JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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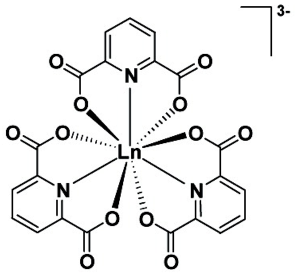
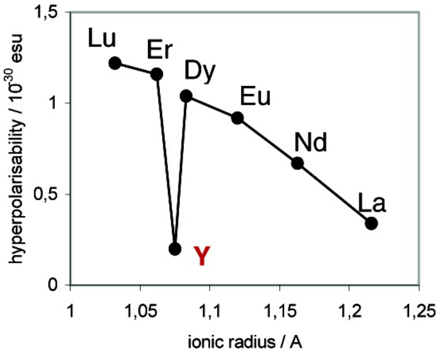
J. Am. Chem. Soc., **2005**, 127 (39), 13474-13475• DOI: 10.1021/ja054065j • Publication Date (Web): 10 September 2005



Ln = La, Nd, Eu, Dy, Er, Lu and Y



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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COMMUNICATIONS

Lanthanide Complexes for Second Order Nonlinear Optics: Evidence for the Direct Contribution of f Electrons to the Quadratic Hyperpolarizability[1]

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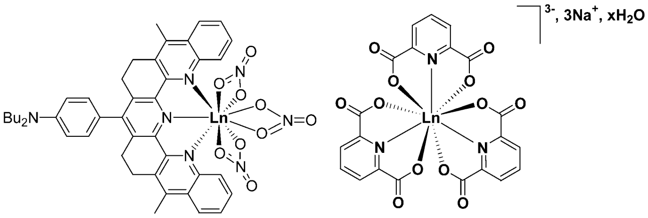
In the last two decades, lanthanide complexes have been extensively used as contrast agents for medical imaging as well as for their catalytic, magnetic, and luminescence properties.[2] By contrast, the study of the nonlinear optical (NLO) properties of lanthanides remains in its infancy and becomes currently an emerging field of research. The third-order NLO properties, i.e. the cubic hyperpolarizability γ, of phthalocyanine lanthanides complexes were first described in pioneering studies by Shirk in 1992[3a] and were recently investigated in polymetallic species.[3b,c] In addition, only few recent articles reported the sensitization of the Eu(III) or Tb(III) luminescence by two-photon excitation.[4] The second-order NLO properties of lanthanide derivatives have received even less attention; to the best of our knowledge, only the Kurtz powder NLO activities of coordination polymers were recently described,[5] and lanthanate complexes have also been used as (NLO-inactive) bulky counteranions in Langmuir−Blodgett films.[6]

In this context, we recently reported the first dipolar lanthanide terpyridyl complex family exhibiting high hyperpolarizability coefficient β (Chart 1) and evidenced a so-called "metal-induced" second-order NLO activity enhancement along the lanthanide series.[1] To get more insight into this intriguing phenomenon, we decided to look at another family of complexes featuring a completely different structure: the tris(dipicolinato)lanthanate $Na_3[Ln(dipic)_3]\cdot xH_2O$ (Chart 1) (Ln = La, Nd, Eu, Dy, Er, Lu, and Y; dipicolinate = pyridyl-2,6-dicarboxylate). Here we demonstrate for the first time the direct contribution of f electrons to the second-order NLO activity.

$Na_3[Ln(dipic)_3]\cdot xH_2O$ complexes are well-known to form an isostructural family in the solid state[7] as well as in water solution.[8] In its ground state, the complexes exibit a non-centrosymmetric propeller-like structure featuring an octupolar D_3-symmetry.[9] Seven complexes were prepared by mixing dipicolinic acid, sodium hydroxide, and $LnCl_3\cdot xH_2O$ in water. The complexes were purified by double crystallization in cold water. After filtration, the crystals were crushed and thoroughly dried in a vacuum at 80 °C. The NMR data are in agreement with those previously reported,[8] and for each complex the number of water molecules was estimated by means of microanalysis and X-ray microfluorescence (Table 1 and Supporting Information Tables S1, S2). The structures of lutetium and yttrium complexes were confirmed by an X-ray diffraction analysis (Figure 1); they are similar to those of other tris(dipicolinato) lanthanate complexes reported in the litterature[7] with small deviations from the octupolar D_3 symmetry. In addition, an overview of 17 $[Ln(dipic)_3]^{3-}$ structures (Ln = La, Ce, Nd, Eu, Dy, Ho, Yb, Lu, and Y) from the Cambridge Crystallographic Data Centre (Table S3 and Figure S1) clearly illustrate that the Ln−N and Ln−O distances regularly decrease from lanthanum to lutetium in agreement with the lanthanide contraction.

Chart 1. Dipolar and Octupolar Complexes



Ln = La, Gd, Dy, Yb

Ln = La, Nd, Eu, Dy, Er, Lu and Y

Table 1. Linear and Nonlinear Optical Data

$Na_3[Ln(dipic)_3]\cdot xH_2O$	λ_{max} nm	ϵ L·mol^{-1}·cm^{-1}	$\langle\beta\rangle$ 10^{-30} esu	$\Delta\beta$
Y ($x = 6$)	279	15920	0.2	0.044
	271	17590		
La ($x = 3$)	278	16320	0.343	0.078
	271	18300		
Nd ($x = 4$)	278	14730	0.67	0.13
	271	16560		
Eu ($x = 4$)	278	14950	0.92	0.22
	270	16470		
Dy ($x = 5$)	278	15720	1.04	0.2
	270	17380		
Er ($x = 5$)	278	15380	1.16	0.27
	270	16990		
Lu ($x = 5$)	279	15750	1.22	0.3
	271	17590		

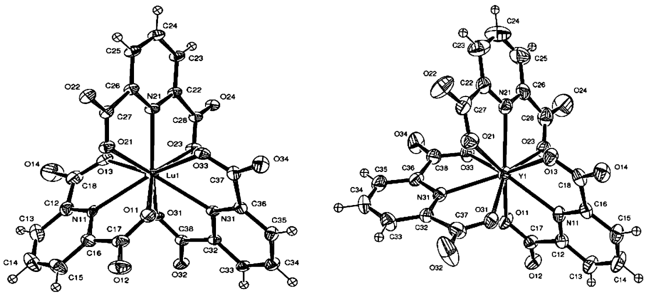


Figure 1. ORTEP drawings of $Na_3[Lu(dipic)_3]\cdot 12H_2O$ and $Na_3[Y(dipic)_3]\cdot 12H_2O$. Sodium atoms and coordinated water molecules are ommited for clarity.

As expected for an isostructural series, all the complexes exhibit the same UV−visible spectrum[1] (Figure 2, Table 1): they show two bands at ca. 270 and 278 nm with similar absorption coefficients

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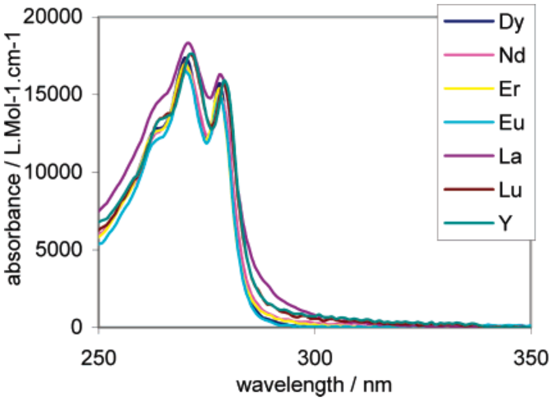

Figure 2. UV−visible spectra of $[Na]_3[Ln(dipic)_3]$ in water.

($15-18 \times 10^3$ L·mol^{-1}·cm^{-1}) which can be assigned to $\pi-\pi^*$ transitions of the coordinated pyridyl ring. Their molecular first hyperpolarizabilities (Table 1) were measured in water solution by using the harmonic light scattering (HLS) technique with a 1.06 μm laser fundamental. All the measurements were performed at the same concentration ($c = 10^{-1}$ mol·L^{-1}) to avoid concentration effects. The intensity of hyper-Rayleigh scattered light from a solution with N molecules per cm^3 of solute and N_S molecules per cm^3 of solvent is given by:

$$I^{2\omega} = G(N_S\langle\beta_S\rangle + N\langle\beta\rangle)(I^{\omega})^2$$

where $\langle\beta\rangle$ (respectively $\langle\beta_S\rangle$) is the orientational average of the second-order hyperpolarizability of the complex (respectively solvent), I^{ω} is the intensity of incident radiation, and G is a coefficient including geometrical factors, local field factors, and other experimental correction terms. To obtain the $\langle\beta\rangle$ values, it was necessary to work in two steps. First, the second-order intensity of the solvent only was measured. The same experiment was then carried out with the solution of the complex. In these two cases, $I^{2\omega}$ versus I^{ω} was plotted. Knowing the $\langle\beta_S\rangle$ value, $\langle\beta\rangle$ was determined by calculating the ratio of the two slopes.

To obtain the most precise results as possible, around 10 slopes for both solvent and solution were plotted for each compound. Then, statistical methods based on Student's *t*-distribution were used to obtain the "real" standard deviation according to this intermediate number of slopes. Errors bars on $\langle\beta\rangle$ ($\Delta\beta$, Table 1) were finally calculated using the uncertainly propagation method and given with a level of confidence of 95%.

As already observed for the dipolar series,[1] the NLO activity regularly increases along the series from lanthanum to lutetium, and it is important to note that the $\langle\beta\rangle$ value of Lu complex is roughly 3.5 times larger that of La. The "metal-induced" NLO activity enhancement is therefore clearly confirmed and appears to be a new intrinsic property of f-block elements. Let us now focus our attention on the particular case of yttrium. Yttrium belongs to group III, has no f electron as does lanthanum, and shows chemical similarities to lanthanides with an ionic radius of 1.075 Å, between those of dysprosium (1.083 Å) and erbium (1.062 Å) (Figure S1).[10] Plotting the variation of $\langle\beta\rangle$ versus the ionic radius as is generally done for lanthanide properties (Figure 3 top), clearly demonstrates the strongly different behavior of yttrium ($\langle\beta(Y)\rangle \ll \langle\beta(Dy)\rangle$ and $\langle\beta(Er)\rangle$) as compared to that of all lanthanide complexes.[11] This result unambiguously indicates that the NLO variation is not driven by geometrical parameters, i.e. the lanthanide contraction. By contrast, plotting $\langle\beta\rangle$ versus an electronic parameter, i.e. the f configuration (Figure 3, bottom) results in a very regular variation with $\langle\beta(Y)\rangle \approx \langle\beta(La)\rangle$.

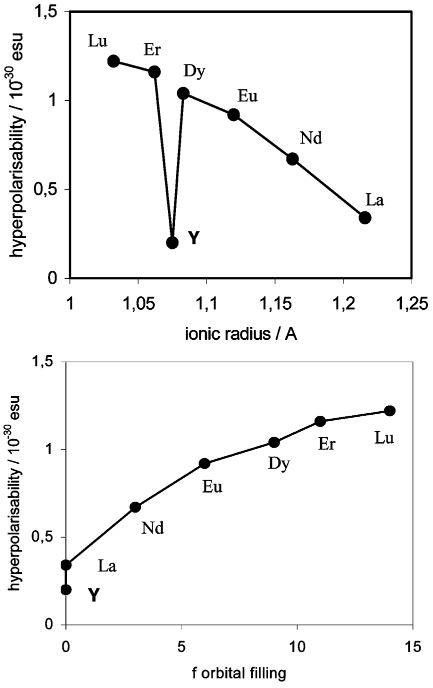

Figure 3. Plot of the hyperpolarizability coefficient β vs ionic radius (top) or f orbital filling (bottom).

In conclusion, this study describes for the first time the NLO properties of multipolar lanthanide complexes, $Na_3[Ln(dipic)_3]$. It confirms the "metal-induced" NLO activity enhancement as a general property of f-block elements and strongly suggests the direct contribution of f electrons to the hyperpolarizability $\langle\beta\rangle$.

Acknowledgment. We are very grateful to Prof. J.-F. Carpentier, R. Réau, and D. Yaron for fruitful discussions.

Supporting Information Available: Experimental data, structure analysis, and crystallographic data in CIF files. This material is available free of charge via the Internet at http://pub.acs.org.

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JA054065J