Molecular Engineering of Octupolar NLO Molecules and Materials Based on Bipyridyl Metal Complexes

OLIVIER MAURY AND HUBERT LE BOZEC*

Institut de Chimie, UMR 6509 CNRS-Université de Rennes1, Campus de Beaulieu, 35042 Rennes Cedex, France

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ABSTRACT

Coordination compounds are of particular interest for the design of new chromophores with large nonlinear optical (NLO) susceptibilities. They offer a wide range of metals with different oxidation states and ligands, which can give rise to tunable electronic properties. Metal ions are excellent templates to build 2D and 3D octupolar NLO-phores. Their associations with functionalized bipyridyl ligands give rise to octahedral and tetrahedral metal complexes with large first-order hyperpolarizabilities. The ability to functionalize these octupoles allows their incorporation into macromolecular architectures such as polymers and metallodendrimers, We also show in this Account two approaches to induce noncentrosymmetry at the macroscopic level, either by supramolecular organization or by the all optical poling procedure.

I. Introduction

Much attention is currently devoted to the search of new molecular materials for optoelectronics because of their potential applications in photonic devices.[1] Extensive

Olivier Maury graduated from the Ecole Nationale Supérieure de Chimie de Paris in 1993 and got his Ph.D. in 1997 under the supervision of M. Ephritikhine (CEA-Saclay). After a postdoctoral position with J.-M. Basset (CPE-Lyon), he got a CNRS position as Chargé de Recherche in 1999 at the University of Rennes. Recently, he moved to the Ecole Normale Supérieure of Lyon in the group of Chantal Andraud. His current research interests concern the design of lanthanides containing molecular materials for optical applications (luminescence and nonlinear optics) toward biological imaging.

Hubert Le Bozec got his Ph.D. in 1981 in Rennes under the supervision of Prof. P. H. Dixneuf. He then spent 1 year in Chapel Hill (North Carolina) in Prof. T. J. Meyer's lab. He is currently Directeur de Recherche of CNRS in Rennes (France). His current research interests are in the area of coordination and organometallic chemistry for NLO and luminescence.
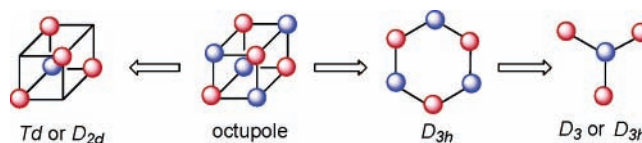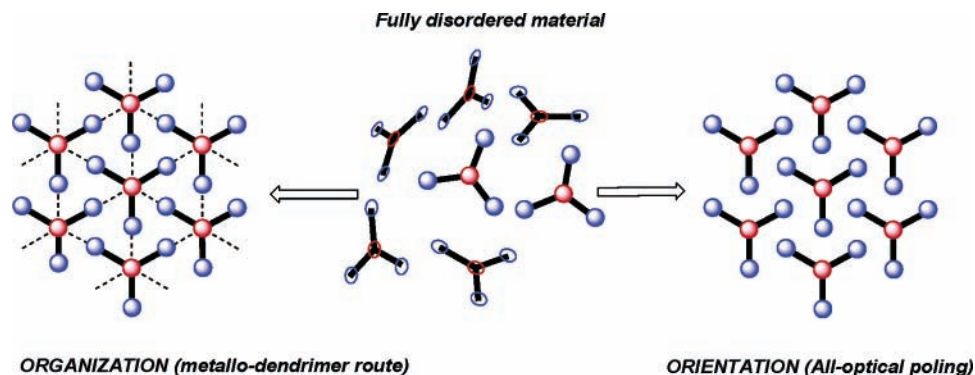
FIGURE 1. Schematic representation of octupolar symmetries.

efforts have been directed toward the design and synthesis of efficient chromophores, which can be incorporated into macroscopic assemblies such as polymers to form materials exhibiting large nonlinear optical (NLO) responses.[2] Traditionnally, such chromophores are noncentrosymmetric dipolar molecules containing donor and acceptor end groups connected through a π backbone.

Beyond this classical dipolar approach, the concept of octupolar nonlinearities was proposed in the early 1990 on the basis of group theoretical and quantum mechanical studies.[2a,3] Recognition of the enlarged potential for nonlinear optics of octupolar molecules has sparked intense research in this new field. Basically, purely octupolar symmetries can be derived from a cubic structure either by projection along a C_3 axis giving rise to the D_{3h} symmetries or by fusion of one type of charge in the center leading to the D_{3h}, D_3, T_d, or D_{2d} symmetries (Figure 1). For molecules belonging to purely octupolar space groups, the vector part of the molecular hyperpolarizability β ($J = 1$) is canceled out and only the octupolar contribution of β ($J = 3$) remains. The advantages of using nondipolar chromophores include easier noncentrosymmetric arrangements and an improved nonlinearity tradeoff. Thus, an increasing number of octupolar organic structures have recently appeared in the literature with the revival of the harmonic light scattering (HLS) technique.[4] Coordination chemistry can also be a powerful tool to build up such octupolar arrangements, and the first demonstration of the potential of transition-metal complexes for NLO was reported by Zyss on Ru(bpy)$_3^{2+}$ of D_3 symmetry.[5] Over the past decade, we have been concerned with the NLO properties of 4,4′-disubstituted-[2,2′]-bipyridine metal complexes.[6] An interesting feature that these ligands offer is their synthetic flexibility that allows fine tuning of the

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* To whom correspondence should be addressed. E-mail: lebozec@univ-rennes1.fr.

Fully disordered material

ORGANIZATION (metallo-dendrimer route)   ORIENTATION (All-optical poling)

FIGURE 2. Organization versus orientation of octupoles.

optical properties through a simple change of the π-conjugated backbone. These ligands are excellent building blocks for the construction of octupolar either octahedral or pseudotetrahedral complexes. In these systems, the metal plays several important roles, which contribute to NLO activity: (i) it is a powerful template to gather ligands in predetermined octupolar arrangements; (ii) it can induce a low-energy metal−ligand charge-transfer transition (MLCT); and (iii) it acts as a Lewis acid to induce a strong intraligand charge-transfer (ILCT) transition.
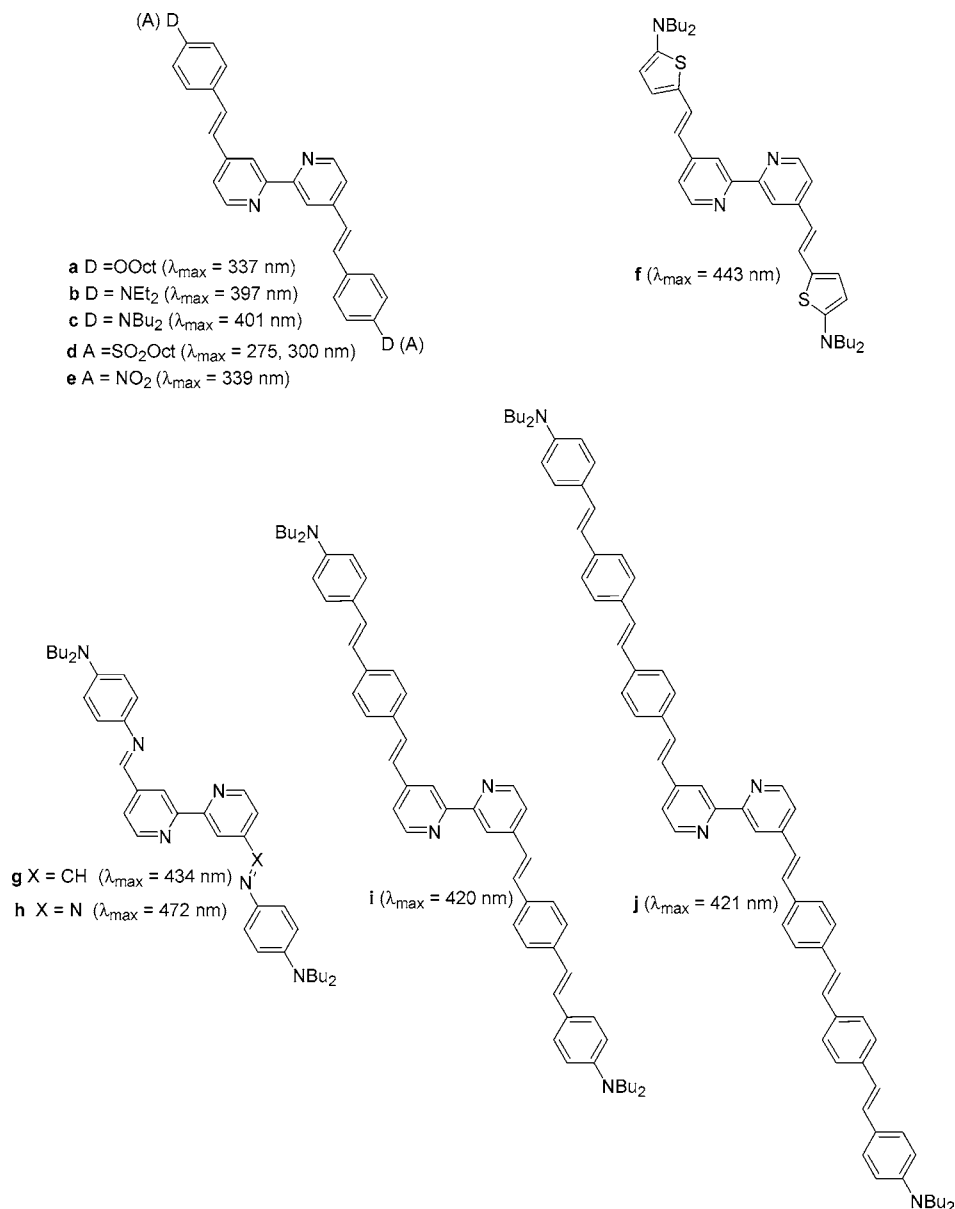
The incorporation and acentric arrangement of NLO-phores into a macroscopic environment constitutes the second step toward the engineering of nonlinear materials and devices. In this regard, several strategies using *dipolar chromophores* have been intensively investigated,[1,2] such as statistical orientation by electrical poling of NLO polymers, predetermined orientation of NLO-phores by using the Langmuir−Blodgett technique, stepwise construction of multilayers or pre-organization of NLO active species within multichromophoric systems. In contrast, construction of macroscopic assemblies featuring *octupolar chromophores* remains in its infancy, particularly as far as macro- and supramolecular architectures are concerned.[7] Such nondipolar materials would be able to overcome the problem of intermolecular dipole−dipole repulsion, which is a major drawback in the realm of electro-optic polymers. The wide possibility offered by bipyridine metal complexes as building blocks for the construction of supramolecular species has prompted us to design multi-octupolar compounds such as polymetallic complexes, metallodendrimers, and metallopolymers. In this Account, we summarize our successful strategies toward the synthesis of molecular and macromolecular octupolar NLO-phores based on metal−bipyridyl chemistry. Two possible ways to engineer an acentric arrangement of octupolar units either by supramolecular macroscopic *organization* (the metallodendrimer route) or by optical *orientation* in polymer films (the all-optical poling technique) are also presented (Figure 2).

II. Design of 4,4′-π-Conjugated-2,2′-bipyridines

We have developed several convenient methods for the preparation of a series of 4,4′-disubstituted-2,2′-bipyridines featuring π-conjugated substituents such as donor-(acceptor) substituted styryl, bistyryl, tristyryl, thienylvinyl,

phenylimino, and azophenyl groups[8,9] (Figure 3). The access to 4,4′-π-donor-styryl-[2,2′]-bipyridines **a**−**c** and 4,4′-dibutylaminothienylvinyl-[2,2′]-bipyridine **f** involved the deprotonation of 4,4′-dimethyl-[2,2′]-bipyridine followed by addition of the corresponding aldehyde. The synthesis of ligands **d** and **e** featuring electron-withdrawing substituents ($Z = -SO_2Oct$ and $-NO_2$) required a Wadworth−Emmons condensation of the appropriate phosphonates with 4,4′-dicarbaldehyde-[2,2′]-bipyridine as the building molecule. To this end, we reported a new two-step synthesis of dicarboxaldehyde-bisimine derivatives by enamination with the Bredereck reagent *tert*-butoxybis(dimethylamino)methane, followed by oxidative cleavage of the enamine double bonds with sodium periodate.[10] The imino-containing bipyridine **g** was quantitatively obtained by a Schiff-base condensation reaction between *N,N*-diethyl-1,4-phenylenediamine and 4,4′-dicarbaldehyde-[2,2′]-bipyridine. The azo-containing bipyridyl ligand **h** was synthesized by diazotation of 4,4′-diamino-[2,2′]-bipyridine with sodium nitrite and the subsequent coupling with *N,N*-dibutylaniline.[11] All of these compounds were characterized by ^{1}H and ^{13}C NMR, and the trans configuration of the C=C, C=N, as well as the N=N linkages was evidenced by an X-ray diffraction analysis.[8] Synthesis of bipyridines featuring extended oligophenylenevinylene π-conjugated backbones (OPV-bpy) **i** and **j**, which are the "styrylogous" of **c**, was achieved by using another methodology, i.e., by means of a double Wadworth−Emmons reaction upon treatment of 4,4′-bis-(phosphonate)-[2,2′]-bipyridine with the corresponding aldehydes.[9]

The optical spectra of "push−pull" molecules containing a donor alkoxy or amino end group are characterized by an intense, structureless, and broad absorption band, which can be assigned to an intramolecular charge-transfer transition (ICT). In contrast, bipyridines featuring an electron-withdrawing group (SO_2Oct or NO_2) can be considered as a "pull−pull" molecule and exhibit maxima in the UV region assigned to $\pi−\pi^*$ transitions. We have studied the effect of the π linker (between the pyridyl and donor end groups) on the optical properties by using the same donor substituent, i.e., a dialkylamino group. An elongation of the conjugated bridge, from **c** to **i**, induces a moderate bathochromic shift [$\Delta\lambda_{max}$(**i** versus **c**) = 19 nm], but no more red shift [$\Delta\lambda_{max}$(**j** versus **i**) = 1 nm] is observed

a D = OOct (λ_{max} = 337 nm)
b D = NEt$_2$ (λ_{max} = 397 nm)
c D = NBu$_2$ (λ_{max} = 401 nm)
d A = SO$_2$Oct (λ_{max} = 275, 300 nm)
e A = NO$_2$ (λ_{max} = 339 nm)

f (λ_{max} = 443 nm)

g X = CH (λ_{max} = 434 nm)
h X = N (λ_{max} = 472 nm)

i (λ_{max} = 420 nm)

j (λ_{max} = 421 nm)

FIGURE 3. 4,4′-π-conjugated-2,2′-bipyridines synthesized and corresponding to UV—vis data in dichloromethane.

for the second homologation. Such saturation in λ_{max} has already been observed for other push—pull OPV derivatives and can be explained by a decrease of the charge-transfer character with the increase of the conjugation length.[12] By contrast, substitution of the phenyl ring in **c** for a thiophene ring in **f** results in a significant bathochromic shift of 42 nm, a typical behavior that is in agreement with other studies on push—pull thiophene stilbene derivatives. The incorporation of nitrogen atoms into the double bond of the transmitter also induces a substantial shift of the ICT transition to a lower energy. Thus, compound **g** (C=N) is red-shifted by 36 nm relative to **c**, and furthermore, **h** (N=N) is red-shifted by 35 nm relative to **g**. Thus, tuning of the electronic absorption properties is made possible by simple modification of the π linker and, with a given donor group such as dialkyl-amino, a substantial red shift of the ICT transition occurs in the following order: phenylazo > thienylvinyl > phenylimino > tristyryl $\approx$ bistyryl > styryl.

III. Octahedral (D_3) and Tetrahedral (D_{2d}) Metallo-octupoles

Figure 4 depicts the generic structure of the D_3 octahedral metallo-octupoles and the different parameters that have been examined.[13] The complexes [M = Zn (**1**), Ru (**2**), Fe (**3**), and Hg (**4**)] were prepared in good yield by refluxing in ethanol the metallic precursors [RuCl$_2$(DMSO)$_4$, ZnOAc$_2$·2H$_2$O, FeCl$_2$·4H$_2$O, and HgCl$_2$) with three equivalents of bipyridines, followed by an anionic metathesis with either sodium hexafluorophosphate or tris(tetrachlorobenzene-diolato)phosphate (TRISPHAT). This latter anion was used to significantly improve the solubility of the resulting complexes.[14] Bipyridyl ligands also allow the design of D_{2d} tetrahedral octupoles by coordination of two bipyridines to metal ions such as Cu^I, Ag^I, or Zn^{II}.[15] The key feature in stabilizing the tetrahedral geometry and protecting the central metal ion against oxidation is the incorporation of either alkyl or aryl substituents at the 6,6′ positions of
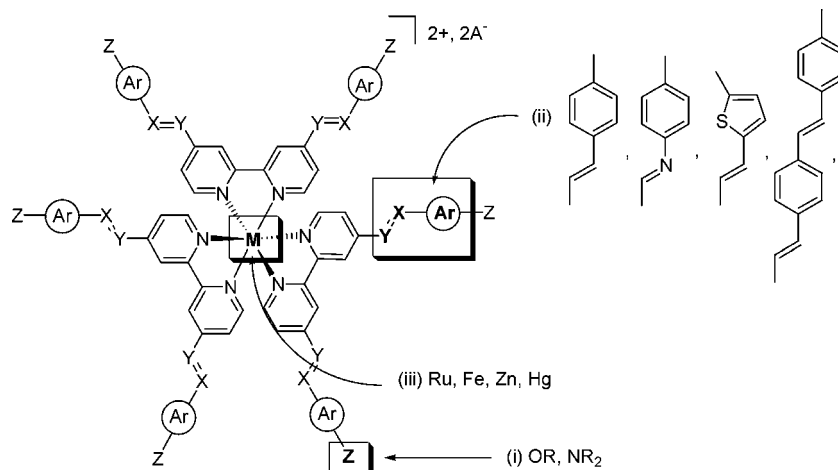
FIGURE 4. Generic structure of the D_3 symmetric family of metallo-octupoles.
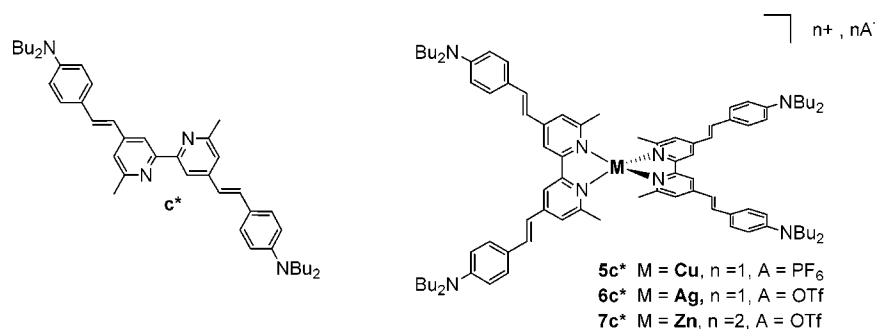

FIGURE 5. Generic structure of the D_{2d} symmetric family of metallo-octupoles.

the bipyridyl ligand. The synthesis of bipyridyl ligands such as **c*** (Figure 5) was achieved by a controlled functionalization of the 4,4′ positions of 4,4′,6,6′-tetramethyl-[2,2′]-bipyridine. Red-orange copper(I), silver(I), and violet zinc(II) complexes **5c***, **6c***, and **7c*** were easily prepared by treatment of [Cu(CH$_3$CN)$_4$][PF$_6$], AgOTf, and Zn(OTf)$_2$ with 2 equiv of ligands **c*** in dichloromethane at room temperature.

Linear Optical Properties. All complexes exhibit strong absorption bands in the visible region, which are sensitive to the nature of the donor group, the π-conjugated backbone, and the metallic core (Table 1 and Figure 6). Two types of transitions can be observed, ILCT and MLCT. The influence of the nature of the ligand on the absorption properties of the related complexes has been investigated in the case of zinc(II) complexes **1**, featuring alkoxy or amino donor groups and styryl, phenylimino, thienylvinyl, or bistyryl transmitters, respectively. UV−vis spectra exhibit a broad intense absorption band assigned to ILCT transition, and no MLCT transition is observed, as expected from the high third ionization potential of zinc. Upon coordination, the acceptor strength of the pyridinic ring is enhanced, resulting in a bathochromic shift of the ILCT transition. For a given donor group such as dibutylamino, a red shift of ca. 70 nm is observed for the Zn^{II} series. Moreover, the energy of this transition steadily decreases when changing the styryl linkage by a bistyryl, phenylimino, or thienylvinyl one, respectively, as found with the corresponding bipyridyl ligands. The influence of the central metallic ion on the linear optical data of

Table 1. Linear and Nonlinear Optical Data of D_3 and D_{2d} Metallo-octupoles

complex	$\lambda_{max}{}^a$ (nm)	e (L mol^{-1} cm^{-1})	$\beta^{1.91\ b}$ $(10^{-30}$ esu)	$\beta_0{}^c$ $(10^{-30}$ esu)
[Zn(**a**)$_3$][TRISPHAT]$_2$, **1a**	382	128 000	250	200
[Zn(**c**)$_3$][PF$_6$]$_2$, **1c**	466	175 000	340	240
[Zn(**f**)$_3$][PF$_6$]$_2$, **1f**	519	50 000	400	260
[Zn(**g**)$_3$][PF$_6$]$_2$, **1g**	506	68 000	310	207
[Zn(**i**)$_3$][TRISPHAT]$_2$, **1i**	482	132 000	870	657
[Ru(**a**)$_3$][TRISPHAT]$_2$, **2a**	387	124 000	270	*d*
	510	51 000		
[Fe(**a**)$_3$][TRISPHAT]$_2$, **3a**	382	141 000	220	*d*
	583	41 000		
[Ru(**c**)$_3$][PF$_6$]$_2$, **2c**	446	142 000	340	*d*
	520	150 000		
[Fe(**c**)$_3$][PF$_6$]$_2$, **3c**	467	168 000	235	*d*
	593	75 000		
[Hg(**c**)$_3$][PF$_6$]$_2$, **4c**	438	160 000		
[Cu(**c***)$_2$][PF$_6$], **5c***	436	106 000	113	86
	480	45 000		
[Ag(**c***)$_2$][OTf], **6c***	431	115 000	90	70
[Zn(**c***)$_2$][OTf]$_2$, **7c***	529	125 000	245	157

^{a} Measured in diluted dichloromethane solution (10^{-5} mol L^{-1}). ^{b} Measured by HLS at 1.91 μm (precision $\pm15\%$) in concentrated dichloromethane solution ($1-5 \times 10^{-3}$ mol L^{-1}). ^{c} Corrected at $\lambda \to \infty$ using the three-level model. ^{d} β_0 value not determined because of the presence of two different ILCT and MLCT transitions.

the [M(bpy)$_3$]$^{2+}$ series (M = Ru, Zn, Fe, and Hg) was examined by using the same bipyridyl ligand (**a** or **c**). The red shift of the ILCT transition induced by complexation can be correlated to the Lewis acidity of the metallic ion: whereas the λ_{ILCT} values of the Ru^{II}, Zn^{II}, and Fe^{II} complexes are roughly similar (Figure 6), that of the Hg^{II}
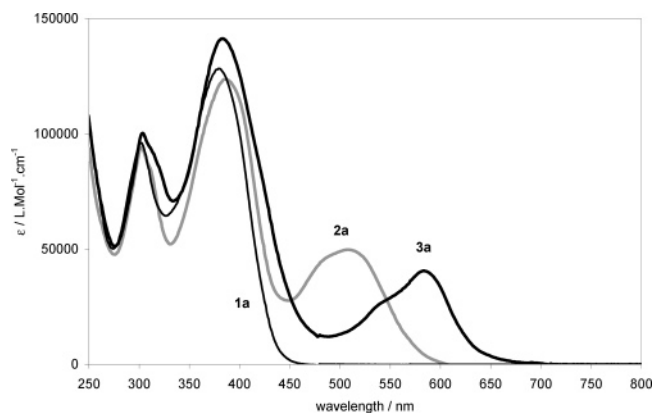
FIGURE 6. UV−vis spectra of complexes **1a** (black), **2a** (gray), and **3a** (bold).

complex decreases significantly, in agreement with the relative Lewis acidity of these metal ions. The influence

of the central metallic ion on λ_{ILCT} is also clearly found for the tetrahedral series $[M(\mathbf{c}^*)_2]^{n+}$ ($M^{n+} = Cu^+$, Ag^+, and Zn^{2+}) (Table 1). The λ_{ILCT} values decrease with the relative Lewis acidity in the order $Zn^{2+} \gg Cu^+ > Ag^+$.

Tris(bipyridyl) ruthenium **2a,c** and iron complexes **3a,c** each show another absorption band arising from the $d\pi(Ru^{II}$ or $Fe^{II}) \rightarrow \pi^*(bpy)$ MLCT transition. The MLCT bands of Fe^{II} complexes ($\lambda_{\text{MLCT}} \approx 590$ nm) are classically found at longer wavelength than those of the corresponding Ru^{II} ($\lambda_{\text{MLCT}} \approx 510$ nm) (Table 1 and Figure 6). The UV−vis spectrum of **2c** exhibits a very broad band with two maxima at 446 and 513 nm corresponding to the overlap of the ILCT and MLCT transitions. In the tetrahedral Cu^I, Ag^I, and Zn^{II} series, only Cu^I complexes show MLCT transitions that are partially overlapped with the ILCT transition.

NLO Properties. Because EFISH requires dipole orientation in solution, it is precluded for purely octupolar
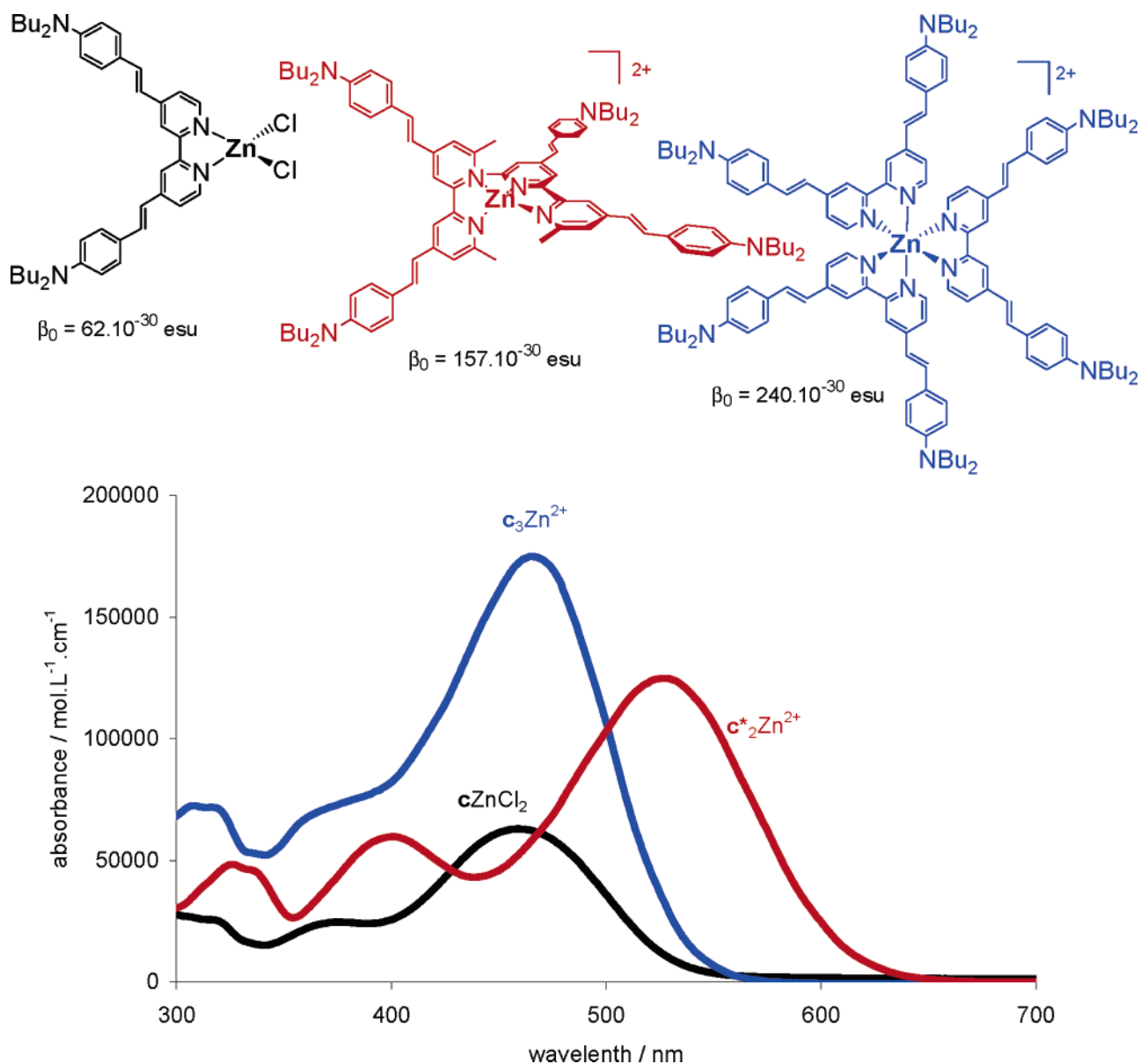

FIGURE 7. Dipolar and octupolar architectures based on zinc(II) complexes.
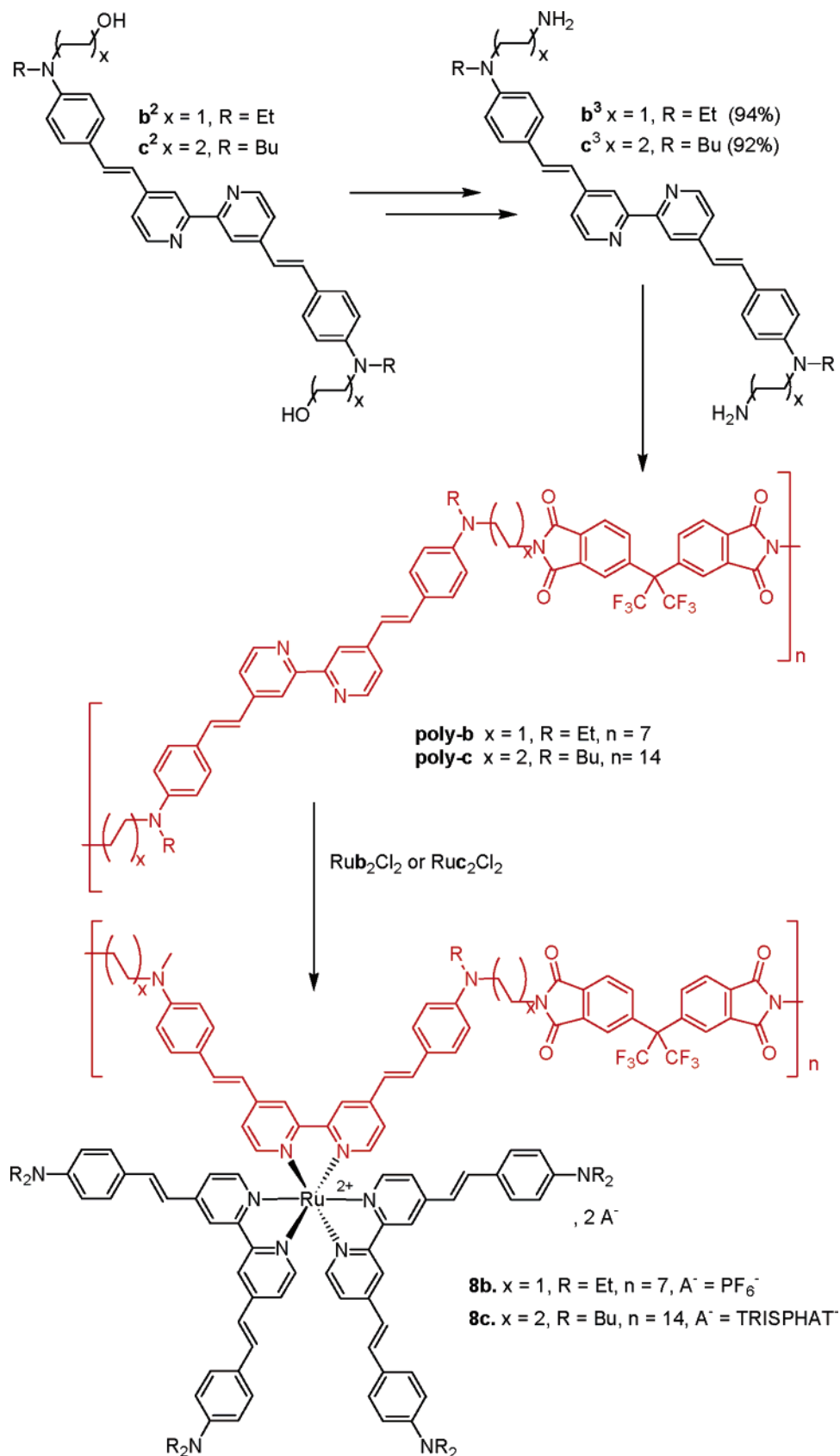
FIGURE 8. Synthesis of polyimide complexes **8b** and **8c**.

molecules. Instead, the HLS technique was used for measuring the molecular hyperpolarizability (β) (Table 1). Two-photon-induced fluorescence may significantly affect

HLS measurements in the visible range, leading to overestimation of hyperpolarizability values. NLO measurements at the infrared-shifted $\lambda = 1.91$ μm fundamental
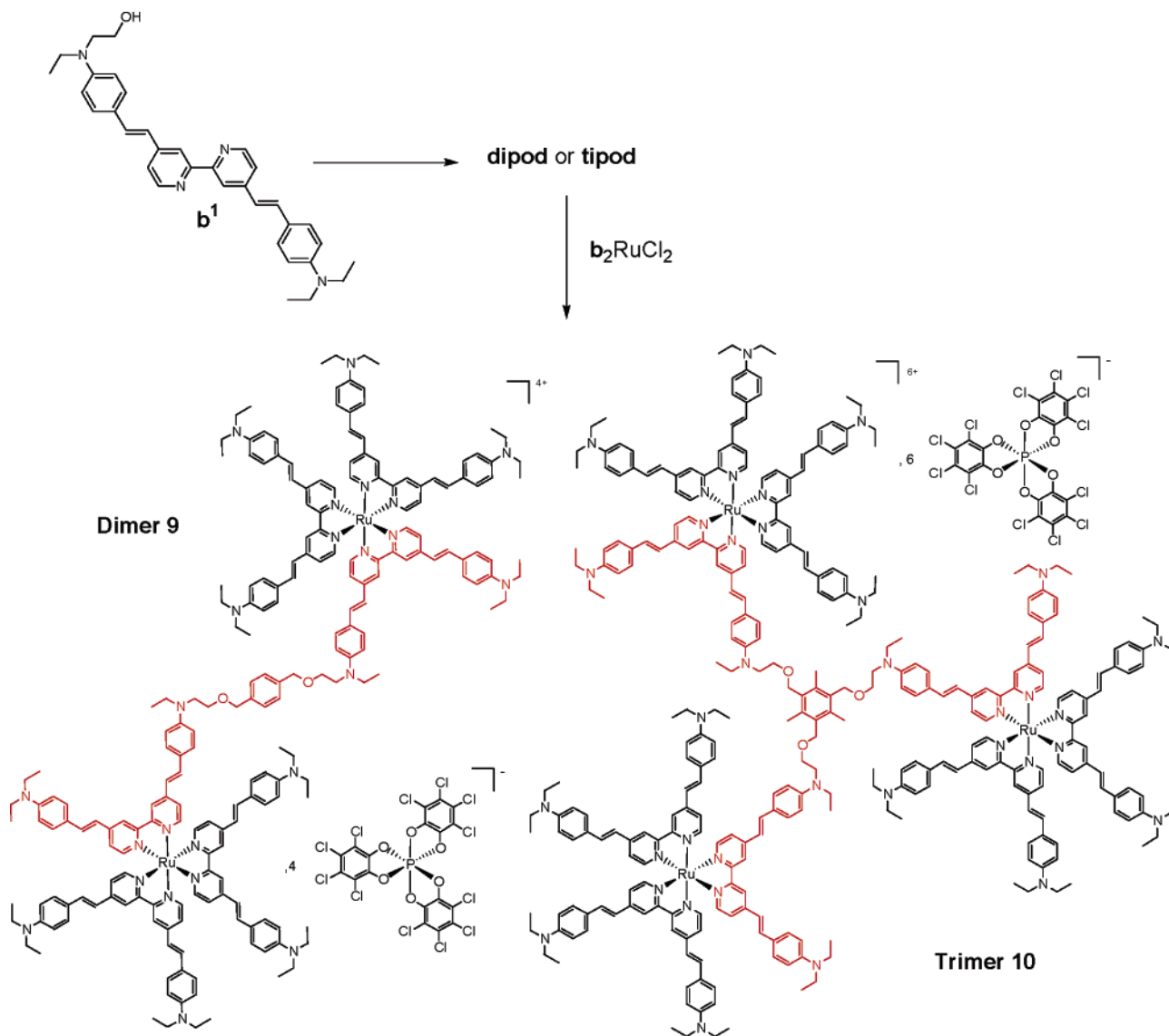
FIGURE 9. Chemical structure of bi- and trimetallic complex **9** and **10** (in red the corresponding **dipod** and **tripod** ligands).

wavelength were performed as the second harmonic wavelength at 955 nm lies in the transparency region of the chromophores, thus making any contribution from the two-photon fluorescence to the HLS signal quite negligible. As is usually observed, the dispersion-free hyperpolarizability coefficient of octupolar chromophores monotonically increases with the increase of the ground-state charge-transfer character,[16] thus by increasing the donor strength of the substituent or by tuning the π-conjugated system. For example, replacing the octyloxy group (**1a**) by a stronger dibutylamino donor group (**1c**) results in a 20% enhancement of β_0, and changing the phenyl ring of the styryl moieties (**1c**) by a thienyl ring (**1f**) leads to a further 10% enhancement of β_0. On the other hand, replacing the C=C bond of the styryl moieties (**1c**) by a C=N bond (**1g**) results in a significant decrease of β_0, despite the important bathochromic shift of the ILCT transition ($\Delta\lambda = 33$ nm): the presence of the nitrogen atom in the π-conjugated system can contribute to localize the charge, hence to decrease the NLO activity. Upon lengthening the conjugation bridge such as in **1g** featuring

two styryl moieties, a 2.7 times enhancement of β_0 is achieved ($\beta_0(\mathbf{1i}) = 657 \times 10^{-30}$ esu versus $\beta_0(\mathbf{1c}) = 241 \times 10^{-30}$ esu). Thus, the nature of the bipyridyl ligand has a significant influence on the NLO activity of the corresponding tris(bipyridyl) metal complexes. However, it clearly appears that the elongation of the π-conjugated backbone is the key parameter to maximize the NLO activity.

As described previously, the influence of the central metal on the linear optical data, especially the red shift of the ILCT transition, can be correlated to the Lewis acidity of the metallic ion. The β_0 value is also strongly correlated to the metal Lewis acidity because that of $[\mathrm{Zn}(\mathbf{c^*})_2]^{2+}$ **7c*** is about twice that of the corresponding copper and silver compounds **5c*** and **6c*** (157 versus 86 and 70×10^{-30} esu, respectively). This result evidences the importance of the metal ion not only as a template to gather ligands in a predetermined octupolar arrangement but also for its participation in NLO activity. Another important aspect of the role of the central metal ion is shown by the peculiar case of

14+ , 14 TRISPHAT⁻
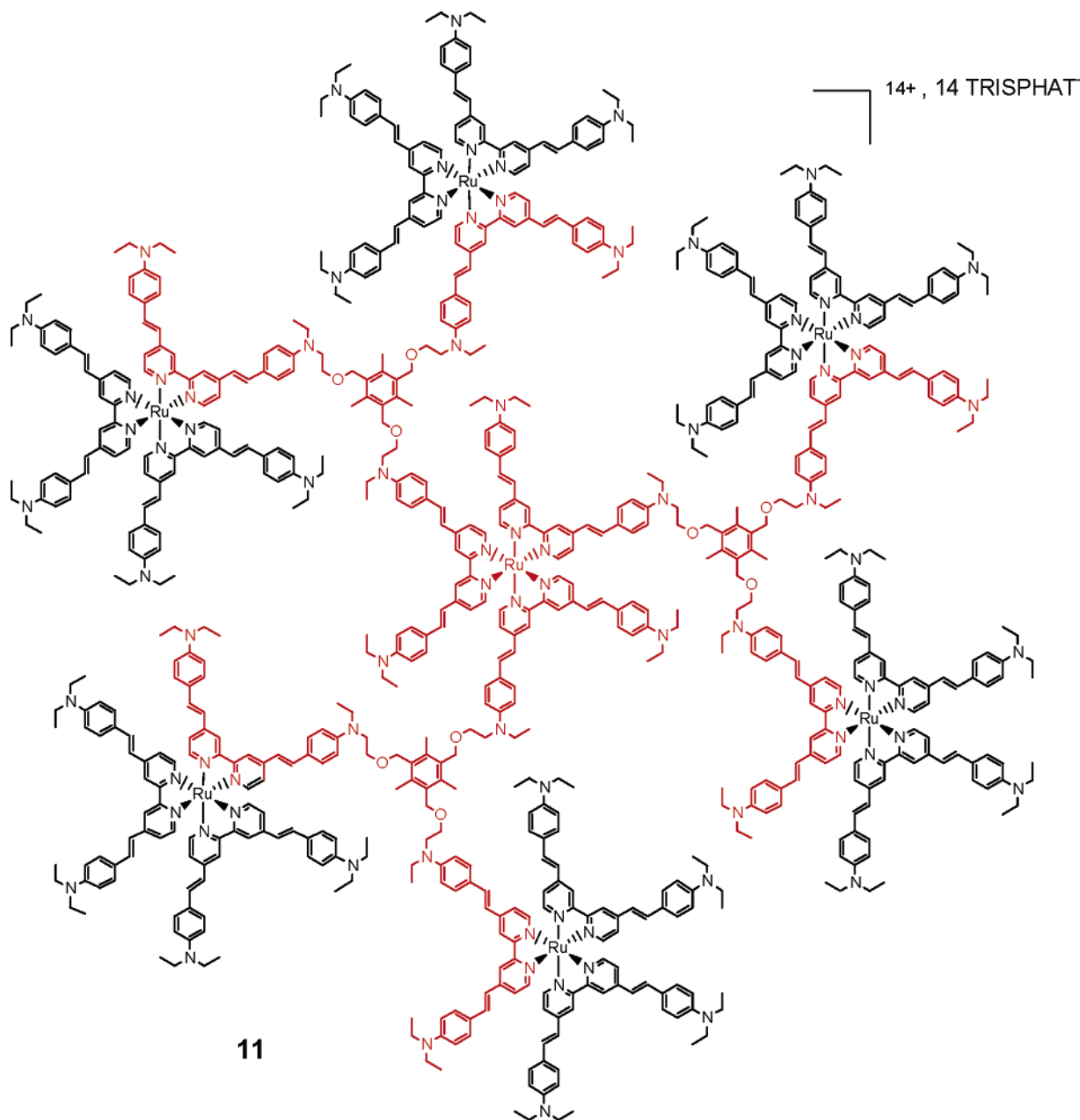
FIGURE 10. Chemical structure of the heptamer **11** (in red, the "complex as ligand" [Ru(**tripod**)₃]²⁺).

zinc(II), which has the ability, because there is no ligand field stabilization effect, to expand its coordination sphere and therefore produce tetrahedral and octahedral complexes with bipyridine ligands.[17] This characteristic provided a unique opportunity to design either dipolar (**c**)ZnCl₂ or octupolar D_{2d} [Zn(**c***)₂][OTf]₂ and D_3 [Zn(**c**)₃][PF₆]₂ molecules by simple controlled combination of one, two, or three bipyridyl ligands with zinc(II) (Figure 7). These complexes are intense dyes exhibiting high molecular extinction coefficients, and the oscillator strength follows a 1:1.8:2.9 ratio (th. 1:2:3) ratio for (**b**)ZnCl₂, **7**, and **1b**, respectively, as expected for noninteracting subchromophores.[4b] Importantly, the β_0 values follow the same tendency and monotonically increase from dipolar to D_3 octupolar compound with respect to the number of subchromophores organized around the Zn^{II} center. An improved transparency/nonlinearity tradeoff is reached for the octahedral complex **1c** as compared to the tetrahedral complex **7c***. Furthermore, these results point out the efficiency of the octupolar strategy because the β_0 value of **1c** is roughly 4 times larger than that of the corresponding dipolar derivative, without the undesirable bathochromic shift of the ILCT transition ($\Delta\lambda = 14$ nm). This is a nice illustration of the superiority of octupoles versus dipoles in terms of nonlinearity without the significant cost of transparency.

In addition to the ILCT transition, ruthenium and iron complexes **2a,c** and **3a,c** each shows an MLCT band in the visible region that also contributes to the NLO activity. In a first approximation, these ILCT and MLCT are roughly parallel but in opposite directions. Electroabsorption spectroscopy was recently used by Vance and Hupp[18] to calculate the contributions from both MLCT and ILCT

transitions to the NLO response on an octupolar ruthenium complex similar to **2b**. They suggested that the total hyperpolarizability (β_{TOT}) results from the summation of the two contributions β_{ILCT} and β_{MLCT}, which are in opposite sign and thus destructively interfere. Because the λ_{ILCT} values of the Ru^{II}, Zn^{II}, and Fe^{II} complexes are roughly similar, one can anticipate that $\beta(Zn) > \beta(Ru) > \beta(Fe)$, because Zn^{II} complexes does not display any MLCT and that of Fe^{II} is red-shifted as compared to that of Ru^{II}. Experimental measurements (Table 1) clearly show that $\beta(Zn) > \beta(Fe)$. However, the β values of Ru^{II} complexes **2a** and **2c** are as large as those of the corresponding Zn^{II} complexes **1a** and **1c** despite the presence of an MLCT transition [$\beta(\mathbf{1c}) = \beta(\mathbf{2c}) = 340 \times 10^{-30}$ esu, $\beta(\mathbf{1a}) = 250 \times 10^{-30}$ esu, and $\beta(\mathbf{2a}) = 270 \times 10^{-30}$ esu]. Thus, the proposed model based on an antagonist contribution of both ILCT and MLCT does not fully rationalize the experimental results.

IV. From Octupoles to Multi-octupoles

Having demonstrated that metal ions can act as powerful templates for the design of octupolar arrangements with large optical nonlinearities, we thought to use the wide possibilities offered by the coordination chemistry of functionalized bipyridines to design multi-octupolar compounds such as polymetallic complexes, metallodendrimers, or metallopolymers with the aim of engineering an acentric arrangement of the octupolar units (Figure 2).

Main-Chain Polyimides Containing Octupolar Ruthenium(II) NLO-phores. Probably the most common approach is the covalent attachment of chromophores to a polymer (side-chain polymers) or their incorporation into the backbone (main-chain polymers).[2a] Among them, aromatic polyimides appear to be very promising materials because of their high thermal stabilities and high glass transition temperatures, and many approaches have been developed to the synthesis of such polymers bearing dipolar chromophores. The covalent incorporation of NLO-phores into polymers generally requires the introduction of appropriate reactive functionalities, such as hydroxyl (OH) or amino (NH$_2$) groups, at the electron-donating site of the chromophore. To achieve the synthesis of the desired polymer, we designed mono- and bishydroxy-substituted 4,4′-bis(dialkylaminostyryl)-2,2′-bipyridines as well as the corresponding bisdiamino-substituted 4,4′-bis-(dialkylaminostyryl)-[2,2′]-bipyridines (Figure 8).[19] Then, combining the diamine derivatives with hexafluoroisopropylidene diphthalic anhydride (6FDA) in NMP at 25 °C, followed by chemical imidization with Ac$_2$O/pyridine, yielded the expected polyimides **poly-b** and **poly-c**. Gel-permeation chromatography gave relatively low molecular weights indicating an average of ca. 7 and 14 bipyridine units in **poly-b** and **poly-c**, respectively.

Ruthenium(II) is an ideal central metal ion to create such polymetallic materials because it has the ability to build stable octahedral D_3 complexes and allows the sequential coordination of bipyridyl ligands. Thus, controlled combination of two 4,4′-dialkylaminostyryl-2,2′-

Table 2. . Linear and Nonlinear Optical Properties of Multimetallic Complexes

compound	$\lambda_{abs}{}^a$ (nm)	e (L mol^{-1} cm^{-1})	β^a (10^{-30} esu)	$\beta(N)/\beta(1)$
monomer	446	142 000	320	1
2b	520	150 000		
dimer	440	258 000	570	1.8
9	511	239 000		
trimer	443	379 000	700	2.2
10	511	354 000		
heptamer	444	693 000	1900	5.9
11	506	648 000		
polymer	445		1300	4.1
8c	513			

^{a} Measured in dichloromethane.
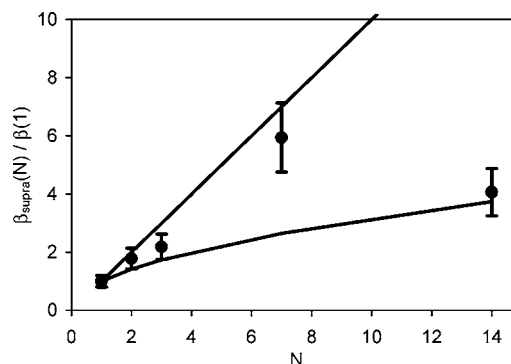
FIGURE 11. Plot of the ratio $\beta_{supra}(N)/\beta(1)$ versus N.

bipyridine "parent" ligands and one macroligand gave rise to the octupolar NLO polyimides 8b and 8c in high yields (>90%) (Figure 8).[20] The UV−vis spectrum is similar to that of the tris(bipyridyl) ruthenium monomers with two maxima at 445 and 513 nm because of the overlapping MLCT and ILCT transitions.

Multimetallic and Metallodendrimer Octupoles. Metallodendrimers constitute a very attractive system, because of their nanoscopic dimensions and their regular, well-defined, and highly branched 3D architecture. In contrast to polymers, these macromolecules can be considered as an ordered ensemble of monomeric building blocks and their geometry can be predetermined by the nature of the connectivity. For that purpose, we have designed multipodal ligands containing two (**dipod**) or three (**tripod**) dialkylaminostyryl-[2,2′]-bipyridine chromophores, precursors to polyoctupoles. Polypyridylmetals are ideal components for the construction of metallodendrimers. An elegant approach has been described based on the "complexes as metals/complexes as ligands" strategy.[21] Therefore, for the design of multi-octupolar complexes, we have applied this concept that required the initial construction of multipodal bipyridyl ligands. The high yield synthesis of the new **dipod** and **tripod** ligands was performed using the monohydroxy-substituted 4,4′-bis-(dialkylaminostyryl)-[2,2′]-bipyridine[22] (Figure 9). The synthetic methodology for the preparation of the bi- and trimetallic compounds **9** and **10** was based on the sequential coordination of the parent ligand 4,4′-bis-(diethylaminostyryl)-[2,2′]-bipyridine and the appropriate multipodal ligands. The heptanuclear species was prepared in excellent yield using the "complexes as metals/
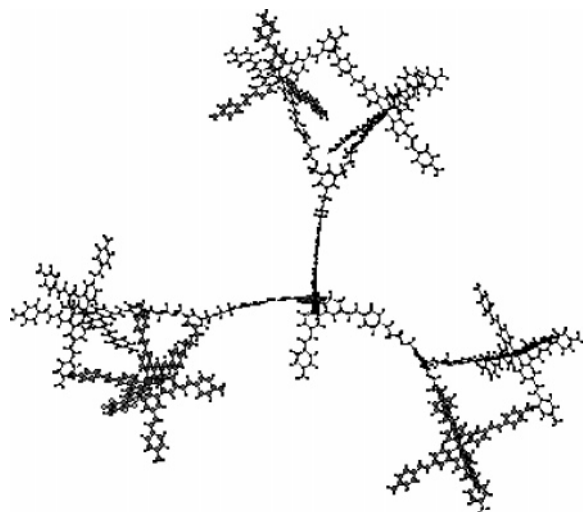
FIGURE 12. Molecular mechanics representation of **11**.

complexes as ligands" strategy. The first step involved the construction of the core building block [Ru(**tripod**)₃]²⁺ (Figure 10). This compound, which contains six free chelating ligands, afforded then the target heptametallic complex 11 by the same route used for the preparation of the bi- and trimetallic compounds. The absorption spectra of these polymetallic compounds were quite similar to that of the parent mononuclear complex with maxima at ca. 510 and 440 nm (Table 2).

NLO Properties. The $\beta^{1.91}$ values of multimetallic species **8**, **9**, **10**, and **11** were rigorously compared to that of monomer **2b** because all these species exhibited very similar absorption spectra and all of the HRS measurements were performed under a similar monomer concentration in dichloromethane solution (Table 2). We have found that the NLO activity increases from monomer ($N = 1$) to dimer ($N = 2$), trimer ($N = 3$), and heptamer

($N = 7$) but decreases from heptamer to polymer ($N = 14$). According to the HLS principle, when the supramolecule is made of N fully disordered monomers, the number N of individual monomers can be inferred from the $\beta_{\text{supra}}(N)/\beta(1) = \sqrt{N}$ relationship, where $\beta(1)$ is the monomer ($N = 1$, **2b**) with first hyperpolarizability. For the polymer **8c**, the experimental hyperpolarizability ratio was about 4.0, thus very close to the theoretical value $\sqrt{14} = 3.7$. Such agreement accounts for the fully disordered assembly of monomeric ruthenium building blocks in the linear polymeric chain, and the increase of β is simply the result of a concentration effect. A totally different behavior was observed for the heptamer **11**, which exhibited a giant first hyperpolarizability of $\beta = 1900 \times 10^{-30}$ esu, although containing half the number of monomeric subunits as compared to **8c**. In that case, the first hyperpolarizability satisfactorily fits with the linear relationship $\beta_{\text{supra}}(N)/\beta(1) = N$ (Figure 11). Such quasilinear dependence is the signature of a quasi-optimized ordering of the individual building blocks in the heptamer. This means that, in a highly ordered dendritic architecture,[22] each monomeric subunit coherently contributes to the HLS response. To illustrate the supramolecular D_3 ordering, we carried out computer modeling of **11** based on molecular mechanic calculations (MMF94). Projection of the heptamer structure along its C_3 axis (Figure 12) clearly suggests octupolar 3-fold symmetry at the supramolecular level. Such octupolar arrangement of octupolar subunits is the optimal octupolar order and results in coherent second harmonic scattering from each individual building block. To the best of our knowledge, this is the first example of supramolecular octupolar self-ordering within a dendritic architecture.[23]
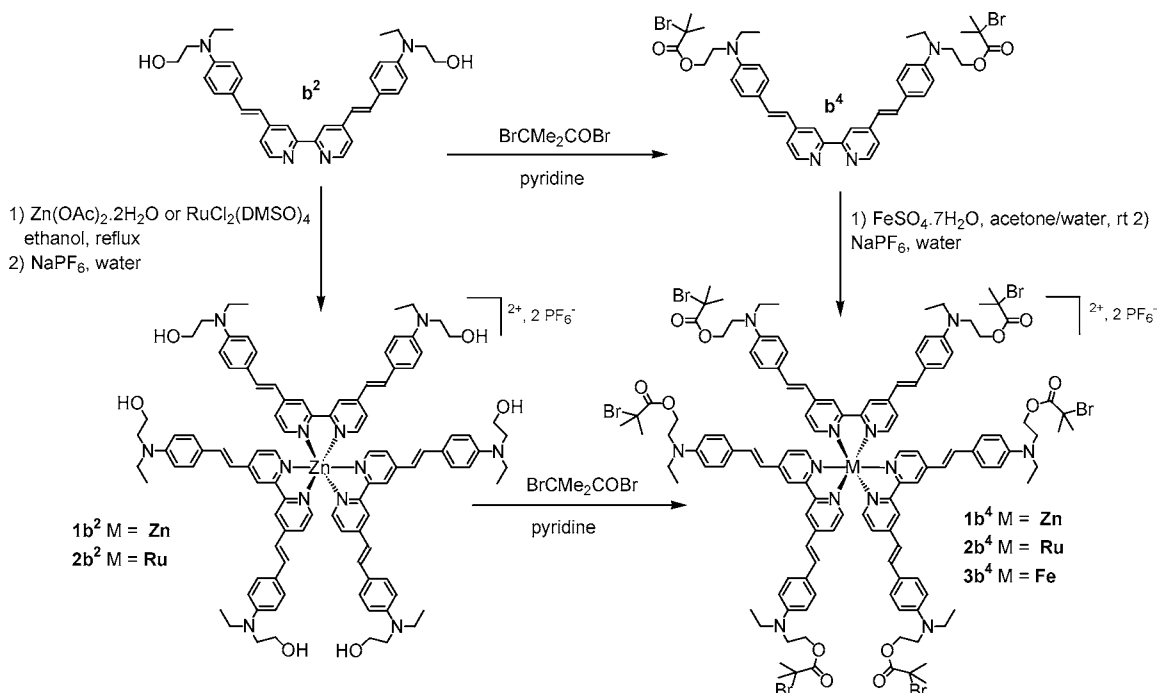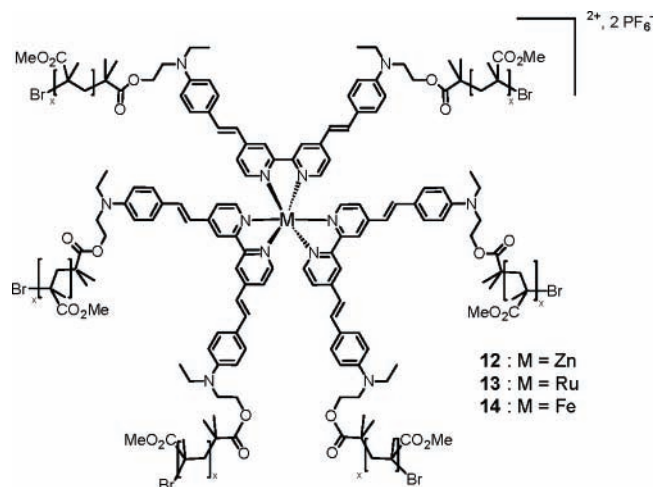

FIGURE 13. Synthesis of ATRP metalloinitiators.

FIGURE 14. Structure of the star-shaped polymers and spin-coated thin films of **12** (orange), **13** (red), and **14** (green).

V. Photoisomerizable Star-Shaped Metallopolymers for Optical Poling

A new challenge is the translation of micro- to macroscopic noncentrosymmetric orientation of octupolar chromophores. Because the traditional electric-field poling, which is the relevant technique for the molecular orientation of dipolar chromophores, is not applicable because of the absence of a permanent dipole moment,

the so-called "all optical poling" technique has to be used to induce noncentrosymmetric ordering of multipolar molecules in polymer films.[24] This rather complex process combines two molecular excitation pathways, respectively, excited at ω and 2ω, that allows for mechanical reorientation of the molecular structure. Basically, this method requires the use of polymer matrixes containing NLO chromophores featuring photoisomerizable moieties such as an azobenzene group, which can undergo reversible trans/cis/trans photoisomerization cycles.

Star-Shaped Metallopolymeric Chromophores. For the preparation of NLO polymers, we used the atom-transfer radical polymerization (ATRP), which has emerged as an excellent technique for the synthesis of well-defined polymers with controlled molecular architecture.[25] For example, this methodology has recently been used by several groups to prepare star-shaped polymers with different metal tris(bipyridyl) reagents as initiators.[26] With the reasonable expectation that this strategy could offer a convenient entry to a variety of octupolar polymeric NLO-phores, we first designed a 2-bromoisobutyroyl-functionalized dialkylaminostyryl bipyridyl ligand and the corresponding zinc, ruthenium, and iron complexes (Figure 13). These complexes are efficient metalloinitiators for the ATRP of MMA in the presence of the Haddleton's catalyst[27] (*N*-propyl-2-pyridylmethanimine/CuBr). The resulting polymers **12**−**14** were obtained as orange (Zn), red (Ru), and green (Fe) flocculent powders, respectively, and kinetic plots of the polymerizations showed a first-order behavior consistent with a living system.[28] It is worth noting that these polymers exhibit absorption and emission properties that are very similar to those of the corresponding monomers **1**−**3c**, clearly indicating that the metallochromophoric structure is conserved upon polymerization. Thin films were obtained by spin-coating onto glass slides, and scanning electron microscopy (SEM) revealed the formation of very uniform films without any
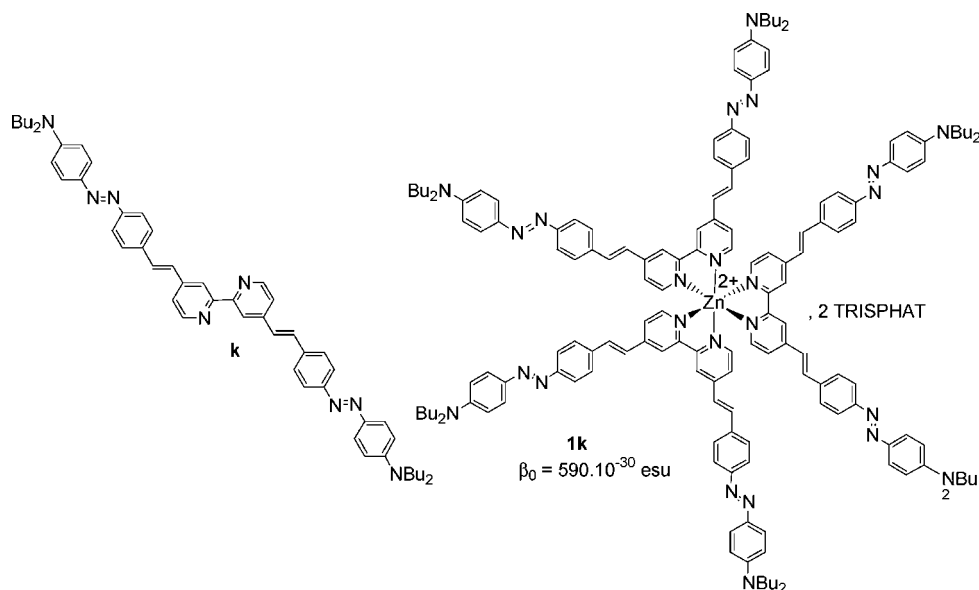
FIGURE 15. Structure of photoisomerizable bipyridyl ligand and corresponding zinc complex.
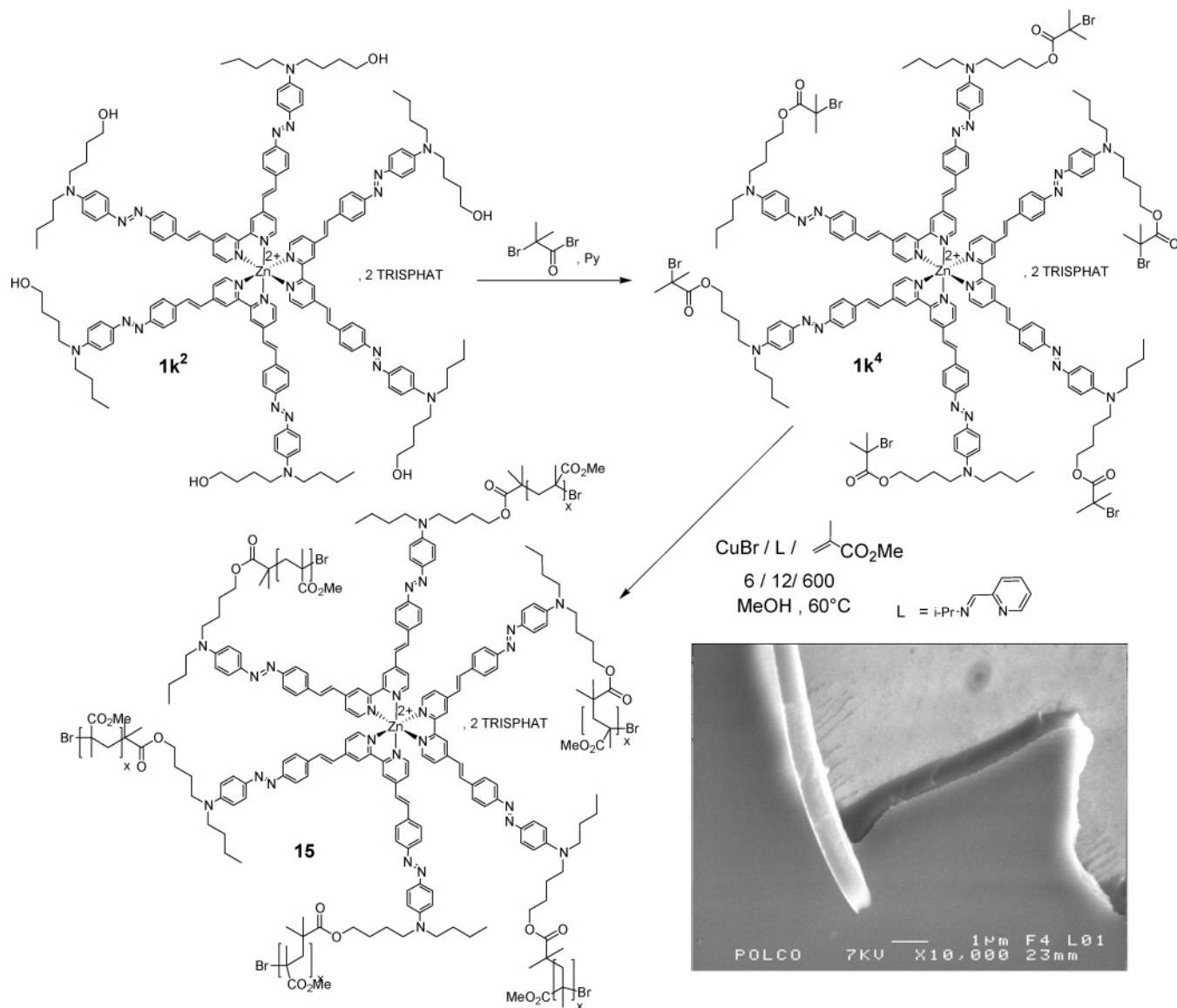
FIGURE 16. Synthesis of the photoisomerizable star-shaped polymer **15** and SEM image of the corresponding film **F₁**.

chromophore aggregation (Figure 14), with the thickness varying approximately between 1 and 2 μm. Solid-state UV−vis spectroscopy unambiguously confirmed that the metallic trisbipyridyl chromophores remain intact within the film.

Macroscopic Orientation of Photoisomerizable NLO Polymers. To carry out the optical poling study, we then prepared the bipyridyl ligand **k** containing two photo-isomerizable azobenzene groups and the corresponding tris(bipyridyl)zinc(II) complex **1k** (Figure 15).[29] Ligand **k** exhibited a broad ILCT transition at 480 nm, which was slightly red-shifted ($\Delta\lambda = 16$ nm) upon Zn^{II} complexation. The NLO activity of **1k** ($\beta_0 = 590 \times 10^{-30}$ esu) was found to be similar to that of **1i**. In chloroform solution, ligand **k** and complex **1k** showed the usual photoisomerization behavior of push−pull azobenzene derivatives, thus an important decrease of the main absorption band in the 480−500 nm region, an increase of absorption around 370 nm, and a monoexponential cis/trans thermal back-reaction kinetic.[30] We subsequently carried out the ATRP

of MMA to prepare the corresponding photoisomerizable star-shaped polymer **15** (Figure 16). The resulting polymer film **F₁** (8%, w/w, relative to PMMA) exhibited a photo-isomerization behavior typical of azo dyes with a biexpo-nential thermal back-reaction kinetic, which is character-istic of the existence of different free volumes around the chromophores (Figure 17).[31] We then investigated the macroscopic optical molecular orientation of this grafted NLO-polymer film and, for comparison, that of a doped **1k**/polycarbonate film **F₂**. Measurements were made using poling fundamental and harmonic wavelengths of 1064 and 532 nm, respectively. The orientation dynamics were followed by measuring every 60 s the second harmonic generated by the poled sample using the 1064 nm field (Figure 18). Interestingly, **F₂** exhibits a 40% higher SHG intensity than **F₁** and a much better stability against relaxation. This preliminary study is very encouraging and suggests that the photoinduced orientation process is in competition with Brownian motion in the polymer. There-fore, grafting the NLO-phore to the polymer chain seems
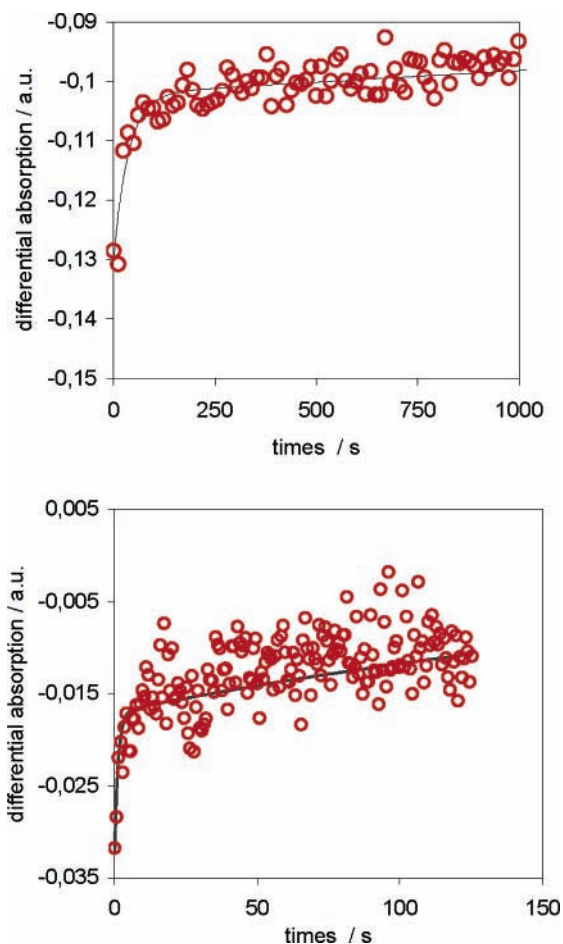
FIGURE 17. Kinetic study of thermal cis—trans relaxation (red circles) and corresponding simulation (black line) at 480 nm wavelengths for the films F_1 (right) and F_2 (left).
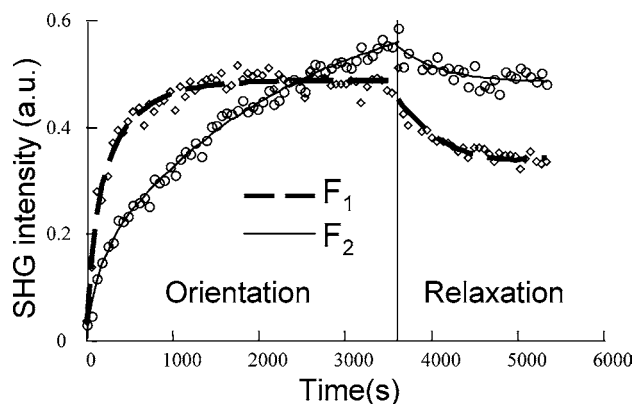
FIGURE 18. Optical orientation and relaxation of F_1 and F_2 under resonant one- and two-photon excitations (○ and ◇) compared to a biexponential plot (lines).

necessary to obtain a higher and more stable photoinduced noncentrosymmetry.

VI. Concluding Remarks

We have shown that coordination chemistry is a versatile tool for the design of either tetrahedral or octahedral octupolar chromophores with large second-order nonlinear optical properties, even larger than most of purely organic octupoles. Their access can be easily achieved by combining bipyridyl ligands with metal ions. The molecular quadratic hyperpolarizability (β) values are strongly influenced by the symmetry of the complexes, the nature of the ligands, and the nature of the metallic centers, which can be exploited to tune the nonlinear response. In this context, the use of trivalent lanthanide metal ions for second-order nonlinear optics seems to be very promising because of their strong Lewis acidity and their ability to accept larger coordination. We are currently working in this direction.[32]

The ability to substitute the pyridine rings with functional groups offers the possibility of making macroscopic assemblies featuring octupolar chromophores such as polymers and dendrimers. We have exemplified a supramolecular octupolar self-ordering within a metallo-dendritic architecture. This result opens attractive perspectives for the construction and control of nanoscale molecules with the goal of miniaturizing photonic devices. Finally, we have demonstrated the effectiveness of the optical poling technique to promote the nonlinear response of octupolar NLO-phores from the molecular to the macroscopic level. This preliminary result is promising and shows the possibility of generating a new class of nonlinear quadratic materials.

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