## Highly stable 7-*N*,*N*-dibutylamino-2-azaphenanthrene and 8-*N*,*N*-dibutylamino-2-azachrysene as a new class of second order NLO-active chromophores<sup>†</sup>

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7-*N*,*N*-Dibutylamino-2-azaphenanthrene (L<sup>3</sup>), 8-*N*,*N*-dibutylamino-2-azachrysene (L<sup>4</sup>) and related Ir(1) complexes or alkylated salts show high second-order NLO responses, as determined by the EFISH technique and DFT calculations. L<sup>4</sup> is appealing as building block for NLO active materials due to its unexpected large  $\mu\beta_{1.907}$ value and its very high thermal stability.

The design and synthesis of new non-linear optical (NLO) chromophores possessing high values of quadratic hyperpolarizabilities  $\beta$  and characterized by chemical, photochemical and thermal stability are of great technology-driven interest.<sup>1</sup> Stilbene and azobenzene based chromophores, well known NLO active molecules already incorporated into electro-optic polymeric systems,<sup>2</sup> present several intrinsic drawbacks due to *cis*-*trans* photoisomerism around the C=C or N=N double bond and photorotamerism of the aromatic rings thus reducing the chromophore NLO activity.<sup>3</sup> Moreover the isolated double bond may be easily oxidized thus interrupting the  $\pi$ -conjugation between the donor and the acceptor groups. These problems can be overcome if the double bond is included in a rigid polyaromatic system, which should ensure not only stability, but also highly electronic delocalization.

In this communication we report the synthesis and the study of the second order NLO properties, measured by the Electric Field Induced Second Harmonic generation (EFISH) technique,<sup>4</sup> of 7-*N*,*N*-dibutylamino-2-azaphenanthrene ( $\mathbf{L}^3$ ) and 8-*N*,*N*dibutylamino-2-azachrysene ( $\mathbf{L}^4$ ) (Fig. 1). For comparison *N*,*N*-dimethyl-4-(pyridin-4-yl)aniline ( $\mathbf{L}^1$ ) and *N*-methyl-*N*hexadecylaminostilbazole ( $\mathbf{L}^2$ )<sup>5</sup> (Fig. 1), the corresponding nonanellated chromophores of  $\mathbf{L}^3$  and  $\mathbf{L}^4$ , respectively, were also investigated. Finally we synthesized *cis*-[Ir(CO)<sub>2</sub>ClL<sup>3</sup>] (IrL<sup>3</sup>) and *cis*-[Ir(CO)<sub>2</sub>ClL<sup>4</sup>] (IrL<sup>4</sup>) complexes and methylated salts to



Fig. 1 Structure of compounds studied.

evaluate the modification of the chromophores electronic properties and their effect on the NLO activity.<sup>6</sup>

Compounds  $L^3$  and  $L^4$  have been reported as intermediates for the preparation of anellated hemicyanine dyes.<sup>7</sup> Compounds used in the present study have been prepared in good yields by careful modification of the known procedure for  $L^3$ , and using a different synthetic approach for  $L^{4.8} L^1$  was obtained using a standard Suzuki coupling and  $L^2$  was prepared as reported.<sup>5</sup> Complexes  $IrL^3$  and  $IrL^4$  have been obtained by reaction of  $L^3$ and  $L^4$  with  $[Ir(CO)_2Cl]_2$  as previously described for similar compounds.<sup>6a,8</sup> The methyl pyridinium salt of  $L^4$  ( $L^4Mel$ ) was prepared by reaction with MeI following a standard procedure.<sup>6b,8</sup> Details of the synthesis and characterization of all the compounds are given in ESI.<sup>†</sup>

The experimental electronic spectra are reported in Table 1, along with their  $\mu\beta_{1.907}$  values measured with the EFISH technique.<sup>4</sup> The theoretical  $\mu$  values (see below) of all compounds are also given together with the experimental values of L<sup>2</sup>, L<sup>3</sup> and L<sup>4.9</sup>

As expected  $L^1$  is characterized by a low value of  $\mu\beta_{1,907}$  in CHCl<sub>3</sub> due to the absence of a complete  $\pi$ -conjugation between the two aromatic rings. However this value increases drastically by a factor of 8.9 if the single bond is included into the polyaromatic scaffold of  $L^3$ . A further increase of  $\beta$  by a factor of 1.4 is obtained upon coordination of  $L^3$  to the "Ir(CO)<sub>2</sub>Cl" moiety which acts as an additive electron–acceptor group producing a red-shift of the ILCT transition (from 347 to 390 nm, Table 1) dominating the NLO response. Remarkably, an increase of the  $\pi$ -conjugation of the free ligand leads to a huge positive effect on the second order NLO response, with an enhancement factor of 4.4 on going from  $L^3$  to  $L^4$ , reaching a  $\mu\beta_{1,907}$  value much higher than that of the related stilbazole  $L^2$ .

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**Table 1** Experimental electronic spectra, EFISH  $\mu\beta_{1.907}$  and  $\mu$  values of  $\mathbf{L}^3$ ,  $\mathbf{L}^4$  and related compounds

Compound	$\lambda/\mathrm{nm}$ [ $\varepsilon/\mathrm{M}^{-1}~\mathrm{cm}^{-1}$ ] <sup>a</sup>	$(10^{-48} \text{ esu})^{a,b}$	$\frac{\mu^c \left(\mu_{\text{theor}}\right)}{(10^{-18} \text{ esu})}$	$\beta_{1.907}$ (10 <sup>-30</sup> esu)
$L^1$	417 [46 500] 506 [9160]	48	2.4	$20^d$
L <sup>2</sup>	381 <sup>6</sup>	223 <sup>6</sup>	$3.7^{6}$	$60^{6}$
L <sup>3</sup>	278 [28 626] 347 [14 397]	430	3.5 (7.6)	$123^d$ (56) <sup>e</sup>
IrL <sup>3</sup>	279 [35 420] 390 [25 670]	620	(16.2)	$(38)^{e}$
$L^4$	305 [41 462] 361 [17 179]	1800	4.2 (8.0)	$(224)^{e}$
IrL <sup>4</sup>	272 [34 541] 421 [12 737]	-2310	(16.9)	$(-137)^{e}$
L <sup>4</sup> MeI	272 [39 886] 285 [37 869] 315 [19 045] 364 [14 386] 473 [26 523]	1820	(18.9)	(96) <sup>e</sup>

<sup>*a*</sup> In CHCl<sub>3</sub> at 10<sup>-4</sup> M with an incident radiation of 1.907  $\mu$ m. <sup>*b*</sup> The error on EFISH measurements is ±10%. <sup>*c*</sup> Experimental  $\mu$  obtained by the Guggenheim method<sup>10</sup> in CHCl<sub>3</sub>; the error is ±1 × 10<sup>-18</sup> esu. <sup>*d*</sup> By using experimental  $\mu$ . <sup>*e*</sup> By using theoretical  $\mu$ . <sup>*f*</sup> There is a band tail at *ca*. 400 nm.

Surprisingly, contrarily to what was observed in the case of stilbazolium salts,<sup>6b,11</sup> methylation of the pyridine ring of  $L^4$  does not affect strongly the second order NLO response although there is a relevant red shift ( $\Delta \lambda_{max} = 112$  nm) of the ILCT transition. This effect might be related to a different orientation of the dipole moment in the two salts, which determines the overall EFISH response. Coordination of  $L^4$  to "Ir(CO)<sub>2</sub>Cl" leads to a slight increase (enhancement factor = 1.2) of the absolute  $\mu \beta_{1.907}$  value which, unexpectedly, becomes negative. This behaviour is in contrast with that observed upon coordination of  $L^2$  to the same Ir(1) moiety where  $\mu \beta_{1.907}$  is enhanced but remains positive, being dominated by an ILCT transition.<sup>5</sup> It is worth noting that the very high  $\mu \beta_{1.907}$  values of  $L^3$  and  $L^4$  are due to large  $\beta_{1.907}$  values since their dipole moments are quite similar to that previously reported<sup>5</sup> for  $L^2$ .

Furthermore of particular interest is the unexpectedly very high thermal stability of  $L^4$  measured by Differential Scanning Calorimetry (DSC) (Fig. 2). The sample was subjected to three reversible cycles of melting and crystallization with a heating rate of 5 °C min<sup>-1</sup> under nitrogen atmosphere. As it is evident

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from the DSC spectrum, the melting and the crystallization peaks show similar intensities within the three cycles thus indicating that there is neither sublimation nor partial decomposition of the product. The decomposition temperature of 434 °C was determined by further heating of the sample over its melting temperature. The very high thermal stability, combined with its high NLO activity, makes  $L^4$  particularly appealing from an applicative point of view. As we have already mentioned NLO chromophores should be highly resistant to thermal degradation for a practical use in electro-optic systems, where temperatures higher than 300 °C are required to process and assemble NLO-active materials into devices.<sup>12</sup>

In order to get insight on the peculiar second order NLO properties of the newly synthesized systems, we carried out DFT (Density Functional Theory) and Time Dependent DFT (TDDFT) computational studies on  $L^3$  and  $L^4$  by means of Gaussian 03 (G03) program package.<sup>13</sup>

The molecular structures of  $L^3$ ,  $L^4$ ,  $IrL^3$  and  $IrL^4$  have been optimized in CHCl<sub>3</sub> using B3LYP exchange-correlation functional, a 6-31G\* basis set for C, H and N and Lanl2DZ basis set with related pseudo-potentials for Ir and Cl. The solvation effects have been included by means of a Polarizable Continuum Model (PCM) as implemented in G03.14 The geometry optimization of  $L^3$  and  $L^4$  provides very similar molecular structures characterized by planarity of the azaphenanthrene and azachrysene and similar CC and CN bond distances (see ESI<sup>†</sup>). The N(butyl)<sub>2</sub> moiety goes out of the plane of the anellated rings by ca.  $6^{\circ}$  for both species, with the two butyl groups oriented in opposite directions. We computed similar dipole moments both in vacuo, 5.2 and 5.6 D, and in CHCl<sub>3</sub> solution, 7.6 and 8.0 D, for  $L^3$  and  $L^4$ , respectively. The optimized IrL<sup>3</sup> and IrL<sup>4</sup> are square planar complexes with the L<sup>3</sup> and  $L^4$  twisted with respect to the square planar coordination plane, by 54° and 65°, respectively (see ESI<sup>+</sup>). From the analysis of the electronic structure of  $L^3$  and  $L^4$  it emerges that the highest occupied orbitals (HOMOs) are of  $\pi$  character and show similar energies and similar charge distribution apart from an increased delocalization due to the presence of four rings in  $L^4$ . The  $L^4$ lowest unoccupied orbitals (LUMOs) of  $\pi^*$  character are, on the other hand, the result of different carbon and nitrogen p orbital combinations with respect to  $L^3$  (see ESI<sup> $\dagger$ </sup>), which is reflected by their different energies. The  $L^4$  LUMO is at lower energy with respect to that of  $L^3$  as a consequence of the increased  $\pi$ -conjugation, leading to a 0.38 eV decrease of the L<sup>4</sup> HOMO-LUMO gap. We then simulated the absorption spectra of both systems by computing the lowest 20 singlet-singlet excitations, the comparison between the experimental and computed spectra of  $L^3$  and  $L^4$  is reported in Fig. 3. The agreement between theory and experiment is good, in the  $L^3$  case we are able to reproduce all the features of the experimental absorption spectrum, and only the lowest absorption band is computed slightly red-shifted by 0.16 eV. For L<sup>4</sup>, the calculated intensity distribution does only qualitatively compare with the experimental absorption bands, even though also in this case the computed transitions nicely fit with the main experimental features, see Fig. 3.

The absorption spectrum of  $L^3$  is characterized by a low-energy band computed at 332 nm and one more intense band at 277 nm, to be compared with the experimental bands at 347 and 287 nm. The lowest transition is calculated as being





Fig. 3 Comparison between theoretical (blue line) and experimental (red line) spectra of  $L^3$  and  $L^4$  with related computed hyperpolarizabilities through a SOS approach in the insets.

a weak HOMO–LUMO excitation at 361 nm, of  $\pi$ – $\pi$ \* character. The transition giving the band at 332 nm is essentially from the HOMO to the LUMO+1 and has charge-transfer character, going from the donor dibutylamino part of the ligand to the acceptor pyridine ring. The absorption band computed at 277 nm is constituted by two main transitions of global  $\pi$ – $\pi$ \* character. The experimental absorption spectrum of L<sup>4</sup> has a quite similar shape with respect to that of L<sup>3</sup>, even though it is red-shifted and it shows the appearance of a band tail at *ca*.400 nm. We computed bands at 353 nm and 312 nm to be compared to the experimental absorption bands at 361 nm and 305 nm.

The band at 353 nm is a charge-transfer transition essentially of HOMO-LUMO+1 character. We computed a weak lower energy transition at 392 nm of charge transfer character, corresponding to the HOMO-LUMO transition, related to the low energy experimental feature and more intense than that of the  $L^3$  ligand, consistently with the experimental spectra. To gain insight into the electronic transitions responsible for the observed quadratic hyperpolarizability  $\beta$  of L<sup>3</sup> and L<sup>4</sup>, we performed a Sum Over States (SOS) analysis.<sup>15</sup> The results, reported as insets of Fig. 3, show in both cases a converged positive value in agreement with the experimental evidence. The ratio of the computed  $\beta$  values of L<sup>3</sup> and L<sup>4</sup> is 2.2, which is in line with the experimental increase of the EFISH  $\beta$  value observed passing from  $L^3$  to  $L^4$ . This increase is mainly due to the red-shifted absorption spectrum of  $L^4$ , related to the HOMO-LUMO gap decrease. Indeed, according to the two-level model,  $\beta$  increases quadratically with decreasing the energy of the electronic transitions. From an in depth analysis of calculated SOS  $\beta$  values, we noticed that the largest contributions to  $\beta$  are provided for both  $L^3$  and  $L^4$  by ILCT transitions. Visualization of the charge transfer processes originating the NLO response is reported in the ESI.<sup> $\dagger$ </sup> We found that for  $L^4$  the lowest energy transition considerably contributes to the calculated  $\beta$ , for L<sup>3</sup> such excited state has almost vanishing contribution to  $\beta$ , due to its higher energy and considerably lower transition dipole moment.

Moreover, at higher energy the 314 nm transition is that mainly responsible for the converged higher  $\beta$  value of  $L^4$  compared to  $L^3$ , indeed the same state in  $L^3$  is characterized by a lower transition dipole moment.

In conclusion  $L^3$  and  $L^4$  are particularly appealing because of their notable values of EFISH  $\mu\beta_{1.097}$  that are likely due to the absence of photorotamerism and photoisomerism processes operating in the corresponding compounds  $L^1$  and  $L^2$ respectively. These properties together with the absence of isolated double bonds ensure the astonishingly high thermal stability of  $L^4$  that makes it a good candidate for the preparation of materials characterized by high second harmonic generation properties. We believe that, because of their relevant technological interest, the results here reported can constitute a springboard for the design of other NLO chromophores of the same family such as 11-*N*,*N*-dibutylamino-3-azapicene and 12-*N*,*N*-dibutylaminobenzo[*m*]-3azapicene with 5 and 6 rings respectively.

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