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An Investigation on the Role of the Nature of Sulfonate Ancillary Ligands on the Strength and Concentration Dependence of the Second-Order NLO Responses in $CHCl_3$ of Zn(II) Complexes with 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$ and 4,4′-*trans*,*trans*-$NC_5H_4(CH{=}CH)_2C_6H_4NMe_2$

Francesca Tessore, Danika Locatelli, Stefania Righetto, Dominique Roberto,* and Renato Ugo

Dipartimento di Chimica Inorganica, Metallorganica e Analitica dell'Università di Milano,
Centro di Eccellenza CIMAINA, Unità di Ricerca di Milano dell'INSTM, and Istituto di Scienze e
Tecnologie Molecolari del CNR, Via G. Venezian 21, I-20133 Milano, Italy

Patrizia Mussini

Dipartimento di Chimica Fisica ed Elettrochimica dell'Università di Milano, and
Centro di Eccellenza CIMAINA, Via G. Venezian 21, I-20133 Milano, Italy

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To evidentiate the role of the nature of sulfonate ancillary ligands on the value of the quadratic hyperpolarizability of Zn(II) complexes with stilbazole-like ligands, the second-order nonlinear optical (NLO) properties of $[ZnY_2(4,4'\text{-}trans\text{-}NC_5H_4CH{=}CHC_6H_4NMe_2)_2]$ complexes ($Y = CF_3SO_3$, CH_3SO_3, or $p\text{-}CH_3C_6H_4SO_3$) are investigated. By working at relatively high concentrations ($>3 \times 10^{-4}$ M), the positive effect of the triflate ligand remains unique while, with nonfluorinated sulfonate ligands, the second-order NLO response is comparable to that of the related complexes with acetate or trifluoroacetate as ancillary ligands. However, at dilutions higher than 10^{-4} M, all of the sulfonate complexes reach huge quadratic hyperpolarizabilities because of solvolysis with the formation of cationic species such as $[ZnY(4,4'\text{-}trans\text{-}NC_5H_4CH{=}CHC_6H_4NMe_2)_2]^+$, characterized by a large second-order NLO response. This view is supported by careful conductivity measurements. The same behavior occurs if 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$ is substituted by 4,4′-*trans*,*trans*-$NC_5H_4(CH{=}CH)_2C_6H_4NMe_2$.

Introduction

Coordination compounds can offer a great diversity of tunable electronic properties acting on their second-order nonlinear optical (NLO) responses.[1−6] For example, the quadratic hyperpolarizability, measured in solution by the electric field induced second harmonic generation (EFISH) technique,[7−10] of π-delocalized nitrogen donor ligands such as 4,4′-*trans* or *trans,trans*-$NC_5H_4(CH{=}CH)_nC_6H_4NMe_2$ (L^1 and L^2 for $n = 1$ and 2, respectively; see Chart 1), increases upon coordination to various metal centers,[11−15] reaching

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* Corresponding author. Fax: +39-02-50314405. E-mail: dominique.roberto@unimi.it.

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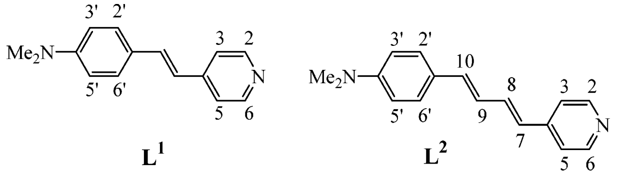
Chart 1



values of the second-order NLO response comparable to that of an organic material such as Disperse Red 1 [*trans*-4,4′-$O_2NC_6H_4$-$N{=}NC_6H_4NEt(CH_2CH_2OH)$], currently used in electro-optic polymers.[16] According to both theoretical[11] and solvatochromic[13] investigations, this significant enhancement seems to be originated mainly by the red shift of the intraligand charge-transfer (ILCT) $n \rightarrow \pi^*$ transition often controlled by increased Lewis acceptor properties of the metal[12] and, therefore, by the ancillary ligands that tune its acceptor properties.[13]

Some of us recently reported, in a preliminary communication,[14] that the quadratic hyperpolarizabilities (measured working in anhydrous chloroform with a nonresonant incident wavelength of 1.907 μm, simplified in the following as 1.91 μm, by the EFISH technique) of $[Zn(CF_3SO_3)_2L_2]$ (L = L^1 and L^2) complexes, at concentrations higher than 1 × 10^{-4} M, are increased by a factor of ca. 3−6 times with respect to that of the related acetate or trifluoroacetate complexes, in agreement with a higher Lewis acidity of the Zn(II) center, expected for the strong electron withdrawing properties of the triflate ligand. At dilutions higher than about 10^{-4} M, the $\beta_{1.91}$ values of these triflate complexes increase abruptly with decreasing concentration, up to huge values, while this effect is not observed for the related acetate or trifluoroacetate complexes. This behavior was attributed to an increased concentration (although very low because EFISH measurements are still possible) of the cation $[Zn(CF_3SO_3)L_2]^+$ produced by strong solvolysis of the triflate ligand, as confirmed by electrical conductivity measurements, which evidenced a sharp conductivity increase at concentrations below 10^{-4} M for triflate complexes only.[14]

These results prompted us to further study whether the relevant increase of the quadratic hyperpolarizability $\beta_{1.91}$ and its unusual concentration dependence are due only to the sulfonate nature of the triflate ligand or if they also require the presence of the strong electron withdrawing CF_3 group. Therefore, we prepared the new complexes $[Zn(CH_3SO_3)_2$(4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2)_2]$ and $[Zn(p\text{-}CH_3C_6H_4SO_3)_2$(4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2)_2]$ and we studied and compared their second-order NLO responses with that of the related triflate complex.

Results and Discussion

A series of $[ZnY_2L_2]$ complexes (Y = sulfonate or acetate ligand; L = L^1 or L^2) were synthesized. The complexes $[Zn(CH_3SO_3)_2L^1{}_2]$ and $[Zn(p\text{-}CH_3C_6H_4SO_3)_2L^1{}_2]$ (L^1 = 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$) were prepared by mixing stoichiometric amounts of $ZnY_2{\cdot}nH_2O$ (Y = CH_3SO_3 or $p\text{-}CH_3C_6H_4SO_3$) and L^1 in CH_2Cl_2 at room temperature, followed by removal of the solvent under a vacuum. The complexes $[Zn(CF_3SO_3)_2L^2]$ (L = L^1 or L^2)[14] were synthesized in the same way. Related complexes with acetate and trifluoroacetate as ancillary ligands and L^1 or L^2 as stilbazole ligands were obtained as reported in the literature.[13]

A large enhancement of the dipole moment μ (see Experimental Section) of $[ZnY_2L^1{}_2]$ complexes occurs by substituting the trifluoroacetate or acetate ligand with the methanesulfonate or paratoluenesulfonate ligand, together with a much higher red shift of the ILCT transition of the stilbazole ligand L^1 ($\Delta\lambda_{max}$ = 101−102 nm with respect to $\Delta\lambda_{max}$ = 2−46 nm).[13] Both the high red shift and the dipole moment enhancement are, however, slightly lower than those reported for the related triflate complex (see Table 1),[14] an expected trend when taking into consideration the superior electron withdrawing properties of the triflate ligand.[17] A much larger red shift of the ILCT transition was reported when comparing $[Zn(CF_3SO_3)_2L^2{}_2]$ ($\Delta\lambda_{max}$ = 123 nm) with $[Zn(CH_3CO_2)_2L^2{}_2]$ ($\Delta\lambda_{max}$ = 10 nm), that is when the stilbazole ligand is characterized by a larger π delocalization.

EFISH measurements, carried out in anhydrous $CHCl_3$ and working with a nonresonant incident wavelength of 1.907 μm and at concentrations higher than 5 × 10^{-4} M, show, despite the much higher red shift of the ILCT transition of L^1, which is suggested as the main origin of the enhancement of the quadratic hyperpolarizability upon the coordination of L^1 to a metal center such as Zn(II),[13] quadratic hyperpolarizability $\beta_{1.91}$ values of $[ZnY_2L^1{}_2]$ (Y = CH_3SO_3 or $p\text{-}CH_3C_6H_4SO_3$) complexes comparable to those of the related Zn(II) complexes with Y = CH_3CO_2 or CF_3CO_2 (Table 1). As a consequence, the values of $\beta_{1.91}$ are quite lower (ca. 3−6 times) than that of the related complex $[Zn(CF_3SO_3)_2L^1{}_2]$.

This latter result is quite unexpected because both the red shift of the ILCT transition of L^1 and the enhancement of the dipole moment of Zn(II) complexes carrying the CH_3SO_3 and $p\text{-}CH_3C_6H_4SO_3$ ligands are more comparable to those of the triflate complex than to those of related complexes carrying the acetate or trifluoroacetate ancillary ligands (Table 1), suggesting a comparable perturbation of the electronic levels of the stilbazole ligand L^1 and a similar charge density distribution of the complexes. Therefore, the presence of the trifluoromethyl group in the sulfonate ancillary ligand seems to be a necessary condition in order to reach a high value of the quadratic hyperpolarizability $\beta_{1.91}$ for the kinds of Zn(II) complexes investigated in this work (Table 1). Despite the significantly lower second-order NLO response, Zn(II) complexes carrying the less-electron-withdrawing ligands CH_3SO_3 or $p\text{-}CH_3C_6H_4SO_3$ do not behave, at dilutions below 10^{-4} M, as the related acetate or trifluoroacetate complexes.[14]

On the contrary, as in the case of the triflate complexes,[14] $\beta_{1.91}$ values, in anhydrous $CHCl_3$, of the methanesulfonate and paratoluenesulfonate complexes are strongly dependent upon concentration (Table 1). At concentrations lower than about 3 × 10^{-4} M, they increase abruptly with decreasing concentration, up to huge values (Figure 1), an effect that

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Table 1. Electronic Spectra, Dipole Moments, and $\beta_{1.91}$ Values of Various Zn(II) Complexes with ′L^1 or ′L^2

complex	concentration 10^{-4} M	$\lambda_{max}{}^a$ (ILCT) nm	μ^a D	$\mu\beta_{1.91}{}^a$ 10^{-30} D cm^5 esu^{-1}	$\beta_{1.91}{}^a$ 10^{-30} cm^5 esu^{-1}	EF^b
$[Zn(CH_3CO_2)_2L^1{}_2]$	1−7	376	8.0	316	39	
$[Zn(CF_3CO_2)_2L^1{}_2]$	1−7	420	10.5	512	49	1.3
$[Zn(CF_3SO_3)_2L^1{}_2]$	10	490	16.7	2715	163	4.2
	5			2720	163	4.2
	1			3670	220	5.6
	0.5			6750	404	10.4
$[Zn(CH_3SO_3)_2L^1{}_2]$	10	475	15.5	450	29	0.7
	5			787	51	1.3
	3			1030	66	1.7
	1			5310	343	8.8
	0.5			9500	613	15.7
$[Zn(p\text{-}CH_3C_6H_4SO_3)_2L^1{}_2]$	8	476	16.0	428	27	0.7
	5			542	34	1.2
	3			1210	76	1.9
	1			3100	194	5.0
	0.5			9230	577	14.8
$[Zn(CH_3CO_2)_2L^2{}_2]$	1−7	406	6.7	680	101	
$[Zn(CF_3SO_3)_2L^2{}_2]$	7	519	14.7	3840	261	2.6
	1			6100	415	4.1

^{a} In anhydrous chloroform. ^{b} EF is the $\beta_{1.91}$ enhancement factor with respect to the related $[Zn(CH_3CO_2)_2L^1{}_2]$ or $[Zn(CH_3CO_2)_2L^22]$ complex, measured as a ratio of the two $\beta_{1.91}$ values.

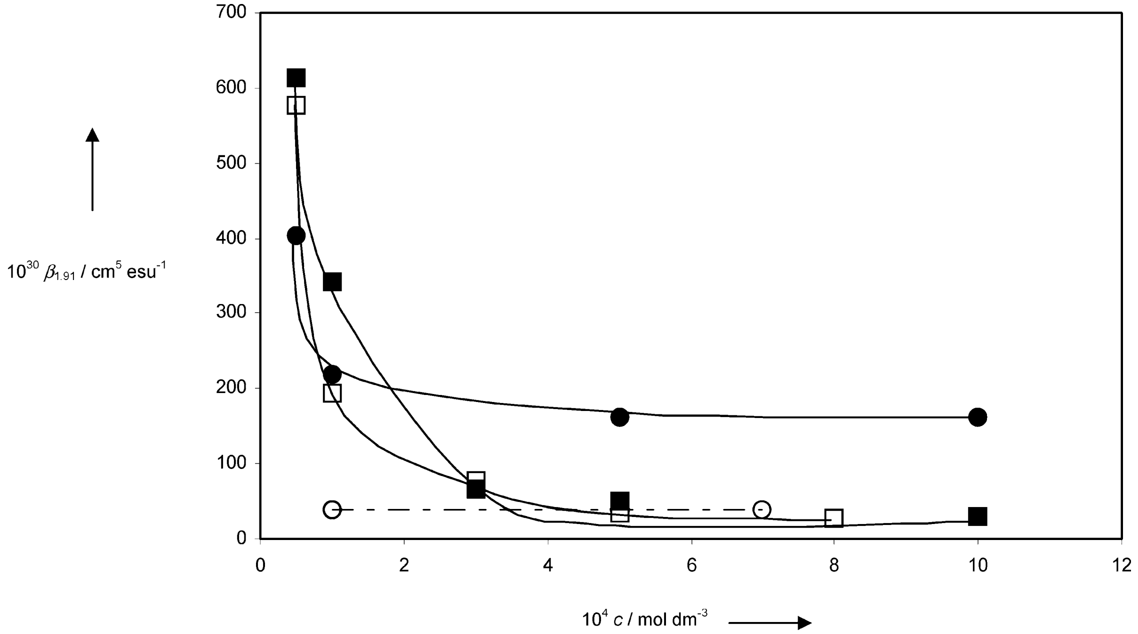

Figure 1. Dependence of $\beta_{1.91}$ upon concentration c for various $[ZnY_2L^1{}_2]$ complexes. ○ = $[Zn(CH_3CO_2)_2L^1{}_2]$; ● = $[Zn(CF_3SO_3)_2L^1{}_2]$; ■ = $[Zn(CH_3SO_3)_2L^1{}_2]$; □ = $[Zn(p\text{-}CH_3C_6H_4SO_3)_2L^1{}_2]$.

was not observed for the related acetate or even trifluoroacetate complexes (Figure 1). This large increase of $\beta_{1.91}$ was already shown not to be the result of inappropriate EFISH measurements resulting from high dilutions and, therefore, a rather small EFISH response. In fact, the $\beta_{1.91}$ value of N-(4-nitro phenyl)-L-prolinol (NPP), taken as a reference that cannot dissociate into ions, measured under the same range of concentrations, was shown to remain unchanged at concentrations below 10^{-4} M.[14] Given the low nucleophilicity of the sulfonate ligands,[17] the above-described behavior of their Zn(II) complexes at low concentrations can be ascribed to some solvolysis with the formation, first, of strong ion pairs, which then slightly dissociate, at higher dilutions, into real ionic species. The hypothesis of an initial strong ion pairing is supported by the observation that it was not possible to carry out EFISH or capacitance measurements when $CHCl_3$ was not completely anhydrous because traces of water favor the instantaneous dissociation of ion pairs into ionic species that, when there are too many, hinder both EFISH and capacitance measurements.

The strong increase of $\beta_{1.91}$ upon high dilutions below 10^{-4} M can then be ascribed, as it was already suggested for the triflate complexes,[14] to an increased concentration of the cation $[ZnYL_2]^+$ (Y = CF_3SO_3, CH_3SO_3, or p-$CH_3C_6H_4SO_3$; L = L^1 or L^2) produced by high dilutions. This latter cationic species, because of the presence of a positive charge and, thus, an increased perturbation of the push−pull character of the stilbazole ligand, should show a much higher second-

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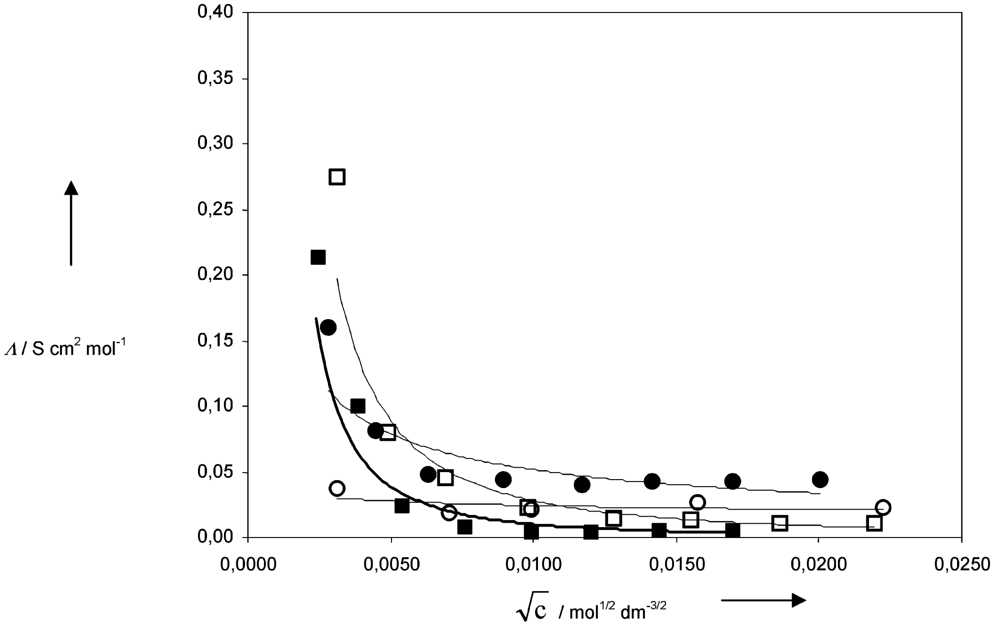

Figure 2. Dependence, in $CHCl_3$ at 298 K, of molar conductance Λ of various $[ZnY_2L^1{}_2]$ complexes versus the square root of the concentration *c*. ○ = $[Zn(CH_3CO_2)_2L^1{}_2]$; ● = $[Zn(CF_3SO_3)_2L^1{}_2]$; ■ = $[Zn(CH_3SO_3)_2L^1{}_2]$; □ = $[Zn(p\text{-}CH_3C_6H_4SO_3)_2L^1{}_2]$.

order NLO response than that of the related undissociated complex. Obviously, a similar process was not observed for the related acetate or even trifluoroacetate complexes, according to the much higher nucleophilic character of these ancillary ligands, when compared to that of the sulfonate ligands.

The hypothesis of an increased ionic dissociation of Zn(II) complexes with sulfonate ligands upon dilution is supported by a careful investigation of the electrical conductivity, in anhydrous $CHCl_3$ solutions (Figure 2), of $[ZnY_2L^1{}_2]$ complexes (Y = CH_3CO_2,[14] CF_3SO_3,[14] CH_3SO_3, or *p*-$CH_3C_6H_4SO_3$). This investigation suggests an increased concentration, by ionic dissociation, of cationic species upon dilution. According to Figure 2, $[ZnY_2L^1{}_2]$ complexes (Y = CH_3CO_2,[14] CH_3SO_3, or *p*-$CH_3C_6H_4SO_3$) are practically undissociated in the concentration range of 1×10^{-3} to 5×10^{-4} M, while the related complex with the triflate ligand shows a slightly higher conductivity, suggesting that, already, some solvolysis with strong ion pairing has occurred. Its conductivity, as we have shown,[14] is in fact much lower than that of ionic species such as tetrabutylammonium triflate and acetate (taken as ionic references). Upon dilution below about 10^{-4} M, only the Zn(II) complexes with sulfonate ligands show a sharp increase of their electrical conductivity, which, on the contrary, remains quite unchanged for the related acetate complex (Figure 2). As above-suggested, such different behavior is due to the much lower nucleophilicity of the sulfonate ligands when compared to that of acetates,[17] thus producing, in the former case, a significant solvolysis with strong ion pairing due to the low dielectric constant and donor properties of chloroform.

It is worth noting that the plot of the molar conductivity versus the square root of the concentration (Figure 2) is, on the whole, very similar to that of $\beta_{1.91}$ versus concentration (Figure 1).

As above-anticipated, the slightly higher conductivity, at concentrations higher than about 5×10^{-4} M, of the Zn(II) complex with the triflate ligand would suggest some slight solvolysis but with parallel strong ion pair formation. Strong ion pairing at relatively high concentrations (ca. 1×10^{-3} to 10^{-4} M) in anhydrous $CHCl_3$ was even proposed for a salt like the iodide of the alkylated cation of 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NBu_2$, to support its significant second-order NLO response, measured by the EFISH technique.[18] It follows that the quite high values of $\beta_{1.91}$, which characterize only the triflate complexes at concentrations higher than about 10^{-4} M,[14] can be ascribed to a slightly increased positive charge located on the stilbazole ligand, produced by solvolysis with parallel strong ion pairing. Such a suggestion of a slight increase of the positive charge on the stilbazole ligands in triflate complexes is in agreement with the slightly higher red shift of their intraligand ILCT transition and their slightly higher dipole moments when compared to the ILCT transitions and dipole moments of the related methanesulfonate or paratoluenesulfonate complexes (Table 1). In any case, the increase of $\beta_{1.91}$ cannot be explained only by the strong inductive effect of the electron withdrawing trifluoromethyl group because such an increase is not observed at all upon comparison with the $\beta_{1.91}$ values of the related Zn(II) complexes carrying the acetate and trifluoroacetate ligands(Table 1).

In conclusion, the unique property of the triflate ancillary ligand of increasing the second-order NLO responses of these kinds of Zn(II) stilbazole complexes must be clearly attributed not to a simple inductive effect but to its extremely low nucleophilic character, when compared not only to acetate or trifluoroacetate ancillary ligands but also to other sulfonate ligands.[17]

Conclusion

In this work, we have produced further evidence that the triflate ligand shows a unique behavior as an ancillary ligand in Zn(II) complexes with stilbazole-like ligands because it significantly increases their second-order NLO responses, measured by the EFISH technique in anhydrous chloroform, even when working at relatively high concentrations.

Such an increase does not occur, in the same range of concentrations, with less-electron-withdrawing sulfonate ligands, despite their significant red shift of the ILCT $n \rightarrow \pi^*$ transition of the stilbazole like ligands, much higher than that of the related complexes with acetate or trifluoroacetate as ancillary ligands. Usually, such a red shift was proposed as the main origin of the increase of the second-order NLO response of complexes with stilbazoles as ligands.[12,13] Therefore, the unexpected low values of the second-order NLO responses of complexes with methanesulfonate or paratoluenesulfonate as ancillary ligands (for instance, at high concentrations, their second-order NLO responses are lower than that of the related acetate complex, as shown in Table 1) would suggest that some process of association occurs at high concentrations, originated by their rather high dipole moment as the origin of their unexpected second-order NLO responses. This process of association cannot occur with complexes with the triflate ligand because, for these, conductivity evidence already supports some solvolysis, with parallel strong ion pairing, even at high concentrations. Only when working at diluted conditions, do all of the Zn(II) complexes with sulfonated ligands behave in the same way with a huge increase of $\beta_{1.91}$. This huge second-order NLO response can be ascribed to an ionic dissociation with the production of cations such as $[ZnY(4,4'\text{-}trans\text{-}NC_5H_4CH{=}CHC_6H_4NMe_2)_2]^+$ ($Y = CF_3SO_3$, CH_3SO_3, or $p\text{-}CH_3C_6H_4SO_3$), characterized by a large second-order NLO response.

In conclusion, ionic dissociation by dilution in anhydrous $CHCl_3$ remains a typical behavior of all Zn(II) complexes carrying an ancillary sulfonate ligand, which is independent of their electron withdrawing character and, therefore, of their nucleophilic properties.

Finally, it is worth pointing out that this work has produced additional evidence that the effect of the concentration *should not* be neglected when investigating the second-order NLO properties of a polar molecule that can theoretically associate or dissociate in a solvent of low polarity. This is an important observation because the concentration used for the experimental determination of the quadratic hyperpolarizability is traditionally not given in the literature, probably because the quadratic hyperpolarizability is considered a molecular property and, therefore, variation with the concentration for a particular molecule would not be expected.

Experimental Section

General Comments. $ZnCl_2 \cdot nH_2O$, $Zn(CF_3SO_3)_2$, 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$ (L^1), and $p\text{-}CH_3C_6H_4SO_3Ag$ were purchased from Sigma-Aldrich and were used without further purification. CH_3SO_3Ag was prepared according to the literature[19] by the reaction of Ag_2CO_3 with CH_3SO_3H, both purchased from Sigma-Aldrich. 4,4′-*trans*,*trans*-$NC_5H_4(CH{=}CH)_2C_6H_4NMe_2$ (L^2) was synthesized according to the literature[12] by the condensation of 4-picoline with *p*-dimethylaminocinnamaldehyde in anhydrous tetrahydrofuran with LDA as a base, followed by the elimination of the hydroxy group with 10% aqueous H_2SO_4. The sulfonate zinc complexes were prepared as described below. Acetate and trifluoroacetate zinc complexes were prepared according to the literature[13] by the reaction of stoichiometric amounts of the corresponding Zn(II) salt and L^1 and L^2. Products were characterized by ^1H NMR, mass (FAB+), and UV−vis spectroscopies and by elemental analysis (carried out in our department). Dipole moments were measured in $CHCl_3$ by using a WTW-DM01 dipolmeter (dielectric constant) coupled with an RX-5000 ATAGO Digital Refractometer (refractive index) and calculated by using the Guggenheim method.[20−22]

For the numbering used in the attribution of the NMR signals, see the structures in Scheme 1.

Synthesis of $[Zn(CF_3SO_3)_2(4,4'\text{-}trans\text{-}NC_5H_4CH{=}CHC_6H_4NMe_2)_2]$. To a suspension of $Zn(CF_3SO_3)_2$ (162 mg; 0.445 mmol) in anhydrous CH_2Cl_2 (50 mL), in a round-bottomed flask under N_2, was added 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$ (200 mg; 0.890 mmol). After the reaction had occurred for 3 h at room temperature, working in the dark (aluminum foil) and under vigorous magnetic stirring conditions, we obtained an orange solution. Evaporation of the solvent afforded a red, powdery product, which was purified by recrystallization from CH_2Cl_2/pentane, leading to pure $[Zn(CF_3SO_3)_2(4,4'\text{-}trans\text{-}NC_5H_4CH{=}CHC_6H_4NMe_2)_2]$ as a bright red solid (332 mg; 0.409; 92%). The product was kept under N_2 in the dark. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 8.46 [d, 4 H, ^3J (H, H) = 6.6 Hz, $2H_2$, $2H_6$], 7.67 [d, 4 H, ^3J (H, H) = 6.7 Hz, $2H_3$, $2H_5$], 7.55 [d, 2 H, J_{trans} (H, H) = 16.0 Hz, $2H_8$], 7.51 [d, 4 H, J_{ortho} (H, H) = 8.7 Hz, $2H_{2'}$, $2H_{6'}$], 6.85 [d, 2 H, J_{trans} (H, H) = 16.0 Hz, $2H_7$], 6.71 [d, 4 H, J_{ortho} (H, H) = 8.9 Hz, $2H_{3'}$, $2H_{5'}$], 3.08 [s, 12 H, $2NMe_2$]. MS (FAB+): *m*/*z* 661 [molecular ion peak − CF_3SO_3]$^+$. Elem Anal. Calcd (%) for $C_{32}H_{32}N_4O_6S_2F_6Zn$ (812.13): C, 47.32; H, 3.97; N, 6.90. Found: C, 47.03; H, 4.04; N, 6.93.

Synthesis of $[Zn(CF_3SO_3)_2(4,4'\text{-}trans,trans\text{-}NC_5H_4(CH{=}CH)_2C_6H_4NMe_2)_2]$. To a suspension of $Zn(CF_3SO_3)_2$ (145 mg; 0.40 mmol) in anhydrous CH_2Cl_2 (50 mL), in a round-bottomed flask under N_2, was added 4,4′-*trans*,*trans*-$NC_5H_4(CH{=}CH)_2C_6H_4NMe_2$ (200 mg; 0.80 mmol). After the reaction had occurred for 3 h at room temperature, working in the dark (aluminum foil) and under vigorous magnetic stirring conditions, we obtained a red solution. Evaporation of the solvent afforded a red, powdery product, which was purified by recrystallization from CH_2Cl_2/pentane, leading to $[Zn(CF_3SO_3)_2(4,4'\text{-}trans,trans\text{-}NC_5H_4(CH{=}CH)_2C_6H_4NMe_2)_2]$ as a dark red solid (327 mg; 0.378 mmol; 95%). The product was kept under N_2 in the dark. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 8.46 [d, 4 H, ^3J (H, H) = 6.8 Hz, $2H_2$, $2H_6$], 7.64 [d, 4 H, ^3J (H, H) = 6.7 Hz, $2H_3$, $2H_5$], 7.46 [dd, 2 H, J_{trans} (H, H) = 15.2 Hz, ^3J (H, H) = 10.6 Hz, $2H_9$], 7.41 [d, 4 H, J_{ortho} (H, H) = 8.9 Hz, $2H_{2'}$, $2H_{6'}$], 6.98 [d, 2 H, J_{trans} (H, H) = 15.2 Hz, $2H_7$], 6.84 [dd, 2 H, J_{trans} (H, H) = 15.4 Hz, ^3J (H, H) = 10.6 Hz, $2H_8$], 6.68 [d, 4 H, J_{ortho} = 8.9 Hz, $2H_{3'}$, $2H_{5'}$], 6.52 [d, 2 H, J_{trans} = 15.3 Hz, $2H_{10}$], 3.04 [s, 12 H, $2NMe_2$]. MS (FAB+): *m*/*z* 713 [molecular ion peak

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$- CF_3SO_3]^+$. Elem Anal. Calcd (%) for $C_{36}H_{36}N_4O_6S_2F_6Zn$ (864.21): C, 51.34; H, 4.68; N, 6.72. Found: C, 51.21; H, 4.55; N, 6.50.

Synthesis of $Zn(CH_3SO_3)_2{\cdot}3H_2O$. The addition of a water solution (5 mL) of CH_3SO_3Ag (241 mg; 1.18 mmol) to a water solution (3 mL) of $ZnCl_2{\cdot}nH_2O$ (81 mg; 0.59 mmol) led to the immediate precipitation of AgCl, which was removed by filtration. Evaporation to dryness of the filtrate, followed by washing with a few milliliters of CH_2Cl_2, afforded $Zn(CH_3SO_3)_2{\cdot}3H_2O$ (157 mg; 0.51 mmol; 86% yield) as a white powder. Elem Anal. Calcd (%) for $C_2H_{12}O_9S_2Zn$ (309.63): C, 7.75; H, 3.91. Found: C, 7.93; H, 4.02.

Synthesis of $[Zn(CH_3SO_3)_2(4,4'$-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2)_2]$. To a suspension of $Zn(CH_3SO_3)_2{\cdot}3H_2O$ (125 mg; 0.40 mmol) in CH_2Cl_2 (90 mL), in a round-bottomed flask under Ar, was added 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$ (181 mg; 0.80 mmol). After the reaction had occurred for 24 h at room temperature, working in the dark (aluminum foil) and under vigorous magnetic stirring conditions, we obtained an orange solution. Evaporation of the solvent afforded, in quantitative yield, $[Zn(CH_3SO_3)_2(4,4'$-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2)_2]$ of satisfactory purity as an orange solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 8.61 [br, 4 H, $2H_2$, $2H_6$], 7.45 [m, 8 H, $2H_3$, $2H_5$, $2H_{2'}$, $2H_{6'}$], 7.32 [d, 2 H, J_{trans} (H, H) = 16.1 Hz, $2H_8$], 6.79 [d, 2 H, J_{trans} (H, H) = 16.1 Hz, $2H_7$], 6.70 [d, 4 H, J_{ortho} = 8.9 Hz, $2H_{3'}$, $2H_{5'}$], 3.02 [s, 12 H, $2NMe_2$], 2.92 [s, 6 H, $2CH_3SO_3$]. MS (FAB+): *m*/*z* 638 [molecular ion peak $- SO_2]^+$, 607 [molecular ion peak $- CH_3SO_3]^+$. Elem Anal. Calcd (%) for $C_{32}H_{38}N_4O_6S_2Zn$: C, 54.58; H, 5.44; N, 7.96. Found: C, 54.69; H, 5.37; N, 8.12.

Synthesis of $Zn(p\text{-}CH_3C_6H_4SO_3)_2{\cdot}2H_2O$. The addition of a water solution (20 mL) of p-$CH_3C_6H_4SO_3Ag$ (610 mg; 2.18 mmol) to a water solution (3 mL) of $ZnCl_2{\cdot}nH_2O$ (149 mg; 1.09 mmol) at room temperature led to the immediate precipitation of AgCl, which, after it was stirred for 20 min, was removed by filtration. Evaporation to dryness of the filtrate afforded $Zn(p\text{-}CH_3C_6H_4SO_3)_2{\cdot}2H_2O$ (353 mg; 0.795 mmol; 73% yield) as a white powder. Elemen Anal. Calcd (%) for $C_{14}H_{18}O_8S_2Zn$ (443.81): C, 37.89; H, 4.09. Found: C, 37.66; H, 4.07.

Synthesis of $[Zn(p\text{-}CH_3C_6H_4SO_3)_2(4,4'$-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2)_2]$. To a suspension of $Zn(p\text{-}CH_3C_6H_4SO_3)_2{\cdot}2H_2O$ (296 mg; 0.667 mmol) in CH_2Cl_2 (100 mL), in a round-bottomed flask under N_2, was added 4,4′-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2$ (302 mg; 1.33 mmol). After the reaction had occurred for 22 h at room temperature, working in the dark (aluminum foil) and under vigorous magnetic stirring conditions, we obtained an orange solution. Evaporation of the solvent afforded, in quantitative yield, $[Zn(p\text{-}CH_3C_6H_4SO_3)_2(4,4'$-*trans*-$NC_5H_4CH{=}CHC_6H_4NMe_2)_2]$ of satisfactory purity as a red solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 8.65 [d, 4 H, ^3J (H, H) = 6.8 Hz, $2H_2$, $2H_{6'}$], 7.76 [d, 4 H, J_{ortho} (H, H) = 7.98 Hz, $2PhSO_3$ ortho to $SO_{3'}$], 7.48 [d, 4 H, ^3J (H, H) = 6.8 Hz, $2H_3$, $2H_5$], 7.46 [d, 4 H, J_{ortho} (H, H) = 8.6 Hz, $2H_{2'}$, $2H_{6'}$], 7.35 [d, 2 H, J_{trans} (H, H) = 16.5 Hz, $2H_8$), 7.13 [d, 4 H, J_{ortho} (H, H) = 7.98 Hz, $2PhSO_3$ meta to SO_3], 6.78 [d, 2 H, J_{trans} = 16.5 Hz, $2H_7$], 6.70 [d, 4 H, J_{ortho} (H, H) = 8.9 Hz, $2H_{3'}$, $2H_{5'}$], 3.04 [s, 12 H, $2NMe_2$], 2.34 [s, 6 H, $2p$-CH_3PhSO_3]. MS (FAB+): *m*/*z* 790 [molecular ion peak $- SO_2]^+$, 683 [molecular ion peak − p-$CH_3C_6H_4SO_3]^+$. Elem Anal. Calcd (%) for $C_{44}H_{46}N_4O_6S_2Zn$ (856.39): C, 61.71; H, 5.41; N, 6.54. Found C, 61.61; H, 5.49; N, 6.67.

EFISH Measurements. The molecular NLO responses of the complexes (Table 1) were measured by the solution-phase direct current electric-field-induced second-harmonic (EFISH) generation method,[7−10] which can provide γ_{EFISH}, that is, the direct information on the molecular NLO properties, through eq 1

$$\gamma_{EFISH} = (\mu\beta_\lambda/5kT) + \gamma(-2\omega;\ \omega,\ \omega,\ 0) \tag{1}$$

where $\mu\beta_\lambda/5kT$ is the dipolar orientational contribution, λ is the fundamental wavelength of the incident photon in the EFISH experiment, $\gamma(-2\omega; \omega, \omega, 0)$, a third-order term at frequency ω of the incident light, is the cubic electronic contribution to γ_{EFISH}, which is negligible for the kinds of molecules that are investigated here, and β_λ is the projection along the dipole moment axis of the vectorial component β_{VEC} of the quadratic hyperpolarizability tensor.[11−15] All of the EFISH measurements were carried out in our department in anhydrous $CHCl_3$ solutions of different concentrations working at a nonresonant incident wavelength of 1.907 mm, using a Q-switched, mode-locked Nd^{3+}:YAG laser, manufactured by Atalaser, equipped with a Raman shifter; the apparatus for the EFISH measurements was made by SOPRA (France).

Electrical Conductivity Measurements. Electrical conductivity measurements were carried out using anhydrous $CHCl_3$ solutions at eight different concentrations, ranging from 6×10^{-6} to 5×10^{-4} M, the upper value being determined by the solubility of the complexes, the lower by the reading capacity of the instrument. For each compound, a mother solution was first prepared at the highest concentration, which was then successively diluted to obtain all of the other solutions. All of the measurements were made at 298 K, using an AMEL 160 conductimeter equipped with an immersion cell with platinated platinum electrodes and glass insulating parts, characterized by a cell constant of ca. 1 cm^{-1} (exactly established at the beginning of the experimental work using a standard aqueous 0.01 M KCl solution).

The molar conductivity Λ (expressed in $\Omega^{-1}\ cm^2\ mol^{-1}$) is given by eq 2

$$\Lambda = \frac{1000\kappa}{c} \tag{2}$$

where c is the concentration of the solution (expressed in mol dm^{-3}) and κ is the specific conductivity in $\Omega^{-1}\ cm^{-1}$, directly obtained by conductance G through eq 3

$$G = \frac{1}{\kappa}\frac{L}{S} \tag{3}$$

where L/S is the cell constant.

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