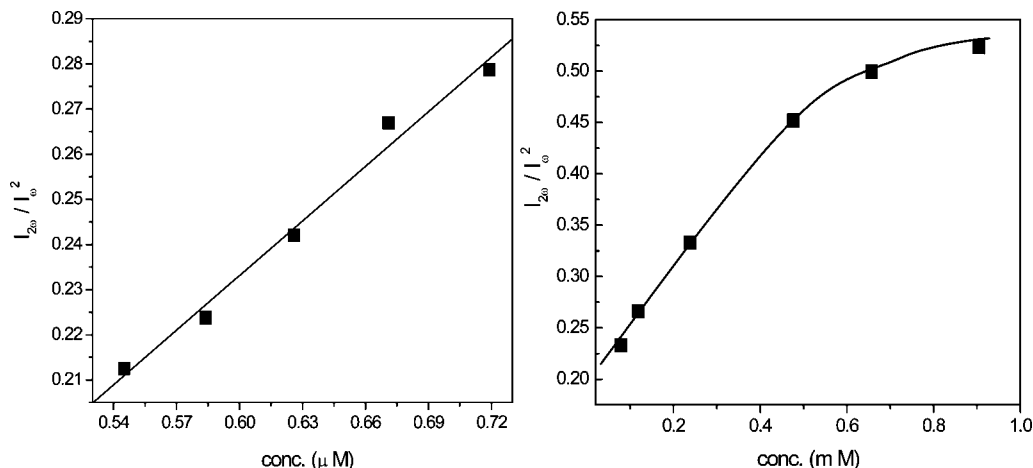


Figure 4. $I_{2\omega}/I_\omega^2$ vs concentration of chromophore **1** in toluene for diluted solutions (left) and moderately concentrated solutions (right).

the same lines, non-Heitler–London contributions are responsible for $\sim 15\%$ increase of the β response and for $\sim 30\%$ increase of the TPA response with respect to the Frenkel exciton contribution.

We now estimate excitonic contributions to the $\langle\beta\rangle$ response calculated at zero frequency ($\langle\beta_0\rangle$), in order to get rid of dispersion effects. At zero frequency, dispersion effects are absent (see inset of Figure 3) so that only a 7% increase of the $\langle\beta\rangle$ response is calculated for **1** in CHCl_3 and **1c** in toluene with respect to **1** in toluene (see Table 1). This increase is still due to the red-shift of the band but only through the decrease of the denominator in the standard sum-over-state formula for the calculation of β_0 .²⁷ For dimer **2**, an increase of 5% is calculated with respect to the additive result, with negligible non-Heitler–London effects. For a linear dimer, we predict a 10% increase of the $\langle\beta_0\rangle$ response due to standard excitonic effects and a supplementary 10% increase due to non-Heitler–London contributions.

The $\langle\beta\rangle$ response of **1** was also measured in moderately concentrated toluene solutions (up 1.5×10^{-3} M): a clear deviation from linearity was found for the SH signal at concentrations higher than $\sim 5 \times 10^{-4}$ M (see Figure 4). This behavior clearly indicates the onset of interactions between dipolar chromophores at these concentrations, with formation of dimers or multimers with much lower $\langle\beta\rangle$ response with respect to the monomeric species. Indeed NMR NOESY experiments at 1 mM concentration of chromophore **1** in C_6D_6 indicate intermolecular through-space coupling between H_2 and H_7 (see Figure 5), accordingly with the formation of multimeric species where monomeric subunits are antiparallelly aligned (Figure 5, bottom panel). In contrast, for millimolar solutions of chromophore **1** in more polar CDCl_3 , only intramolecular through-space couplings can be observed, indicative that no association occurs. Consistently, the HRS response stays linear over a wide concentration range in CHCl_3 .

Further evidence for the formation of dimeric units is provided by structure determination of **1** in the solid state by X-ray crystallography (Figure 6). Indeed along the a -axis chains are formed where dimers are packed face-to-face, in antiparallel fashion, and successive dimers are translated along the molecular plane (see Figure 6, bottom panel). Molecules in the dimers are 3.4 Å apart, whereas the distance between successive dimers is 3.9 Å. In the dimers, the benzene ring and the heterocycle are positioned on top of each other, supporting what was found in solution NMR studies of concentrated samples of dye **1** in a low-polarity environment.

Discussion and Conclusions

Our results show that environmental effects and experimental conditions strongly affect NLO properties of samples and that a careful modeling of relevant interactions makes it possible to predict the properties of samples in the operating conditions encountered in the various applications.

Interactions with a polar environment or a charge basically alter the transition energy of polar chromophores, with a direct effect on the (hyper)polarizabilities due to the presence of transition energies in the sum-over-states expressions. But another, indirect effect can be even more important: if the (hyper)polarizability is measured near to a resonance, the response has a strong dispersion with respect to the incident frequency so that small shifts of the transition energies can lead to big variations of the response, as already observed for other push–pull chromophores.⁹ Zero-frequency responses are free from dispersion effects so that they offer a measure of the direct effect of the band shift.

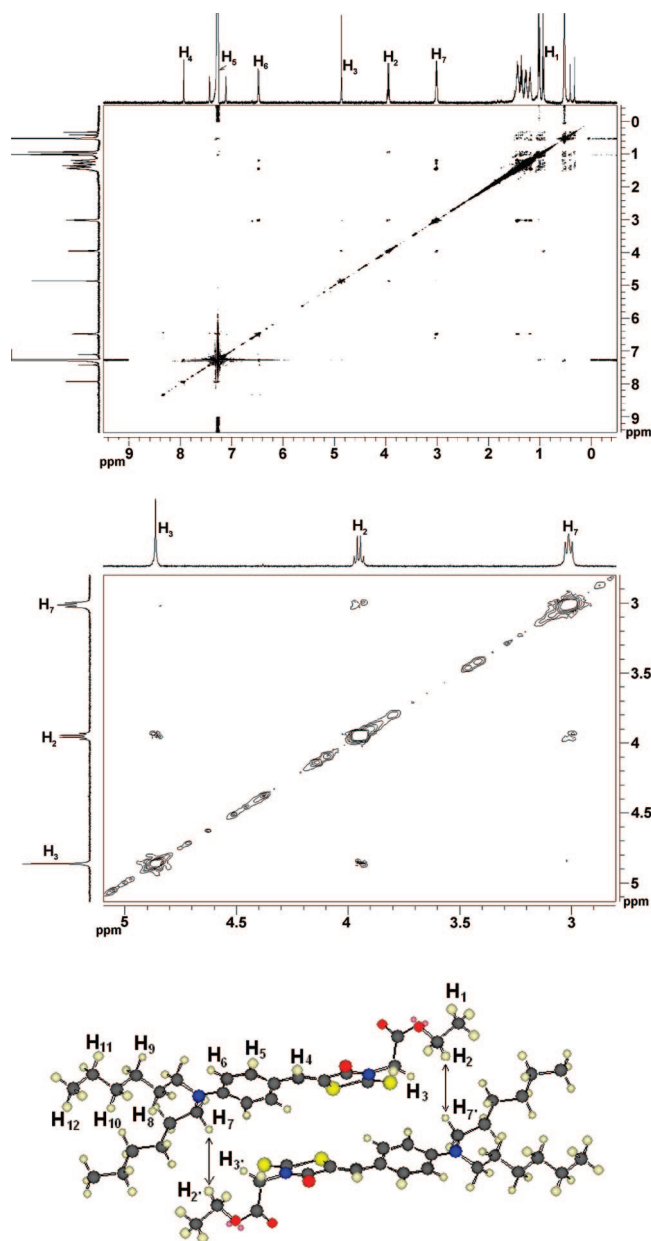


Figure 5. NOESY NMR spectra of a millimolar solution of chromophore **1** in benzene- d_6 at 298 K: full spectrum and selected area. Bottom: structural model for a dimeric unit of chromophore **1** derived from MM2 optimization and NMR study. The arrows indicate spatial proximities as evidenced by NOESY cross-coupling peaks.

Effects due to interchromophoric interactions are more subtle. In fact they are collective excitonic effects altering not only the energy of the states but also their nature (delocalization). These effects are then liable to provoke major quantitative and qualitative changes in the NLO responses. Our analysis of HRS results allows distinguishing true excitonic effects from dispersion effects. Indeed, variations in the β and TPA response of dimers with respect to additive results are strongly affected by the proximity to the two-photon resonance. In regions of steep dispersion of the responses (such as at 1064 nm for the chromophores investigated in the present paper), variations as big as 70% and 200% are expected for the β and the TPA response, respectively. True excitonic effects in the β response can be evaluated by choosing a completely dispersionless frequency: at zero frequency the amplification of β_0 for dimers become $\leq 20\%$. For resonant properties, such as TPA cross sections, another criterion must be set, as, for example,

comparing TPA cross sections at their maxima. In this way, modulations amounting up to 40% for TPA maxima are calculated and observed for dimers with respect to the monomer.¹⁹ Non-Heitler–London contributions are found to be important for the β and the TPA response of dimers, accounting for up to $\sim 50\%$ of the total excitonic effect for β_0 and up to $\sim 70\%$ for the TPA maxima. We can then conclude that excitonic effects are more important the higher the order of nonlinearity is.¹⁸ In particular, non-Heitler–London contributions are almost irrelevant for linear spectra,¹⁹ whereas they can be substantial for nonlinear responses. Moreover, the importance of excitonic contributions is strongly related to the geometry of the dimer, as shown by comparison between our dimer **2** and the hypothetical linear dimer. These findings could also help in rationalizing deviations from additive behavior observed for other covalent dimers, as discussed in ref 10. It is also worthwhile to stress here that deviations from predictions of the Frenkel exciton model were already observed for covalent dimers based on the paracyclophane moiety:²⁸ in that case, the failure of the exciton model was to be ascribed to strong through-space charge-transfer interactions due to the close vicinity of the two chromophores (~ 3.3 Å), whereas this cannot be the case for our dimer, where the interchromophore distance is much higher, on the order of 7 Å.¹⁹

Interchromophore interactions between dipolar chromophores come into play not only in molecular dimers, but also in concentrated samples, where the molecular density is high enough to induce proximity between chromophores. Our results for solutions of **1** in moderately concentrated solutions (10^{-4} – 10^{-3} M) suggest that already at a concentration of $\sim 5 \times 10^{-4}$ M chromophores start to associate and do not behave as isolated chromophores (Figures 4 and 5). Given the dipolar character of chromophore **1** ($\mu = \sim 7$ – 9 D)^{5,29} and previous studies carried out on different polar push–pull chromophores,³⁰ aggregation in solution is expected to occur in low-polarity environments due to dipole–dipole interactions:



where \mathbf{M} represent the monomeric species and \mathbf{N} the aggregate (composed by n molecules). The simplest aggregation equilibrium would be a dimerization ($n = 2$), an equilibrium between multiple species also being possible.

Equilibrium 5 gives rise to an HRS response which can be written as

$$I_{2\omega}/I_{\omega}^2 = Gc_{\text{solute}}\{(1-x)\langle\beta_{\mathbf{M}}^2\rangle + x/n\langle\beta_{\mathbf{N}}^2\rangle\} \quad (6)$$

where G is a instrument factor and c_{solute} is the nominal operating concentration of the solution; x is the fraction of monomer **1** which is aggregated at the operating concentration, $\beta_{\mathbf{M}}$ is the response of the isolated (monomeric) chromophore **1** in toluene (experimentally determined for chromophore **1** in diluted toluene solution), and $\beta_{\mathbf{N}}$ is the response of the aggregate. We performed numerical simulations of the $I_{2\omega}/I_{\omega}^2$ response, by using the $\beta_{\mathbf{M}}$ value derived at low concentrations and trying different aggregation numbers. At each time, we fixed $\beta_{\mathbf{N}}$ to 0, according to the idea that dipolar chromophores tend to aggregate in antiparallel fashion and take preferentially even n number values. Trying to reproduce the experimental behavior observed as a function of concentration, we derived the best aggregation equilibrium constant for each n value. Results are reported in Figure 7, for $n = 2, 4, 8$. These results suggest that the aggregation equilibrium responsible for the nonlinear dependence of the β response on the concentration is not a simple dimerization: for a dimerization equilibrium we would expect a slight and smooth deviation from linearity. The experimental behavior is much better reproduced for higher aggregation numbers: in particular, $n = 8$ allows us to describe the quick decrease of slope at concentration $\sim 5 \times 10^{-4}$ M after a linear behavior at lower concentrations. The aggregation equilibrium constant corresponding to the best fit corresponds to $x = \sim 0.45$ for $c_{\text{solute}} = 10^{-3}$ M.

The concentration range where we observe interchromophore interactions effects corresponds to 10^{23} – 10^{24} molecules/m³.

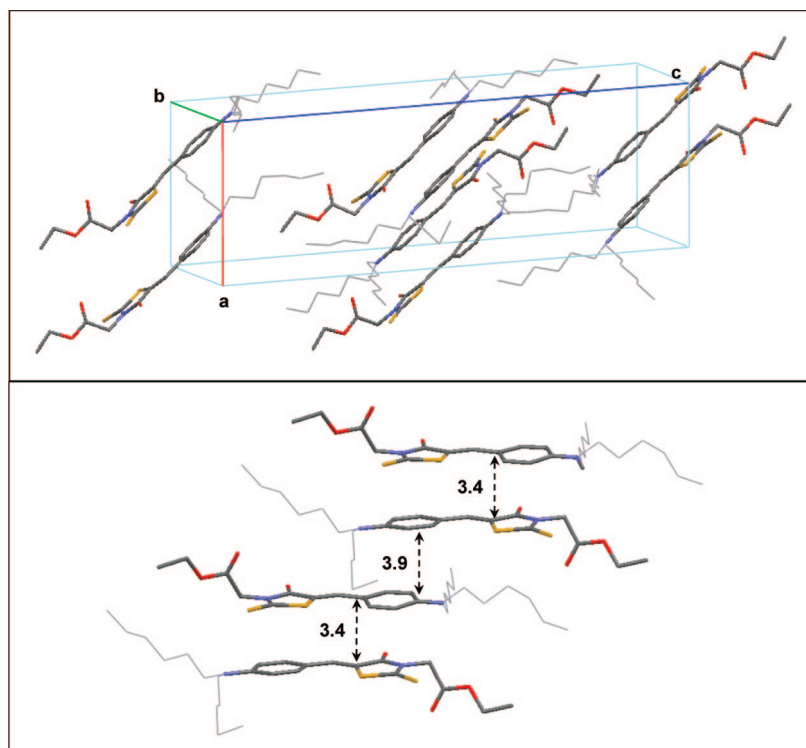


Figure 6. X-ray crystal structure of compound **1**. Top panel: crystal packing. Bottom panel: view of the dimerized chain along the a -axis. For graphical reasons, hexyl chains have been drawn with thinner lines.

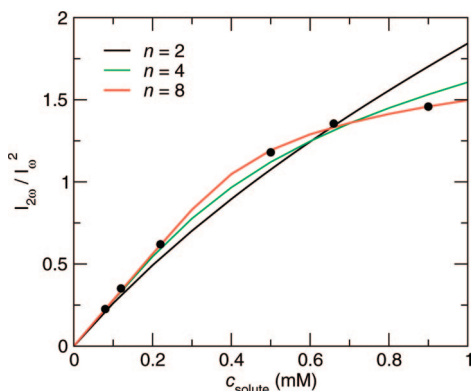


Figure 7. $I_{2\omega}/I_{\omega}^2$ vs concentration of chromophore **1** in toluene. Symbols, experimental data; lines, numerical simulations for β_M set to the value extrapolated at low concentration, $\beta_N = 0$ and different aggregation numbers (n). Aggregation equilibrium constant $K = 400 \text{ M}^{-1}$ for $n = 2$, $K = 10^9 \text{ M}^{-3}$ for $n = 4$, and $K = 9 \times 10^{21} \text{ M}^{-7}$ for $n = 8$.

These concentration values are quite low if compared with typical chromophore loadings in polymeric matrixes for photorefractive applications (10^{26} – 10^{27} molecules/ m^3) and typical crystal densities (10^{27} molecules/ m^3 in our case). These loadings also usually correspond to the maximum loading in order not to have negative interchromophore interactions. The reason why we find that already at much lower concentrations interchromophore interactions are dominant is possibly the low dielectric constant of toluene (2.4) with respect to typical polymeric matrixes (~ 4). Indeed, the same concentration-dependent studies (HRS and NMR) on CHCl_3 solutions (dielectric constant of 4.8) showed that no aggregation effects take place up to the 10^{-2} M concentration range.

This study provides demonstration that interchromophore interactions play an important role in determining the overall β response of dipolar chromophores in low-polarity environments. These interactions promote self-orientation of the chromophores in a folded manner ($0 < \alpha < 90^\circ$) within dimers where the proximity and enchainment between chromophores is forced. Intermolecular interactions are also responsible for spontaneous association of chromophores in antiparallel or quasi-antiparallel fashion, leading to aggregates with low β value in moderately concentrated solutions (i.e., 10^{-3} M) of low-polarity solvents. The self-orientation process allows excitonic effect to occur, thus modifying the β responses of each subunit of the multimers and, as a consequence, the macroscopic response. Interestingly, this modification will strongly depend on the reciprocal orientation of the chromophores within the dimers (as already observed for other covalent dimers),¹⁰ the antiparallel one leading to small variations of the β response. At opposite, if the dipolar chromophores are constrained in a linear geometry, much larger excitonic contribution shall be achieved. This means that forcing either internally (via covalent bonds) or externally (using, for instance, a supramolecular host) a dimerization/aggregation in a linear geometry³¹ is a good strategy for enhanced second-order NLO responses. The present study thus shows that interchromophore interaction effects should definitely be considered when such polar/polarizable chromophores are used in real conditions: important and nontrivial effects are expected not only in the case of intermolecular charge-transfer phenomena²⁸ but also when interactions have a purely electrostatic origin. Aggregation and self-orientation processes can lead to markedly different β response as compared to noninteracting monomeric species. This is particularly true when push–pull

chromophores are used in low-polarity environments and confinement conditions.

Besides interchromophoric effects, the presence of a positive charge in close proximity to the NLO chromophore was also found to strongly influence the NLO response of the model push–pull chromophore **1**. In a low-polarity environment, the β response doubles due to the presence of the positive charge located nearby the donating moiety. This clearly demonstrates that the NLO response derived from experiments in solutions does not account for the real response in biological environments where Coulombic effects due to charges are expected to come into play (membranes, polyelectrolytes, ...). Such effects are particularly relevant for membrane markers designed for SHG monitoring of membrane potentials.²

In summary, we investigated the NLO properties of a polar chromophore in different external and supramolecular environments. Our combined experimental and theoretical approach demonstrates important polarity and charge effects on the β response of polarizable molecules and nontrivial effects stemming from interchromophore interactions in molecular dimers and in moderately concentrated samples in low-polarity environment. Besides self-orientation, interchromophore interactions can be responsible for important excitonic effects. Our theoretical model allows distinguishing and evaluating standard (Frenkel exciton model) and non-Heitler–London excitonic contributions. Interestingly, the importance of excitonic effects and the contribution of non-Heitler–London interactions increase with the order of nonlinearity and strongly depend on the reciprocal orientation of chromophores. Correctly modeling the properties of molecules in the real conditions of use is not only of fundamental interest but also instrumental for the efficient design of molecular probes and devices.

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