



Self-ordered dendrimers based on multi-octupolar ruthenium complexes for quadratic nonlinear optics

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Available online 4 January 2005

Abstract

A quasi-optimized supramolecular octupolar ordering has been achieved in a metallodendrimer made of several ruthenium tris-bipyridine complexes displaying high nonlinear optical efficiency. This acentric organization is evidenced by Harmonic Light scattering at 1.9 μm , where a coherent second harmonic emission from each dendrimer unit is compared to the fully incoherent harmonic signal from a disordered linear polymer containing the same nonlinear complexes. These results show the interest of a controlled coordination strategy to build supramolecules and dendritic structures, with promising perspectives towards nanoscale applications in photonics.

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Pacs: 42.65; 42.70; 61.46; 78.40.Me

Keywords: Dendrimers; Nonlinear optics; Harmonic light scattering; Metal complexes; Hyperpolarizability; Self-organization

1. Introduction

The noncentrosymmetric organization of dyes in molecular materials for quadratic nonlinear optics (NLO) is a critical challenge for efficient material

elaboration and subsequent device applications [1]. In that respect, various strategies have been explored for a long time, encompassing electrical poling of NLO-polymers [2] via dipole-DC field coupling, or self-organization of active chromophores via the Langmuir–Blodgett technique [3], or self-organized multilayers [4]. Another method to elaborate noncentrosymmetric materials is the nanoscale ordering of NLO units within a multi-chromophoric system, resulting in the availability

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of “preorganized” structures with huge individual NLO responses. Promising reports have been published in the case of dipolar bis-chromophoric molecules [5–7] and of four dipolar units in calix [4]-arene derivatives [8]. Self-organization schemes involving a higher number of dipolar chromophores within supramolecular architectures like β -cyclodextrin [9] or dendrimers [10] have also been investigated and may open a new route to the design and elaboration of acentric nano-objects where exceptionally large first-order hyperpolarizabilities β and dipole moments are intrinsically associated.

All these approaches are dealing with one-dimensional, strongly dipolar molecules. Beyond this classical dipolar scheme, a new concept of octupolar nonlinearities was recently proposed on the basis of group theory and quantum mechanical studies [11]. For molecules belonging to purely octupolar space groups such as D_3 , D_{3h} , D_2 and T_d , the vector part ($\beta_{J=1}$) of the first-order hyperpolarizability β tensor vanishes and only the octupolar part $\beta_{J=3}$ remains. Thus, an increasing number of two- and three-dimensional octupolar molecules such as benzene derivatives, crystal violet and similar carbocations, cyanine salts and biphenyl derivatives have been investigated [12].

Recently, organometallic and coordination compounds have also received increasing attention as potential NLO materials [13]. Noncentrosymmetric structures can be obtained upon coordination of different ligands to a metal centre. Among the variety of metallo-octupoles studied, tris(dialkylaminostyryl-[2,2']-bipyridine)zinc(II) or ruthenium(II) complexes exhibit the best trade-off between NLO activity and thermal/chemical stability [14]. Moreover, ruthenium(II) has the ability to form heteroleptic complexes upon sequential coordination of different bipyridyl ligands [15].

Non-dipolar (octupolar) materials would be able to overcome the problem of intermolecular dipole–dipole interactions [11]. However, whereas octupolar nonlinearities have been widely evidenced in individual molecules [16], their extension to supramolecular architectures still remains a challenging issue [17]. We have previously shown the interest of metal complexes which can play the

role of very powerful templates for the engineering of various octupolar arrangements exhibiting high NLO responses [18]. In the frame of this work, we proposed to use the rich possibilities offered by the supramolecular coordination chemistry [19] to conceive and elaborate multi-octupolar molecules like polymetallic complexes, metallo-dendrimers or metallo-polymers [20]. Therefore, for the design of multi-octupolar complexes, we sought to apply this concept which requires the initial construction of multipodal ligands based on dialkylaminostyryl-[2,2']-bipyridine (DAASbpy).

In the present paper we describe the synthesis and characterization of new polyimide, dipodal and tripodal ligands containing the DAASbpy moieties, and their further complexation to Ru(II) ions. These ligands are shown to be very good building blocks for the elaboration of polymetallic octupolar structures (dimer, trimer, heptamer and polymer) [21]. Their UV-visible absorption and second-order nonlinear optical properties are investigated with respect to those of the corresponding monometallic units. NLO studies, based on harmonic light scattering (HLS) measurements performed at 1.91 μm fundamental wavelength clearly evidences a quasi-optimized acentric supramolecular ordering in a dendrimer containing seven ruthenium(II) complexes.

2. Experimental

The synthesis of the dipod and tripod ligands **c** and **d** was made using the mono-hydroxy substituted 4,4'-bis(dialkylaminostyryl)-2,2'-bipyridine **b** as starting material (Fig. 1). These ligands were prepared by treating α,α' -dibromo-p-xylene and 2,4,6-tris(bromomethyl)mesitylene, respectively, with ligand **b** in the presence of sodium hydride in dimethylformamide (DMF). The synthetic methodology for the preparation of the multimetallic compounds was based on the sequential coordination of the “parent” ligand **a** bearing two identical dialkylamino groups and the appropriate multipodal bipyridyl ligands. The bi- and tri-metallic complexes **2** and **3** were obtained by refluxing the ligands **c** and **d** and $\text{Ru}(\mathbf{a})_2\text{Cl}_2$ in DMF, followed by an exchange of the chloride

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