mental analysis calcd (%) for C$_{664}$H$_{1136}$Cl$_{32}$Ru$_{16}$O$_{16}$P$_{32}$N$_{30}$: C 58.90, H 8.46; found: C 58.73, H 8.61.

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[17] Single crystals of **2A** from CH$_2$Cl$_2$/pentane at 4°C; monoclinic; space group *P*2$_1$/*c*; *a* = 25.0209(4), *b* = 9.3092(1), *c* = 18.5033(2) Å; *β* = 93.8485(5)°; *V* = 4300.2(2) Å^3, *ρ*$_{calcd}$ = 1.304 mg m^{-3} for *Z* = 4; *R*$_1$ = 0.034; *w*R$_2$ = 0.105; *R*$_{int}$ = 0.0235. CCDC-194781 (**2A**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit @ccdc.cam.ac.uk).

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Concentration Affects NLO Behavior

Large, Concentration-Dependent Enhancement of the Quadratic Hyperpolarizability of [Zn(CH$_3$CO$_2$)$_2$(L)$_2$] in CHCl$_3$ on Substitution of Acetate by Triflate**
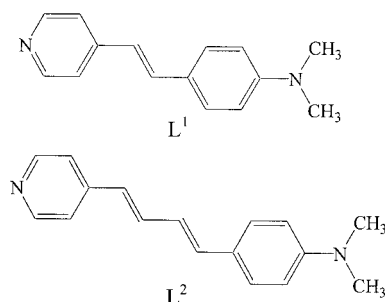
Francesca Tessore, Dominique Roberto, Renato Ugo, Patrizia Mussini, Silvio Quici, Isabelle Ledoux-Rak, and Joseph Zyss*

Organometallic and coordination compounds can offer a great diversity of tunable electronic properties that act on their second-order nonlinear optical (NLO) response.[1] The quadratic hyperpolarizability, measured by the electric field

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induced second harmonic (EFISH) generation technique,[2] of push–pull stilbazole ligands such as 4,4'-*trans* or *trans,trans*-$NC_5H_4(CH=CH)_nC_6H_4NMe_2$ ($n = 1$ and 2 for L = L^1 and L^2, respectively) usually increases on coordination to various acceptor centers.[3] According to both theoretical[3b] and

Figure 1. Dependence of $\beta_{1.91}$ on concentration for $[Zn(CH_3COO)_2L_2^1]$ (○), $[Zn(CF_3SO_3)_2L_2^1]$ (●), and NPP (reference; ◇) in anhydrous $CHCl_3$.

solvatochromic[3e] investigations, this enhancement mainly originates from the red shift of the intraligand charge transfer (ILCT) n→π* transition, which is often controlled by the increased Lewis acceptor properties of the metal atom[3d] and therefore by the ancillary ligands that tune these properties.[3e] However, up to now the effect of a very strong electron-withdrawing ancillary ligand such as the triflate anion has not been investigated.

A large enhancement of the dipole moment μ of $[ZnX_2L_2]$ complexes (X = CH_3CO_2, CF_3CO_2, CF_3SO_3) in anhydrous $CHCl_3$[4] occurs on coordination of the triflate ligand, together with a red shift of the ILCT transition of the stilbazoles L^1 or L^2 that is much larger ($\Delta\lambda_{max} = 116–123$ nm) than usually occurs on coordination to "$Zn(CH_3CO_2)_2$" or "$ZnCl_2$" ($\Delta\lambda_{max} = 2–36$ nm, Table 1)[3e] or, despite the well-known positive effect of chelation[3e] on coordination to the Zn^{II} complexes of electronically related chelating ligands such as 4-dialkylaminostyryl-2,2'-bipyridine (59–72 nm)[5a, b] or 4,4'-bis(dialkylaminophenylazo)-2,2'-bipyridine and 4,4'-bis(dialkylaminophenylimino)-2,2'-bipyridine ($\Delta\lambda_{max} = 45–58$ nm).[5c] Consistent with such a large red shift, the quadratic hyperpolarizability $\beta_{1.91}$, measured in anhydrous $CHCl_3$ at an incident wavelength of 1.907 μm by the EFISH technique,[2] of $[Zn(CF_3SO_3)_2L_2]$ (L = L^1, L^2) complexes is much higher than that of related Zn^{II} complexes with Cl, CH_3CO_2, and
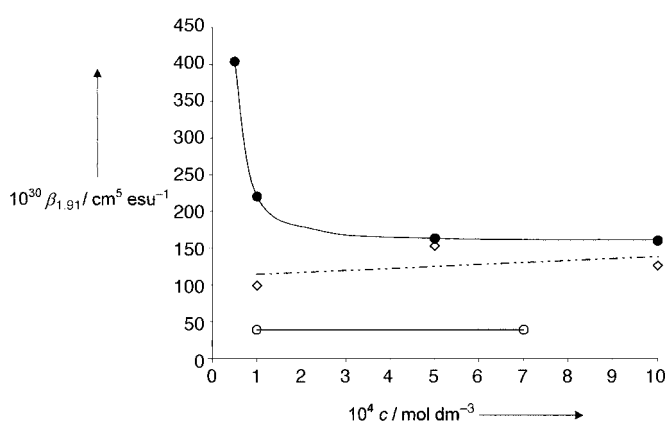
CF_3CO_2 ancillary ligands (Table 1).[3e] This increase in the second-order NLO response is far higher than those reported up to now for the coordination of these push–pull stilbazoles to various metal centers or even to the very strong Lewis acid BF_3.[3a–e]

Surprisingly, the $\beta_{1.91}$ value of these triflate complexes is dependent on concentration (Table 1). At concentrations below about 10^{-4} M, it increases abruptly with decreasing concentration, and reaches very large values (Figure 1), an effect that is not observed for the acetate or trifluoroacetate complexes (Table 1). This large increase does not result from inappropriate EFISH measurements owing to high dilution, since $\beta_{1.91}$ of *N*-(4-nitrophenyl)-L-prolinol (NPP), taken as reference and measured under the same conditions by the EFISH technique,[2] remains unchanged even at a concentration of 10^{-4} M (Figure 1).

Given the weak nucleophilicity of the triflate anion, these results could be explained by some solvolysis of strong ion pairs, as suggested by the fact that it was not possible to carry out EFISH[2] or capacitance measurements[4] when $CHCl_3$ was not completely anhydrous, because traces of water lead to dissociation of strong ion pairs into ionic species which hinder EFISH and capacitance measurements. Careful investigations of the electrical conductivity of anhydrous $CHCl_3$ solutions (Figure 2) of $[ZnX_2L_2]$ complexes (X = CH_3CO_2, CF_3CO_2, CF_3SO_3) are in agreement with this proposal. According to Figure 2, both $[Zn(CH_3CO_2)_2L_2^1]$ and $[Zn(CH_3CO_2)_2L_2^2]$ are practically undissociated in the concentration range $10^{-3}–10^{-4}$ M, while the complexes with the triflate ligand show a slightly higher conductivity, but much lower than that of reference ionic species such as tetrabutylammonium triflate and acetate. The conductivities of these two salts are comparable, so that we can safely assume that in anhydrous $CHCl_3$ both triflate and acetate anions have comparable ionic mobilities.

Table 1: Electronic spectra, dipole moments, and $\beta_{1.91}$ values of various $[ZnX_2L_2^1]$ and $[ZnX_2L_2^2]$ complexes (X = CH_3CO_2, CF_3CO_2, CF_3SO_3).

Complex	$10^4 c$ [M]	λ_{max} [nm][a]	μ [D][a]	$10^{30}\mu\beta_{1.91}$ [D cm^5 esu^{-1}][a]	$10^{30}\beta_{1.91}$ [cm^5 esu^{-1}][a]	EF[b]
$[Zn(CH_3CO_2)_2L_2^1]$	1–7	376[3e]	8.0[3e]	316	39	–
$[Zn(CF_3CO_2)_2L_2^1]$	1–7	420[3e]	10.5[3e]	512	49	1.3
$[Zn(CF_3SO_3)_2L_2^1]$	10	490	16.7	2715	163	4.2
	5			2720	163	4.2
	1			3670	220	5.6
	0.5			6750	404	10.4
$[Zn(CH_3CO_2)_2L_2^2]$	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 $\beta_{1.91}$ enhancement factor with respect to the related $[Zn(CH_3CO_2)_2L_2]$ complex, that is, $\beta_{1.91}([ZnX_2L_2])/\beta_{1.91}([Zn(CH_3CO_2)_2L_2])$.
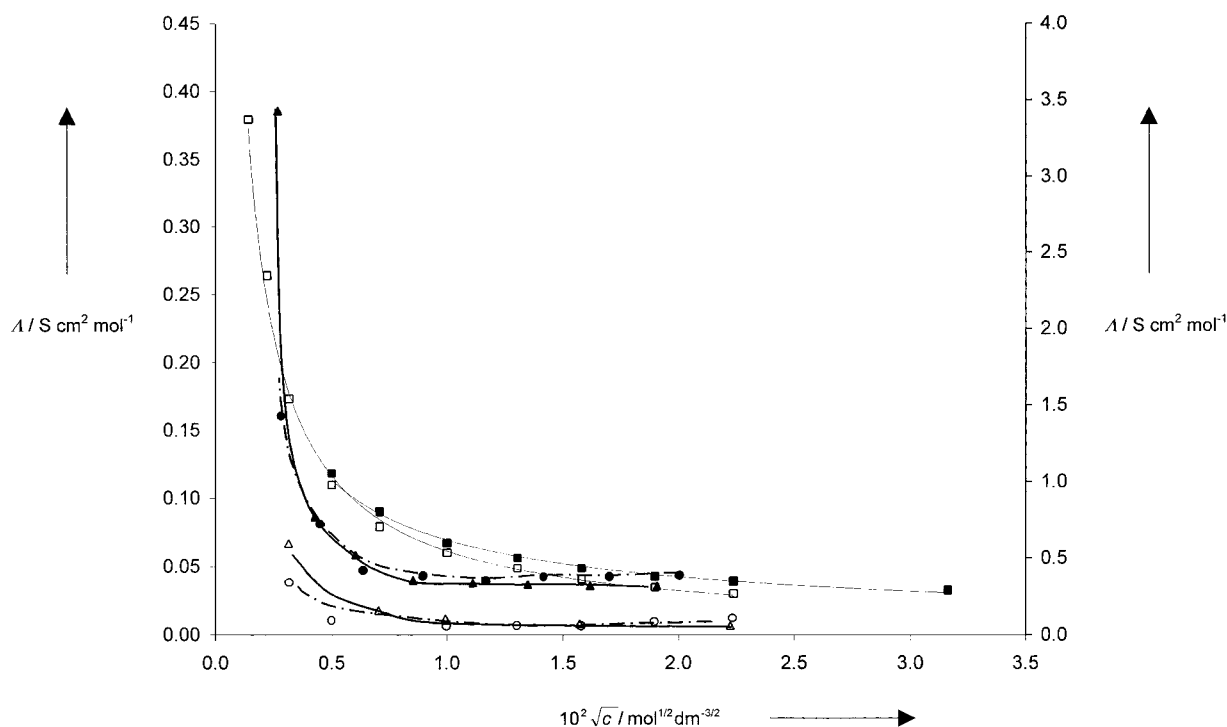
Figure 2. Dependence of molar conductances Λ of zinc acetate and triflate complexes of ligands L^1 and L^2 (left *y* axis) and of tetrabutylammonium acetate and triflate salts (right *y* axis) on the square root of the concentration *c* in anhydrous $CHCl_3$ at 298 K. $\bigcirc = [Zn(CH_3COO)_2L_2^1]$, $\triangle = [Zn(CH_3COO)_2L_2^2]$, $\bullet = [Zn(CF_3SO_3)_2L_2^1]$, $\blacktriangle = [Zn(CF_3SO_3)_2L_2^2]$; $\square = [Bu_4N]CH_3COO$, $\blacksquare = [Bu_4N]CF_3SO_3$.

Therefore, the slight but significant conductivity enhancement observed on passing from acetate to triflate ancillary ligands (Figure 2) confirms the hypothesis of some solvolysis of the triflate anion with concomitant strong ion pairing. Strong ion pairing in anhydrous $CHCl_3$ was already proposed to explain the significant second-order NLO response, measured by the EFISH technique,[2] for the iodide salt of the alkylated cation of 4,4′-*trans*-$NC_5H_4CH=CHC_6H_4NBu_2$.[6] Accordingly, the sharp conductivity increase towards limiting values for triflate complexes at concentrations below 10^{-4}M indicates a sharp increase in the degree of ionization, as expected for increased dissociation of ion pairs with increasing dilution. It is noteworthy that the molar conductivity versus concentration trend (Figure 2) is similar to that of $\beta_{1.91}$ versus concentration (Figure 1). Therefore, the large increase in $\beta_{1.91}$ at very low concentrations must be attributed to increased dissociation of strong ion pairs owing to solvolysis of the triflate ligand.

Nevertheless, the $\beta_{1.91}$ values of $[Zn(CF_3SO_3)_2L_2]$ complexes at concentrations above 10^{-4}M are already three to six times higher than those of the related acetate or trifluoroacetate complexes (Table 1). This unusual result supports a mechanism for increasing the positive charge on the stilbazole system, such as ion pairing, which should favor the unusually high red shift of their ILCT transitions. In fact this increase cannot be explained solely by the stronger inductive electron-withdrawing effect of triflate relative to trifluoroacetate. Consequently, an increased concentration (albeit still very low, because the EFISH measurement is possible) of the free cation $[Zn(CF_3SO_3)_2L_2]^+$, which, as expected for a localized positive charge, must have a very high $\beta_{1.91}$ value, is the origin of the large $\beta_{1.91}$ value at high dilution.

A possible general role of the triflate ligand in increasing the quadratic hyperpolarizability, measured in anhydrous $CHCl_3$ solution, of complexes of ligands L^1 or L^2 with other metals or of Zn^{II} complexes with chelating nitrogen-donor π-delocalized ligands[3e,5] is under investigation, as is the effect on the second-order NLO response of Zn^{II} complexes of ligands L^1 or L^2 and less strongly electron withdrawing sulfonated ancillary ligands, to determine whether the strong increase in the quadratic hyperpolarizability results only from the sulfonate nature of the ligand, or whether it also requires a strongly electron-withdrawing CF_3 group. Although the concentration used for the experimental determination of the quadratic hyperpolarizability is traditionally not reported, probably because it is a molecular property which should not vary with concentration, here we have provided clear evidence that quadratic hyperpolarizabilities can be strongly concentration dependent.

Experimental Section

Complexes $[ZnX_2L_2]$ ($X = CH_3CO_2$, CF_3CO_2, CF_3SO_3; $L = L^1$ or L^2) were prepared[3e] by allowing a stoichiometric mixture of $ZnX_2 \cdot x H_2O$ (kept under vacuum at 100°C for 3 h) and L in CH_2Cl_2 to stir at room temperature in the dark for 3 h. Removal of the solvent under vacuum and recrystallization from dichloromethane/pentane afforded the complexes, which were stored under N_2 in the dark and characterized by elemental analysis, ^{1}H NMR spectroscopy, and mass spectrometry (FAB +). EFISH measurements[3d, e] were carried out in anhydrous $CHCl_3$ (purchased from Fluka and used without further

treatment) at an incident wavelength of 1.907 μm. Dipole moments μ were determined in anhydrous $CHCl_3$ by the Guggenheim method.[4] All solutions for EFISH, conductivity, and capacitance measurements were used immediately after preparation.

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Dual Stereoselectivity of 1-(2′-Carboxy)benzyl 2-Deoxyglycosides as Glycosyl Donors in the Direct Construction of 2-Deoxyglycosyl Linkages**

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2-Deoxyglycosides are found as the integral part of many important natural products.[1] The stereocontrolled construction of 2-deoxyglycosyl linkages is more challenging than that of usual glycosyl linkages as the 2-deoxyglycosyl donors lack the stereodirecting substituent at C2 and the resulting glycosides are more acid-labile. Although the synthesis of 2-deoxy-α-glycopyranosides is relatively easier, the construction of 2-deoxy-β-glycopyranosyl linkages is a far more challenging problem[2] as the axial addition of a glycosyl acceptor to the oxocarbenium ion intermediate is a favorable process owing to the anomeric effect.[3] Therefore, the frequently used method for the synthesis of 2-deoxy-β-glycopyranosides employs the glycosyl donors with equatorial heteroatom substituents at C2 that can participate during glycosylation to direct the incoming acceptor to the β-face and are removed at a later stage.[4] Nevertheless, a direct and efficient method for the construction of the 2-deoxy-β-glycopyranosyl linkage by using a 2-deoxyglycopyranosyl donor would be more efficient and practical than the indirect methods. Although a few methods (e.g. glycosylation mediated by silver silicate[5] or silver zeolite,[6] the 2-deoxyglycosyl phosphite/TMSOTf (TMSOTf = trimethylsilyl trifluoromethanesulfonate) method,[7] and the glycosylation of 2-deoxyglycosyl fluoride with TiF_4[8] or $SnCl_2$,[9]) have been devised, the direct synthesis of 2-deoxy-β-glycopyranosides from 2-deoxyglycosyl donors still remains a difficult task. We have previously introduced (2′-carboxy)benzyl (CB) glycosides as glycosyl donors for the efficient β-mannopyranosylation.[10] We applied this CB glycoside methodology to the direct synthesis of 2-deoxyglycopyranosides and herein report the preparation of CB 2-deoxyglycosides from glycals and their α- or β-stereoselectivity (dual stereoselectivity) as glycosyl donors in the glycosylation reaction, depending on their protecting groups.

CB 2-deoxyglucoside **4** was readily obtained from the tribenzylglucal **1** as shown in Scheme 1. CB 4,6-*O*-benzylidene-2-deoxyglucoside **7**, on the other hand, was prepared from a 3,4,6-tri-*O*-acetyl-D-glucal via 2-deoxyglycosyl bromide **5**.[13] Glycosylations of the CB 2-deoxyglycosyl donors **4** and **7** were performed with primary alcohol acceptors **8–12** and with secondary alcohol acceptors **13–17**. Glycosylation of the benzyl-protected donor **4** with primary alcohol acceptors

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