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First lanthanide dipolar complexes for second-order nonlinear optics†

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New push–pull NLO-phores based on lanthanide complexes (Ln = La, Gd, Dy, Yb) featuring an annelated dibutylaminophenyl functionalised terpyridyl ligand have been synthesised and shown to exhibit large first-order hyperpolarizability.

Whereas lanthanide complexes have attracted considerable attention for their luminescent properties arising from *f–f* transitions, as well as for their magnetic properties and biological applications,[1] much less is known about their potentialities in the field of second-order nonlinear optics (NLO). To the best of our knowledge only the Kurtz powder NLO activity of a europium-containing coordination polymer was recently reported.[2] Langmuir–Blodgett films of stilbazolium chromophores with lanthanate complexes as bulky counter-anions were also studied for their second harmonic generation properties.[3] Over the last decade, we have been concerned with the second-order nonlinear optics of dipolar and octupolar coordination complexes.[4] We have mainly focused our attention on the NLO properties of molecular,[4a,b] macro-[4c] and supra-[4d] molecular 4,4′-disubstituted-[2,2′]-bipyridine transition metal complexes. In these systems the metal plays two important roles which both contribute to NLO activity: (i) it is a powerful template to gather ligands in a predetermined non centrosymmetric arrangement and (ii) it acts as a Lewis acid to induce a strong Intra-Ligand Charge Transfer (ILCT) transition. These observations prompted us to investigate the NLO properties of trivalent lanthanide metal ions because of their strong Lewis acidity and their ability to accept large coordinance (8–12), resulting in unusual geometries. Herein, we report on the synthesis, radiocrystallographic structure and optical properties of a series of dipolar lanthanide complexes (Ln = La, Gd, Dy, Yb) featuring a functionalized annelated terpyridyl ligand and we demonstrate for the first time that rare-earth complexes can behave as efficient NLO-phores.

The terpyridyl-type ligand **L** (Fig. 1), whose synthesis will be described elsewhere, is functionalized by a dibutylaminophenyl group at the *para* position of the central pyridyl ring in order to induce an intra-ligand charge transfer from the amino donor to the central pyridine acceptor moieties. In addition, this ligand contains two dimethylene bridges (annelation) between the central pyridine and the lateral quinoline moieties in order to avoid any *cisoid–transoid* isomerization and thus to stabilize the resulting complexes against competitive coordination of solvent ligands such as water.[5]

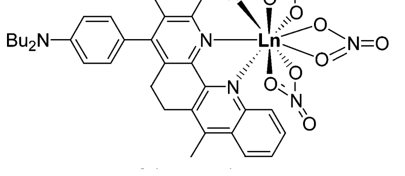

Fig. 1 Structure of the complexes.

This tridentate ligand **L** was used to prepare in good yield the corresponding **L***Ln* $(NO_3)_3$ (*Ln* = La, Gd, Dy, Yb) complexes by addition of a dichloromethane solution of **L** to one equivalent of hydrated lanthanide nitrate dissolved in acetonitrile (Fig. 1).[6] The ligand **L** and corresponding complexes were fully characterized by ^{1}H NMR, UV-visible spectroscopy, elemental analysis.† The ^{1}H NMR spectrum of the ligand exhibits only one set of signals in agreement with the C_2-symmetric structure of the molecule. While lanthanum complexation induces only minor modification of the NMR spectrum, the other paramagnetic lanthanide complexes display ^{1}H NMR signals which are spread over *ca.* 150 ppm (−95 to 47 ppm for dysprosium and −6 to 114 ppm for ytterbium). Only one set of signals is observed in CD_2Cl_2 solution even at low temperature, clearly indicating the formation of a single species in solution with an average C_2-symmetric architecture.

In the case of gadolinium, we were able to prepare crystals as thin orange needles, suitable for X-ray diffraction analysis, by cooling down an acetonitrile solution of $\mathbf{L}Gd(NO_3)_3$. The radiocrystallographic structure of $\mathbf{L}Gd(NO_3)_3{\cdot}CH_3CN$ is shown in Fig. 2.‡[6] The structure consists of a neutral molecule in which the gadolinium is nonacoordinated, bonded to six O-atoms from the bidentate nitrato moieties and to three N-atoms of the terpyridyl ligand. As already observed,[6] the Gd–N distance is shorter in the case of the central pyridine as compared to the lateral ones. This

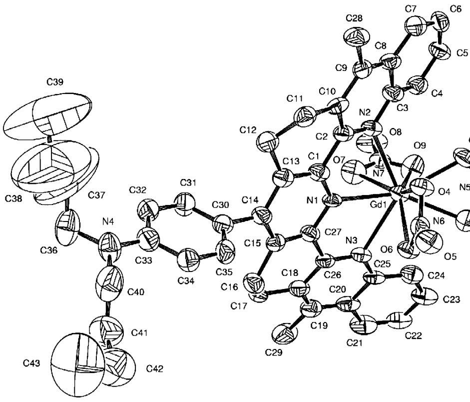

Fig. 2 ORTEP drawing of [$\mathbf{L}Gd(NO_3)_3{\cdot}CH_3CN$] with ellipsoid at 30% probability, acetonitrile and hydrogen atoms were omitted for clarity. Selected distances Gd–N(1) 2.445(9) Å, Gd–N(2) 2.551(8) Å, Gd–N(3) 2.573(8) Å, Gd–O(1) 2.503(8) Å, Gd–O(3) 2.459(8) Å, Gd–O(4) 2.437(7) Å, Gd–O(6) 2.485(7) Å, Gd–O(7) 2.460(9) Å, Gd–O(9) 2.446(9) Å.

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† Electronic supplementary information (ESI) available: synthesis and complete characterisation of the ligand and related complexes. See http://www.rsc.org/suppdata/cc/b4/b407073a/

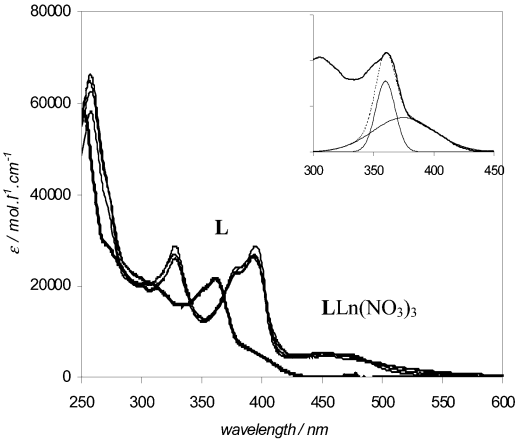

Fig. 3 UV-visible spectra of the ligand (deconvolution inset) and of related complexes.

Table 1 Linear and nonlinear optical data for the ligand and related complexes

	λ_{ILCT} $\lambda_{\pi-\pi^*}$[a] (nm)	ε (L mol^{-1}. cm^{-1})	$v_{1/2\ (ILCT)}$ (cm^{-1})	f[b]	$\beta^{1.91c}$ (10^{-30} esu)	β_0 (10^{-30} esu)
L	376	7500	4294	0.14		
	361	21800				
L*La*(NO$_3$)$_3$	453	5400	6055	0.14	186	136
	391	24500				
L*Gd*(NO$_3$)$_3$	452	5800	4550	0.12	246	180
	393	26900				
L*Dy*(NO$_3$)$_3$	450	5400	5825	0.14	260	190
	394	26700				
L*Yb*(NO$_3$)$_3$	452	5150	5465	0.12	288	211
	394	28850				

[a] Measured in dilute dichloromethane solution (1×10^{-5} mol L^{-1}). [b] The oscillator strength is deduced from the UV-visible spectra according to $f = 4.319 \times 10^{-9}.\varepsilon.v_{1/2}$. [c] Measured by HLS using λ = 1.91 µm as fundamental wavelength in concentrated dichloromethane solution (1×10^{-2} mol L^{-1}), experimental error ±15%.

closer interaction allows the metal to be more deeply located in the ligand cavity, minimizing the steric repulsion with the quinolic protons H4 and H24 (H(4)–O(3) = 2.291 Å; H(24)–O(1) = 2.573 Å).

The UV-visible spectrum of **L** (Fig. 3, Table 1) reveals an absorption maximum at 361 nm corresponding to the π–π* transition, characteristic of the dimethylene annelated terpyridyl moieties,[5b] overlapped with a broad band at 376 nm (Fig. 3, deconvolution in inset) assigned to the intra-ligand charge transfer transition from the dibutylamino donor group to the central pyridinic acceptor fragment. Lanthanide complexation results in a moderate bathochromic shift of the π–π* transition ($\Delta\lambda$ = 32 nm) and a strong one for the ILCT transition ($\Delta\lambda$ = 76 nm) in agreement with the high Lewis acidity of the *f*-elements. In addition, this bathochromic shift is insensitive to the nature of the lanthanide core, confirming the already observed similar ionochromic effect along the *4f* block elements.[7] It is important to note that the oscillator strength (*f*) of the ILCT transition is conserved upon complexation, the lowering of the extinction coefficient being compensated by a broadening of the band.

The molecular hyperpolarizability coefficient β and the corresponding dispersion free hyperpolarizability β_0 for the four lanthanide complexes are reported in Table 1. β measurements were performed by the Harmonic Light Scattering (HLS) method at 1.91 µm to avoid any possible 2-photon absorption induced fluorescence phenomena.[4d] It is worth noting that the NLO activity apparently increases steadily along the lanthanide series, but the differences are within the experimental error. The β_0 values are high, between 136 and 211 × 10^{-30} esu, and are considerably larger for the Gd, Dy and Yb complexes than for their La counterpart [β_0(Yb) is roughly 1.5 times that of β_0(La)]. Generally, according to the two-level model,[8] a change in the NLO activity of a given molecule is correlated with a modification of the linear absorption properties. Therefore this result is quite surprising, since all complexes display a similar structure and exactly the same UV-visible spectrum. So, the observed NLO activity enhancement can not be explained by an increase of the Lewis acidity along the lanthanide series. This "metal-induced" NLO activity enhancement is particularly interesting in terms of transparency/nonlinearity trade-off because improved β values are reached without any cost in transparency.

In conclusion, this preliminary communication describes the first investigation of "push–pull" lanthanide complexes for second-order nonlinear optics. It appears that lanthanide complexes can behave as efficient NLO-phores and that the NLO activity depends on the nature of the rare-earth itself. This discovery opens new perspectives in molecular engineering for NLO studies and for the design of new multifunctional materials combining NLO and luminescence properties.

Notes and references

‡ Crystal data for $C_{43}H_{44}N_4Gd(NO_3)_3 \cdot CH_3CN$: M_r = 1001.17, trigonal, $R\bar{3}$, a = 48.4150(1) Å, c = 10.6278(2) Å, V = 21574.2(7) Å^{-3}, Z = 18, D_x = 1.387 Mg m^{-3}, λ(MoKα) = 0.71073 Å, μ = 14.43 cm^{-1}, F(000) = 9162, T = 120 K. 554 variables and 5438 observations with $I > 2.0\sigma(I)$; calc $w = 1/[\sigma^2(F_o^2) + (0.16P)^2 + 11.50P]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting R = 0.094, R_w = 0.242 and S_w = 0.939, $\Delta\rho < 1.8$ e Å^{-3}. CCDC 229762. See http://www.rsc.org/suppdata/cc/b4/b407073a/ for crystallographic data in .cif or other electronic format.

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