Cyclometallated iridium(III) complexes with substituted 1,10-phenanthrolines: a new class of highly active organometallic second order NLO-phores with excellent transparency with respect to second harmonic emission

Claudia Dragonetti,[a] Stefania Righetto,[a] Dominique Roberto,*[ab] Renato Ugo,[a] Adriana Valore,[a] Simona Fantacci,[c] Antonio Sgamellotti[c] and Filippo De Angelis*[c]

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[Ir(ppy)$_2$(5-R-1,10-phen)][PF$_6$] (ppy = cyclometallated 2-phenylpyridine, phen = phenanthroline, R = H, Me, NMe$_2$, NO$_2$) and [Ir(ppy)$_2$(4-R′,7-R′-1,10-phen)][PF$_6$] (R′ = Me, Ph) complexes are characterized by one of the highest second order NLO response (measured by the EFISH technique) reported for a metal complex, mainly due (as suggested by a theoretical SOS-TDDFT investigation) to MLCT processes from the ppy–Ir based moiety acting as donor push system to π* orbitals of phen, acting as an acceptor pull system; the good transparency to the second harmonic emission renders these NLO-phores appealing as building blocks for molecular materials with second harmonic generation.

Molecular chromophores with second order non linear optical (NLO) properties have attracted increasing interest for their potential as building blocks of NLO materials for optical telecommunications and optical data storage.[1] In particular, organometallic and coordination NLO-phores may offer additional flexibility, when compared to classical push–pull organic NLO-phores, by introducing either a perturbation of the electronic properties of the organic ligand NLO-phores or adding new NLO active electronic charge-transfer transitions with energies and intensities that are tunable by virtue of the nature, oxidation state and coordination sphere of the metal centre.[2] Thus, coordination to a metal centre of organic NLO-phores such as stilbazoles, bipyridines, phenanthrolines and terpyridines bearing a NR$_2$ donor group produces a significant increase in their quadratic hyperpolarizability, due to a red-shift of the intraligand charge-transfer transition (ILCT). In comparison, the second order NLO response of metal complexes carrying the NLO-phores bearing an electron acceptor substituent is mainly controlled by metal to ligand charge-transfer transitions (MLCT).[2a,2e] The presence of various charge-transfer processes between an active NLO π delocalised ligand such as for terpyridine and a metal centre is a way to produce tunable and significant second order NLO responses.[2e]

Recently ionic cyclometallated Ir(III) complexes with chelated π delocalised ligands such as bipyridines[3] or phenanthrolines[4] have shown interesting photoemissive properties with potential applications in electroluminescent devices. Some recent Density Functional Theory (DFT) investigations on this kind of new luminescent Ir(III) complex[3,4] have shown that the HOMO (highest occupied molecular orbital) is mainly an antibonding combination of Ir (t_{2g}) orbitals and π orbitals of the cyclometallated ligand while the LUMO (lowest unoccupied molecular orbital) is π* antibonding orbital of the π delocalised chelated ligand (bipyridine or phenanthroline). Therefore transitions between HOMO and LUMO have a significant charge-transfer character so that these complexes could be new NLO-phores with the cyclometallated moiety acting as donor towards the π delocalised chelated ligand acting as acceptor. This hypothesis prompted us to investigate the second order NLO response of [Ir(ppy)$_2$(5-R-1,10-phen)][PF$_6$] (R = H, Me, NMe$_2$, NO$_2$) and [Ir(ppy)$_2$(4-R′,7-R′-1,10-phen)][PF$_6$] (R′ = Me, Ph), that we recently investigated for their luminescent properties.[4c] The quadratic hyperpolarizability of these complexes was measured by the EFISH (Electric Field Induced Second Harmonic generation) technique[5] working with a non resonant 1907 nm incident wavelength in a low polarity solvent like CH$_2$Cl$_2$, which allows by ion-pairing the extension of the use of this technique to ionic compounds.[2e] It turned out that these Ir(III) complexes show a large negative second order NLO response (Table 1, $\mu\beta_{1907}$ ranging from -1270 to -2230×10^{-30} D cm^5 esu^{-1}). Most notably, they do not show strong absorptions above 450 nm (Table 1; Fig. 1 and 2) so that a significant second harmonic generation may be obtained without any significant cost in transparency towards the strength of its emission, a crucial aspect in the design of NLO-phores.[1] Transitions below 350 nm are reported to be MLCT transitions from a Ir(III) based orbital to the π* antibonding orbitals of the phen.[3,4] In accordance, the highest absolute $\mu\beta_{1907}$ value is for the complex carrying the phen with the strong electron-withdrawing group NO$_2$, as expected for increased acceptor properties of the π* antibonding orbitals of the phen. Equally important, an increase in the π-delocalisation of the phen ligand leads to a positive effect on the second order NLO response as evidenced by comparing [Ir(ppy)$_2$(4-Ph,7-Ph-1,10-phen)][PF$_6$] and [Ir(ppy)$_2$(4-Me,7-Me-1,10-phen)][PF$_6$] (Table 1). Strangely enough, in these NLO-phores, a phen with a strong electron donor group like NMe$_2$, as

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[a] *Dip CIMA, Università di Milano, UdR dell'INSTM di Milano, via Venezian 21, I-20133, Milano, Italy. E-mail: dominique.roberto@unimi.it*
[b] *ISTM-CNR, via Venezian 21, I-20133, Milano, Italy*
[c] *ISTM-CNR, c/o Dip. di Chimica, via Elce di Sotto 8, I-06123, Perugia, Italy. E-mail: filippo@thch.unipg.it*

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Table 1 Electronic absorption spectra and EFISH $\mu\beta_{1907}$ values obtained in CH_2Cl_2 solution of various cyclometallated Ir(III) complexes

Compound		Absorption maxima (nm) [$\varepsilon/M^{-1}\ cm^{-1}$]^a	EFISH $\mu\beta_{1.907}{}^b/10^{-30}$ D cm^5 esu^{-1}
$[Ir(ppy)_2(5\text{-}R\text{-}1,10\text{-}phen)][PF_6]$	R = Me	255 (sh), 268 [60300], 333 (sh), 377 [8070]^c	−1565
	R = NMe_2	252 (sh), 264 [81400], 334 (sh)^c	−1330
	R = NO_2	254 (sh), 264 [86900], 378 [12400]^c	−2230
	R = H	252 (sh), 264 [58500], 377 [9130]^c	−1270
$Ir(ppy)_2(4\text{-}R',7\text{-}R'\text{-}1,10\text{-}phen)][PF_6]$	R′ = Ph.	269 [51300], 282 (sh), 385 [9020]^c	−1997
	R′ = Me	255 (sh), 265 [73000], 375 (sh)^c	−1454

^{a} Ref. 4*c*. ^{b} measurements carried out in CH_2Cl_2 at 10^{-3} M; the error of the EFISH measurements is ±10%. ^{c} There is a band tail above 400 nm up to *ca.* 500–550 nm.

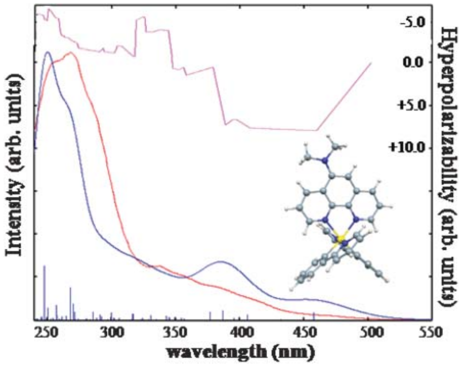

Fig. 1 Experimental (CH_2Cl_2; red) and calculated (blue) absorption spectra and various contributions to the computed quadratic hyperpolarizability (magenta) for the complex with NMe_2.

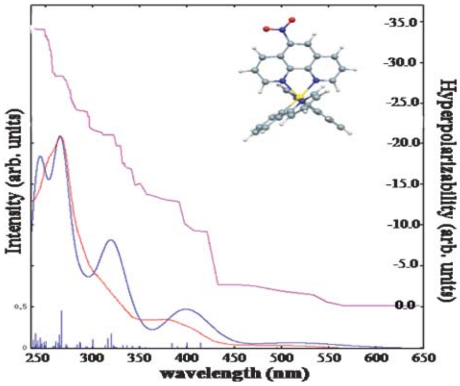

Fig. 2 Experimental (CH_2Cl_2; red) and calculated (blue) absorption spectra and various contributions to the computed quadratic hyperpolarizability (magenta) for the complex with NO_2.

in $[Ir(ppy)_2(5\text{-}NMe_2\text{-}1,10\text{-}phen)][PF_6]$, still acts as a pull acceptor site.

To confirm our hypothesis on the electronic factors governing the second order NLO response of these NLO-phores, we performed DFT calculations, taking as framework a structure with the metal placed in the origin and the phen oriented along the *z* direction.[6] Such a DFT approach is described in detail in our work on the luminescent properties of these Ir(III) complexes.[4c] Here we have extended the theoretical investigation to the evaluation of the origin and strength of their second order NLO properties. Therefore for cationic $[Ir(ppy)_2(5\text{-}R\text{-}1,10\text{-}phen)]^+$ (R = NMe_2, NO_2) we calculated and characterized the excited states and therefore the origin of their absorption spectrum and second order NLO properties by TDDFT calculations.[6]

For both species the HOMO is, as expected,[3,4] an antibonding combination of $Ir(t_{2g})$ and ppy(π) orbitals followed, in order of decreasing energy, by additional combinations of $Ir(t_{2g})$ and ppy(π) orbitals, with decreasing ppy character.[4c] In the presence of a NMe_2 group, the increased electron donation on the phen leads to a destabilization of one phen π-bonding orbital, which shifts at higher energy as HOMO-1 just below the HOMO. For this latter complex, the LUMO and the LUMO + 1 are a couple of phen π* orbitals, while at higher energies the LUMO + 2 and LUMO + 3 are a couple of ppy π* orbitals. In the complex with a phen carrying a NO_2 group, these two phen π* LUMOs strongly mix with the NO_2 antibonding orbital, producing a strong stabilization of all the phen π* orbitals, which leads to reduction by more than 1 eV of the HOMO–LUMO gap compared to the complex with the phen carrying a NMe_2 group. The lowest 85 singlet–singlet excitation energies, transition dipole moments, oscillator strengths and excited state dipole moments of the complexes carrying a phen with NMe_2 and NO_2 groups have been calculated by TDDFT,[6] thus allowing the simulation of the absorption spectra up to below 250 nm and the determination of the excited states responsible of the second order NLO properties by means of the Sum Over States (SOS) approach.[8] In Fig. 1 and 2 the experimental and computed absorption spectra of the two complexes show a good agreement, in terms of absolute band positions and relative intensities, especially taking into account the rather limited dimensions of the basis set and the neglect of spin–orbit coupling in the excitation energies. For the complex with a NMe_2-substituted phen, the presence of a high-lying phen π bonding HOMO − 1 translates into a ILCT transition with sizable intensity ($f = 0.082$) calculated at 458 nm, originating from the high energy phen HOMO − 1 to the phen π* LUMO + 1. A significant ($f = 0.063$) MLCT transition from the Ir–ppy based HOMO to the ppy π* LUMO + 2 at 406 nm is followed at higher energy by strong ($f = 0.108$ and 0.096) ILCT and MLCT transitions at 387 and 377 nm, respectively, corresponding to the significant band tail extending above 400 nm in the experimental spectrum (Fig. 1). For the complex with the NO_2-substituted phen, a considerable red-shift of the absorption spectrum is observed. The low energy spectral portion is characterized by transitions of low intensity ($f = 0.012$ and 0.016) at 544 and 495 nm, both corresponding to MLCT excitations from the HOMOs to the LUMO of mixed phen–NO_2 π* character. At higher energy (414, 400 and 384 nm) three (f = 0.066, 0.067 and 0.059) MLCT transitions from the Ir–ppy based HOMOs to the phen π* LUMO + 1, the ppy π* LUMO + 3 and again the phen π* LUMO + 1 respectively are calculated, corresponding to the 378 nm absorption of the experimental spectrum (Fig. 2).

Finally we calculated the contribution of each excited state to the static quadratic hyperpolarizability by means of the SOS method.[8,9] In Fig. 1 and 2 the contribution to the quadratic hyperpolarizability as a function of the excited state wavelength of the various transitions for the Ir(III) based NLO-phores carrying NMe_2– and NO_2–phen is reported. For the complex with a NO_2 group, the quadratic hyperpolarizability is exclusively the sum of negative contributions, resulting in an overall negative value, as experimentally found. For the complex with a NMe_2 group, however, counteracting positive and negative contributions to the quadratic hyperpolarizability are calculated, the latter determining the negative sign of the converged final value, as experimentally found. In agreement with experimental evidence, the calculated quadratic hyperpolarizability for the complex with a NMe_2 group is *ca.* 5 times lower than that calculated for the corresponding complex with a NO_2 group. Indeed, considering dipole moments calculated for the NMe_2 (12.6 D) and NO_2 (4.1 D) cationic complexes, we derive $\beta_{1.907}$ experimental values of -106 and -543×10^{-30} D cm^5 esu^{-1}, respectively.

For the complex with a NMe_2 group, the largest positive contributions to the quadratic hyperpolarizability are due to the ILCT transitions at 458–387–316 nm, while the largest negative contributions are due to the MLCT transitions at 377–343 nm. The opposite sign of the ILCT and MLCT contributions derives from the positive or negative difference between ground and excited states dipole moments.[11] In chemical terms the ILCT contribution is due to a charge-transfer from a π phen orbital involving the NMe_2 group to a π* antibonding of the phen ring, while the MLCT contribution is due to a charge-transfer from a ppy–Ir based HOMO orbital to π* levels of the phen or of the ppy. In the case of the Ir(III) complex with a NO_2 group, on the other hand, the largest contributions to the quadratic hyperpolarizability arise from transitions to the π* phen calculated at 414 and 384 nm, both of MLCT character with a large variation of excited state dipole moment compared to that of the ground state, with smaller contributions deriving from other transitions to the π* phen calculated at 544 and 495 nm also of MLCT character. For both complexes, MLCT transitions involving the π* ppy orbitals, although giving rise to significantly intense contributions to the absorption spectrum, do not contribute too much to the second order NLO response due to the negligible variation of the excited state dipole moment compared to the ground state one.

In conclusion, these Ir(III) complexes are a new kind of second order NLO-phores with a response mainly controlled by MLCT transitions from the HOMOs ppy–Ir based donor orbital of the cyclometallated moiety to the LUMOs π* acceptor orbitals of the phen, independently from the donor or acceptor properties of the phen substituent. These new ionic NLO-phores are characterized by a strong second order NLO response. Their negative $\mu\beta_{1.907}$ values are, as absolute values, much higher than those, also measured by EFISH, of ionic NLO-phores such as quaternary stilbazolium salts.[12] Notably, this large and tunable response is obtained at no significant cost of transparency with respect to the second harmonic emission, even working with a 1065 nm incident wavelength. We are extending our investigation to other cyclometallated Ir(III) moieties or other chelated π delocalized ligands, in order to tune the NLO response by acting on the energy of HOMO orbitals (cyclometallated Ir(III) moiety) or of LUMO orbitals (π delocalized chelated ligand).

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