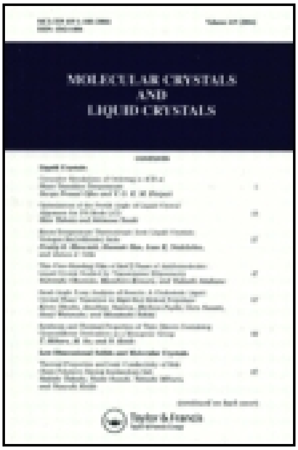

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Polyfluorene Based Coordination Compounds for Nonlinear Absorption

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Polyfluorene Based Coordination Compounds for Nonlinear Absorption

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We report here the nonlinear absorption properties of different coordination compounds (M = Eu, Zn), based on the bifluorene system. Measurements were performed in chloroform between 450 and 650 nm for nanosecond time duration pulses. The nonlinear absorption is attributed to a three-photon absorption process involving a first two-photon absorption step followed by an excited state absorption process. The three-photon absorption efficiency of these complexes was shown to be similar to that of the bifluorene for a same concentration in bifluorene, with furthermore an excellent thermal stability.

Keywords: coordination compounds; excitonic coupling; fluorene; nonlinear absorption

INTRODUCTION

A lot of investigations focusing on optical limiting materials for the protection of eyes and optical systems against tunable nanosecond lasers in the visible have already been reported [1]. Efficient nonlinear absorbers, based on two-photon absorption (TPA) process, were found [2–4]. The most frequent strategy used centrosymmetric molecules substituted by donor groups [5–8], while a new approach involving

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unsubstituted molecules, such as the Stilbene3 (a bistilbene) [9] or linear polyfluorenes derivatives [10–11] appears very promising in terms of TPA cross-sections and nonlinear absorption for the visible [12]. The origin of these promising properties was ascribed to strong excitonic coupling interactions between monomers, enhancing strongly the TPA cross-sections of these linear oligomers molecules.

A new approach to optimize oligomers nonlinear absorption properties based on excitonic coupling is the introduction of these systems in dendritic systems (Figure 1), in order to study the role of the dimensionality of the molecule on the coupling interactions. The dimensionality of the molecule will depend on the central binding core : a first approach was considered by the introduction of fluorene oligomers in two-dimension dendrimers, in which the dimensionality is given by a central benzene ring [13]. Their response is higher than that of their linear analog fluorene oligomers.

The approach proposed in this paper consists in using three-dimension systems, in which fluorene oligomers are bound in the three

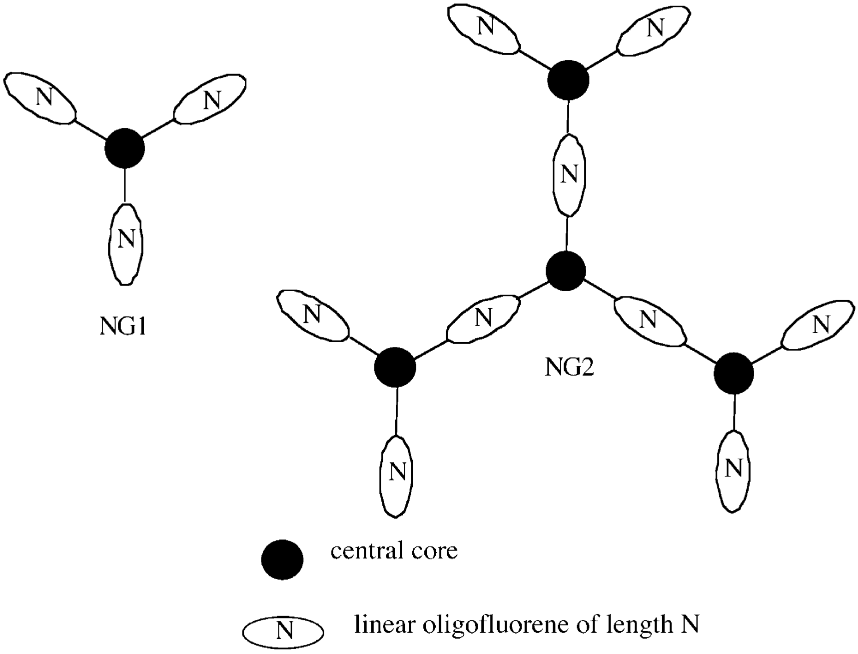

FIGURE 1 General structures of first and second generations dendritic systems of oligofluorenes of length N (**NG1** and **NG2** respectively).

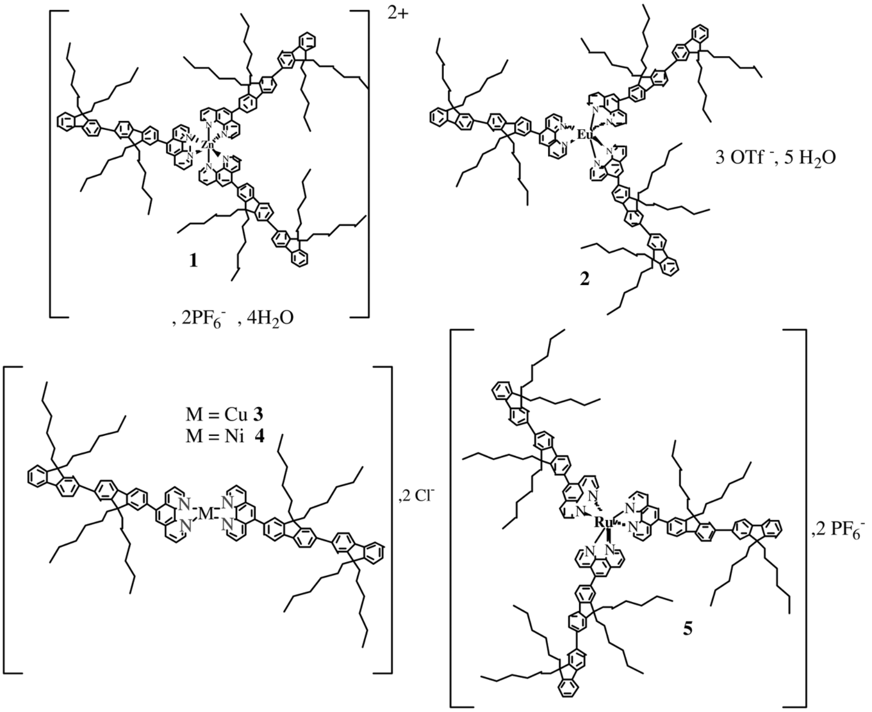

FIGURE 2 Molecular structures of complexes **1–5**.

directions of the space by means of a metal. We present linear and nonlinear absorption properties of dendrimers of first generation of different complexes containing two fluorene units.

EXPERIMENTAL

The complexes 1–7 (Figures 2, 3) synthesis will be described elsewhere.

The three-photon absorption spectra were obtained, at constant fluence by wavelength scanning, from a collimated beam (210 µm $HW1/e^2M$) of a Nd:YAG pumped optical parametric oscillator, which produces 2.6 ns pulses (full width at half maximum : FWHM) in the 450–650 nm range. All experiments have been carried out at room temperature under ambient atmosphere.

In nanosecond regime, the nonlinear absorption can be described in a two-step three-photon absorption process [4]. When the excited-state lifetime τ_{01} is much shorter than the laser pulse time-duration ($\tau_{pulse} = 2.6$ ns (FWHM)), the instantaneous molecular response may

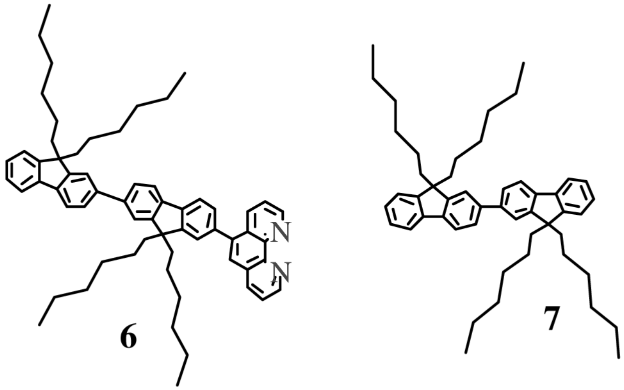

FIGURE 3 Molecular structures of organic molecules **6–7**.

be applied, and the three-photon absorption coefficient α_3 is defined following Eq. (1) and given by Eq. (2).

$$\frac{dI}{dz} = -\alpha_3 I^3 \tag{1}$$

$$\alpha_3 = \frac{N}{V}\frac{\sigma_{TPA}\sigma_{1n}\tau_{01}}{2(\hbar\omega)^2} \tag{2}$$

N/V is the chromophore concentration, σ_{TPA} and σ_{1n} are respectively the TPA and the ESA cross-sections in the solvent, and ω the laser pulsation. The optimization of α_3 requires the simultaneous optimization of all these parameters.

Experimentally, this three-photon absorption coefficient is obtained from nonlinear transmission measurements by numerically inverting the transmission formula (3), in which L is the sample thickness.

$$T_E = \iint \frac{1}{\sqrt{1 + 2\alpha_3 L I^2(r,t)}} dr\, dt \tag{3}$$

RESULTS AND DISCUSSION

Linear absorption spectra of complexes **1–4** are displayed in Figure 4, while wavelengths maxima are reported in Table I in comparison with the organic ligand **5** and the bifluorene molecule **6**. Zn and Eu complexes **1** and **2** are colorless, while Cu or Ni systems present a slightly green colour. Accordingly, at studied concentrations (nearly at 10^{-5} $g{\cdot}L^{-1}$), all spectra of complexes **1–4** present a good transparency in

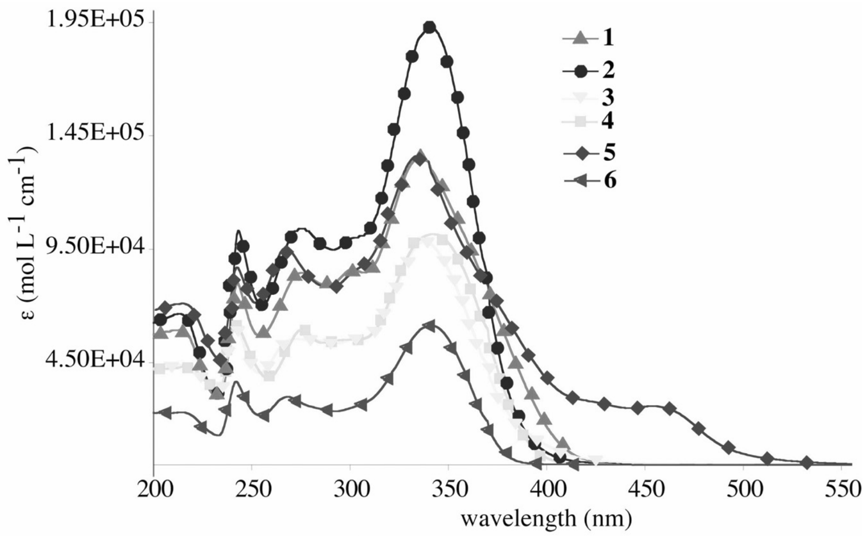

FIGURE 4 Linear absorption spectra of systems **1–6** in chloroform.

the visible. The linear absorption spectra of these complexes present a main band close to 350 nm similar to that observed in the case of the corresponding ligand **6**. This behaviour allows to assume a weak metal-ligand charge transfer (MLCT) process in systems **1–4**. In contrast, the Ru complexe **5**, which has an orange colour, presents a

TABLE I Relevant Data of Systems **1–7;** Molecular Mass (M), Linear Absorption Maximum (λ_{abs}), Molar Extinction Coefficient ε, Three-Photon Absorption Coefficient α_3 measured at 100 g/L in the Chloroform, Three-Photon Absorption Coefficient Normalized to the Bifluorene Concentration α_3' (see Eq. (5)).

System	M^a	$\lambda_{\text{abs}}{}^b$	ε^c	$\alpha_3{}^d$ ($\lambda_{3\text{PA}}{}^b$)	$\alpha_3'{}^d$
1	2963	335	145220	850 (532)	1870
2	3273	341	158850	1140 (516)	1260
3	1877	339	105560		
4	1854	342	108550		
5	2927	459	27070		
		334	145240		
6	845	341	61400	2200 (532)	2800
7	667	330^e	53570^e	1890 (521)	1890

^{a}g.mol^{-1} ; ^{b}nm; ^{c}mol. L^{-1} cm^{-1}; ^{d} cm^3.GW^{-2}; ^{e} Ref. 14.

MLCT band at 460 nm in addition to the ligand band. Consequently, only complexes **1** and **2**, which are uncoloured and present the best transparency in the visible range, will be studied for nonlinear absorption effects in the visible.

The three-photon absorption spectra for complexes **1-2** are presented in Figure 5 between 450 and 650 nm in comparison with their organic ligand **6** and the bifluorene molecule **7**. Broad bands were obtained for the α_3 spectral distribution. Complexes **1-2** and the ligand **6** present a main band at nearly the same wavelength than that of the bifluorene **7** (520–530 nm) with further weaker structures at longer wavelengths. The most efficient molecules are the organic molecules **6** and **7**, with α_3 values of nearly 2000 cm^3/GW^2 for a concentration of 100 g/L in chloroform, while both complexes **1** and **2** present α_3 values of the same order of magnitude, but two times less high (Table I).

The lack of MLCT process in **1** and **2**, deduced from above linear absorption properties, allows to assume that nonlinear absorption properties of complexes could arise mainly from the response of the organic ligand **6**. Futhermore, the influence of the 1,10-phenanthro line group of this molecule on its nonlinear absorption properties will be neglected, due to the weak efficiency of this substituent as a donor group (illustrated by the weak bathochromic effect in the linear

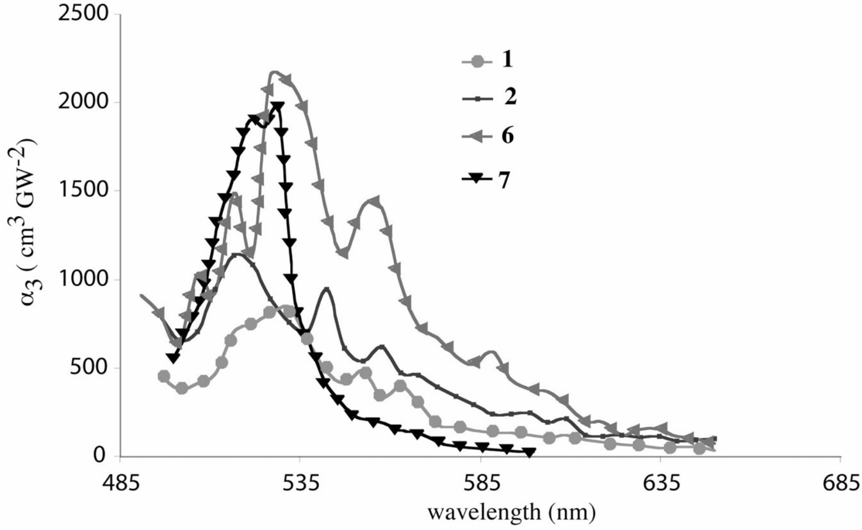

FIGURE 5 Three-photon absorption spectra of systems **1**, **2**, **6** and **7** at c = 100 g/L in chloroform.

absorption spectrum, with respect to that of the bifluorene **7**, as shown in Table I); the nonlinear absorption response of the molecule **6** can be then attributed to the response of the bifluorene system **7**. Accordingly, in order to deduce the role on nonlinear absorption of the 3D distribution of the three bifluorene systems around Zn and Eu metals in complexes **1** and **2** respectively, we have compared nonlinear absorption properties of theses complexes with those of organic systems **6** and **7** at similar concentrations of bifluorene in each system. The three-photon absorption coefficient α'_3 normalized to the number of moles per liter of the bifluorene **7** was determined from the coefficient k given by the relationship (4) and using Eq. (5). In Eq. (4), M is the molecular mass of the system, as given in Table I, and M' the molecular mass of the bifluorene **7**. The factor α is equal to 1 for molecules **6** and **7**, while this parameter takes the value of 3 in the case of the coordination complexes **1** and **2** in order to take into account of the three ligands around the metal.

$$k = \frac{M}{\alpha M'} \tag{4}$$

$$\alpha'_3 = k\alpha_3 \tag{5}$$

Maxima values of α'_3 are reported in Table I for systems **1**, **2** and **6**, **7**. In good agreement with the above assumption, the organic molecule **6** presents a very close α'_3 value at its maximum than that of **7** (2800 and 1900 cm^3/GW^2 respectively) ; similarly complexes **1** and **2** present very close values of α'_3 than **7** (1300 and 1900 cm^3/GW^2). The 3D repartition of bifluorene molecules around the europium or the zinc does not provide further interactions to enhance nonlinear absorption properties of this molecule, at least for this first generation of these 3D dendritric systems.

CONCLUSION

Nonlinear absorption properties of first generation 3D fluorene oligomers complexes were studied. All these systems are transparent in the visible range due to the lack of MLCT phenomenon.

These systems are efficient nonlinear absorbers in the green range. Although their response is similar than that of their linear analog fluorene oligomers for a same concentration of oligomers, due to no further excitonic interactions in 3D molecules, these coordination complexes present better thermal and chemical stabilities than their organic parents, which is a great advantage for their use in practical applications.

The study of TPA properties of these systems is in progress in order to support above conclusions. The study of higher generations of dendritic coordination complexes is also in progress to induce higher 3D interactions between fluorene oligomers.

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