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Zinc(II) as a Versatile Template for the Design of Dipolar and Octupolar NLO-phores

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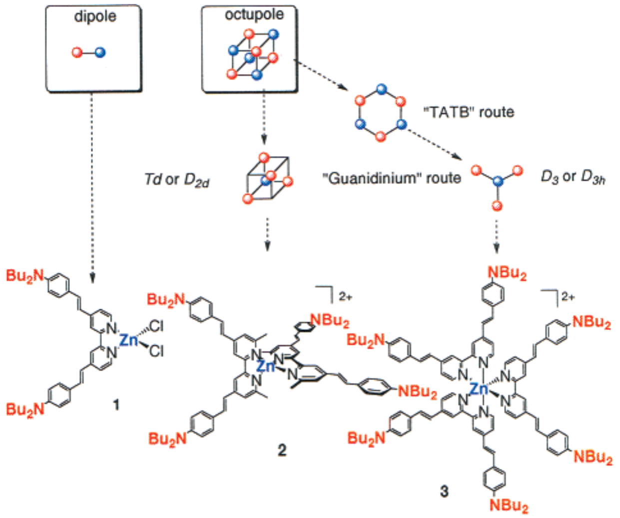
Received January 25, 2002

Interest in nonlinear optics has led to the design of numerous chromophores with large molecular hyperpolarizability β, mainly monodimensional (1D) dipolar chromophores.[1] Recognition in the early 1990s of the enlarged potential for nonlinear optics of octupolar molecules has triggered the emergence of a new field of research.[2] Basically, purely octupolar symmetries can be derived from a cubic Td structure either by projection along a C_3 axis giving rise to the D_{3h} or D_3 symmetries ("TATB route") or by fusion of one type of charge in the barycenter leading to the D_{3h}, D_3, T_d, or D_{2d} symmetries ("guanidinium route") (Scheme 1). Thus, an increasing number of 2D and 3D nondipolar molecular structures have recently appeared in the literature with the revival and development of the harmonic light scattering technique (HLS).[3]

Metal ions are powerful 3D templates, which can gather ligands to build a variety of predetermined stereochemical (octupolar) arrangements. In this context, 4,4′-bis(dialkylaminostyryl)-[2,2′]-bipyridine ligands have been recently used for the molecular engineering of octupolar D_3 ruthenium(II)[4] and D_{2d} copper(I)[5] complexes, due to their well-defined coordination with these metal ions. By contrast, since there is no ligand field stabilization effect, zinc(II) has the ability to expand its coordination sphere and therefore is known to give tetrahedral complexes or octahedral complexes with diimine ligands. Herein we would like to show that this characteristic provides a unique opportunity to design either dipolar or octupolar D_{2d} and D_3 molecules by simple controlled combination of one, two, or three bipyridyl ligands with zinc(II). In addition, these new octupolar chromophores display very large off-resonant first-order hyperpolarizabilities and present an improved transparency/nonlinearity tradeoff as compared to the corresponding dipolar molecule.

The dipolar zinc(II) complex **1** has already been described elsewhere[6] and was obtained upon room-temperature treatment of $ZnCl_2 \cdot 2H_2O$ with one equivalent of 4,4′-bis(dibutylaminostyryl)-[2,2′]-bipyridine **a** in dichloromethane. The tris(bipyridyl) zinc(II) complex **3** was readily obtained in 83% yield by refluxing 3 equiv of **a** with $ZnCl_2 \cdot 2H_2O$ in ethanol, followed by an exchange of the chloride with hexafluorophosphate counterions. The synthesis of the bis(bipyridyl) zinc(II) complex **2** was quantitatively achieved by reacting at room temperature $Zn(OTf)_2$ with 2 equiv of the α,α′-methyl substituted bipyridyl ligand **b**, which was used in place of **a** in order to ensure the pseudotetrahedral D_{2d} symmetry (Scheme 1).[7] The structure of **2** and **3** was unambiguously confirmed by ^1H, and ^{13}C NMR spectroscopy and elemental analysis.

Scheme 1



These complexes exhibit intense intraligand charge transfer (ILCT) in the visible region as depicted in Figure 1. The complexation is accompanied by a bathochromic shift which is sensitive to the structure of the Zn(II) complexes. Compared to the free ligands **a** ($\lambda_{max} = 401$ nm) or **b** ($\lambda_{max} = 397$ nm), the neutral Zn(II) complex **1** has a red-shift ($\Delta\lambda = 58$ nm) smaller than the dicationic complexes **2** ($\Delta\lambda = 131$ nm) and **3** ($\Delta\lambda = 65$ nm). Concerning **2** and **3**, the bathochromic shift depends on the number of coordinated ligands and decreases substantially as the ligand-to-metal ratio increases. Moreover, complexes **1**−**3** are intense dyes exhibiting high molecular extinction coefficients. The oscillator strengths[8] (Table 1) follow a 1:1:1.8:2.9 ratio for **a**, **1**, **2**, and **3**, respectively, as expected for noninteracting subchromophores (1:1:2:3).[3c−d] This is in agreement with the absence of an extended delocalization through Zn^{2+} between the bipyridyl subchromophoric units in **2** and **3**. These new octupolar complexes possess good thermal stability with 10% weight losses ($T_{d_{10}}$ determined by TGA) occurring above 300 °C.

The molecular hyperpolarizability coefficient β and the corresponding dispersion free hyperpolarizability β_0 for compounds **1**−**3** are reported in Table 1. For the neutral dipolar compound **1**, $\mu\beta$ was determined by the electric-field-induced second harmonic generation (EFISH) method at $\lambda = 1.34$ μm as fundamental wavelength,[6] and β was then deduced by measuring the dipole moment μ by means of the Guggenheim model. β measurements of octupolar complexes **2** and **3** were performed by the harmonic light scattering (HLS) method at 1.91 μm. As the harmonic wavelength at 955 nm is far enough from the $\lambda_{cut-off}$ of these complexes, any contribution of two-photon-induced fluorescence

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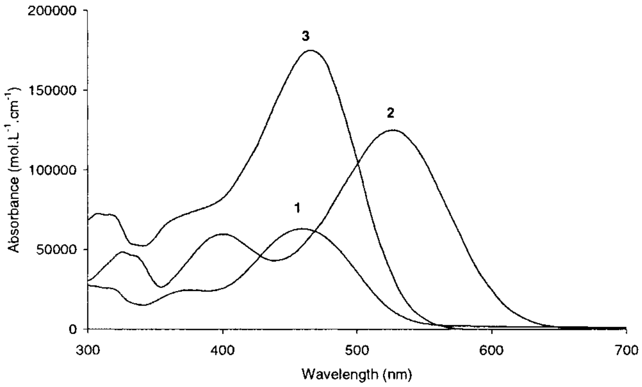

Figure 1. UV−visible spectra of complexes **1**−**3**.

Table 1. Linear and Nonlinear Optical Data

cmpd	λ_{max} (nm)	ϵ (mol·L^{-1}·cm^{-1})	$\nu_{1/2}$ (cm^{-1})	f	β (10^{-30}esu)	β_0 (10^{-30}esu)	T_{d10} (°C)
a	401	65000	4280	1.22			380
b	397	61000	4348	1.15			368
aZnCl$_2$ **1**	459	62000	4490	1.22	172[a]	62	399
b$_2$Zn^{2+} **2**	529	125000	3825	2.07	245[b]	157	308
a$_3$Zn^{2+} **3**	466	175000	4544	3.48	340[b]	241	330

[a] Measured by EFISH (precision ±10%) at 1.34 μm in a 10^{-3} mol·L^{-1} chloroform solution; $\mu \cdot \beta = 1830 \times 10^{-30}$ esu[5] with $\mu = 10.65$ D. [b] Measured by HRS (precision ±15%) in a (1−5)·10^{-2} mol·L^{-1} dichloromethane solution at 1.91 μm.

to the HLS signal can be considered as negligible. HLS measurements were carried out in concentrated dichloromethane solution ($1-5 \times 10^{-2}$ mol·L^{-1}) with a concentrated solution of ethyl-violet as reference ($\beta^{1.91} = 170 \times 10^{-30}$ esu). Interestingly, the off-resonant β_0 values (Table 1) monotonically increase from **1** to **3** with respect to the number of subchromophores organized around the Zn(II) center. The β_0 value of **2** is about 2-fold larger than that of the recently reported tetrahedral Cu^{I}(**b**)$_2^{+}$ complex ($\beta_0 = 78 \times 10^{-30}$ esu).[5] This result is consistent with the better acceptor strength of Zn^{2+} versus Cu^{+} and the absence of an antagonist MLCT transition in **2**. An improved transparency/nonlinearity tradeoff is reached for the octahedral complex **3** as compared to that for the tetrahedral complex **2**. Moreover, these results point out the efficiency of the octupolar strategy since **3** exhibits a β_0 value that is roughly 4 times larger than that of the corresponding dipolar derivative **1**, without the undesirable bathochromic shift of the ILCT transition [$\Delta\lambda$(**3** vs **1**) = 7 nm]. It is also worth noting that **3** exhibits a very large β_0 value of 241×10^{-30} esu (comparable to that of the ruthenium analogous complex[9]), which is to the best of our knowledge the largest ever reported for octupolar molecules.[10] The enhanced molecular NLO activity of D_3 metallo-octupoles as compared to those of the most efficient D_{3h} organic octupoles can be related to the ability of Zn^{2+} to organize three subchromophores or six intraligand charge transfers, whereas the central benzene ring in D_{3h} organic octupoles allows the spatial arrangement of only three charge transfers.

In conclusion, this study shows that the possibility of expanding the coordination number renders Zn^{2+} very effective for the simple and easy design of (1D) dipolar structures or (3D) octupolar structures. Moreover, the results illustrate the superiority of octupoles versus dipoles in terms of nonlinearity without significant cost of transparency. Their good thermal stability and large first hyperpolarizability make them attractive candidates for nonlinear optical materials.

Acknowledgment. We thank the Région Bretagne (PRIR 99CC10) and the CNRS for financial support. K.S. is grateful to the French Ministry of Education for a fellowship.

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(8) The oscillator strength f is estimated by the following relationship: $f = 4.319 \times 10^{-9} \cdot \epsilon \cdot \nu_{1/2}$ where $\nu_{1/2}$ represents the half-height bandwidth (cm^{-1}).

(9) More recent measurements concerning [**a**$_3$Ru][PF$_6$]$_2$ give fluorescence-free β_0 of ca. 240×10^{-30}esu see ref 4c.

(10) The most efficient D_{3h} organic octupoles featuring extended conjugated pathway are: 1,3,5-triscyano-2,4,6-tris(dibutylaminobistyryl)benzene ($\lambda_{max} = 470$ nm, $\beta^{1.56} = 219 \times 10^{-30}$esu, $\beta_0 = 116 \times 10^{-30}$esu), see ref 3 g−h; 1,3,5-tris(methylsulfonylbistyryl)benzene ($\lambda_{max} = 377$ nm, $\beta^{1.34} = 250 \times 10^{-30}$esu, $\beta_0 = 157 \times 10^{-30}$esu), see ref 3j; and 4,9,14-tris(4′-(di-4-methoxyphenyl)aminophenylethynyl)truxenone ($\lambda_{max} = 509$ nm, $\beta_0^{xxx} = 169 \times 10^{-30}$esu, $\beta_0 = 104 \times 10^{-30}$esu), see ref 3b.

JA025705A