Novel ruthenium(II) complexes with substituted 1,10-phenanthroline or 4,5-diazafluorene linked to a fullerene as highly active second order NLO chromophores†

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Various Ru(II) complexes with substituted 1,10-phenanthroline or 4,5-diazafluorene are characterized by a good to very large second order NLO response, as determined by EFISH. Among these complexes, [Ru(9-fulleriden-4,5-diazafluorene)$(PPh_3)_2Cl_2$] is particularly appealing due to its huge second-order NLO response and its transparency to the second harmonic generation. The structure of *cis*-Cl,*trans*-PPh_3-[Ru(5-NO_2-1,10-phen)$(PPh_3)_2Cl_2$)] was determined by single-crystal X-ray diffraction.

Introduction

Coordination complexes with second-order non-linear optical (NLO) properties are of particular interest as new molecular materials for electro-optical and optical applications.[1] In particular, the presence of a metal centre can offer electronic flexibility by introducing charge-transfer transitions, metal to ligand (MLCT) or ligand to metal (LMCT), usually at low energy and of relatively high intensity, tunable by virtue of its nature, oxidation state and coordination sphere, or by shifting to lower energy the internal charge transfer transitions (ILCT) of organic push-pull ligands.[2]

Recently, we reported[3] that various cationic cyclometallated Ir(III) complexes with a substituted 1,10 phenanthroline show one of the highest second-order NLO responses (measured as $\mu\beta_{1.907}$ by the Electric Field Induced Second Harmonic generation (EFISH) method)[4] reported for metal complexes. Such a high response was attributed mainly to a MLCT process from the orbitals of the cyclometallated Ir(III) system, acting as the donor, to the π* orbitals of the phenanthroline ligand, acting as the acceptor system.[3]

These findings and the observation that the presence of a redox-active metal centre such as Ru(II) could provide a redox-switchable modulation of the NLO responses,[5] prompted us to investigate the second-order non linear optical properties of some neutral Ru(II) complexes with substituted 1,10-phenanthroline or 4,5-diazafluorene. In particular it was appealing to investigate the effect on the π* acceptor properties of the 4,5-diazafluorene ligand of a substituent such as the highly polarisable and non conventional electron withdrawing C_{60}-fullerene system.[6] Therefore we investigated 4,5-diazafluorene as the ligand to which the C_{60} unit is connected through a cyclopropane group, which allows a facile electronic communication between the fullerene and the ligand (periconjugation).[7]

Results and discussion

We prepared, characterized and investigated the second-order NLO properties of all of the Ru(II) complexes reported in Fig. 1.

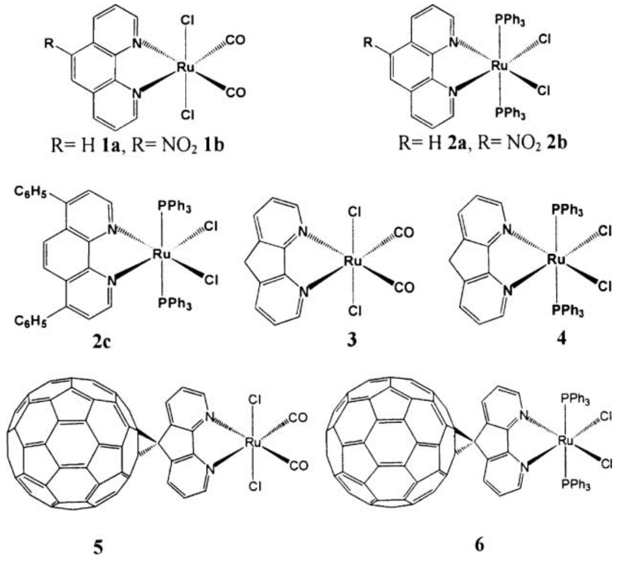

Fig. 1 General structure of the investigated Ru(II) NLO chromophores.

The known complexes *trans*-Cl,*cis*-CO-[Ru(1,10-phen)$(CO)_2Cl_2$][8] (**1a**, phen = phenanthroline) and *cis*-Cl,*trans*-PPh_3-[Ru(1,10-phen)$(PPh_3)_2Cl_2$)][9] (**2a**) and the new complexes *trans*-Cl,*cis*-CO-[Ru(5-NO_2-1,10-phen)$(CO)_2Cl_2$)] (**1b**), *cis*-Cl,*trans*-PPh_3-[Ru(5-NO_2-1,10-phen)$(PPh_3)_2Cl_2$)] (**2b**) and *cis*-Cl,*trans*-PPh_3-[Ru(4,7-diphenyl-1,10-phen)$(PPh_3)_2Cl_2$] (**2c**) were prepared by reaction of $[Ru(CO)_2Cl_2]_n$ or $[Ru(PPh_3)_3Cl_2]$ with the substituted 1,10-phenanthroline following the synthetic procedure reported

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in the literature[10–11] (see Experimental). The new complexes *trans*-Cl,*cis*-CO-[Ru(4,5-diaz)$(CO)_2Cl_2$] (**3**, diaz = diazafluorene), *cis*-Cl,*trans*-PPh_3-[Ru(4,5-diaz)$(PPh_3)_2Cl_2$)] (**4**), *trans*-Cl,*cis*-CO-[Ru(9-fulleriden-4,5-diaz)$(CO)_2Cl_2$] (**5**) and *cis*-Cl,*trans*-PPh_3-[Ru(9-fulleriden-4,5-diaz)$(PPh_3)_2Cl_2$] (**6**) were prepared in the same way by reaction with 4,5-diazafluorene[12] or 9-fulleriden-4,5-diazafluorene.[13] The geometry of the various isomers was established on the basis of IR and NMR evidence (see Experimental).[14] The structure of complex **2b** was determined by single-crystal X-ray diffraction and has been shown to contain the octahedral Ru(II) ion surrounded by two *trans* triphenylphospine ligands, two *cis* chloride ions and the phenanthroline ligand in the equatorial plane of the octahedron (See Fig. 2).

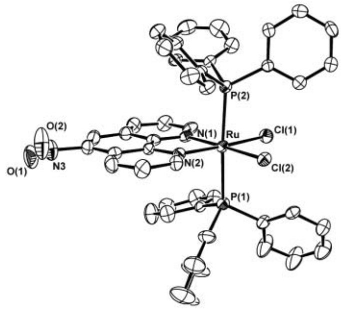

Fig. 2 ORTEP view of Complex **2b**. Displacement ellipsoids are drawn at 30% probability.

The trends of the electronic spectra of the prepared complexes are, as expected, similar to those reported for this kind of complex[14] (Table 1). In the case of **1a**, **1b**, and **3**, with two *cis* CO ligands, there is a band below 350 nm typical of internal pπ → pπ* transitions of the aromatic system of 1,10-phenanthroline or 4,5-diazafluorene together, at lower energy, with a broad weak shoulder (366–380 nm). A relatively strong band (459–507 nm) is typical of complexes **2a**, **2b**, **2c**, and **4**, with two *trans* phosphine ligands. These absorptions at relatively low energy are in the range reported for dπ → pπ* MLCT transitions from Ru(II) to pyridine, bipyridine or phenanthroline ligands.[10,14] When a C_{60} fullerene moiety is linked to the 4,5-diazafluorene ligand (**5** and **6**), the band below 350 nm becomes strong due to the presence of the fullerene moiety,[15] while the band at around 479–482 nm is, as for **1a** and **2a**, **1b** and **2b**, **3** and **4**, much stronger in the presence of two phosphines (**6**) instead of two CO (**5**) (Table 1).

Table 1 Absorption maxima and $\mu\beta_{1.907}$ values of Ru(II) complexes

Complex	Absorption maxima[a]/ nm [ε/M^{-1} cm^{-1}]	EFISH $\mu\beta_{1.907}{}^{a,b}$/10^{-48} esu
1a	272 [8400] 370 (sh, w, br)	−696
1b	273 [25 500] 380 (sh, w, br)	−730
2a	271 [39 500] 329 (sh, vw), 459 [4900]	−1585[c]
2b	273 [35 100] 336 (sh, vw), 507 [5000]	−2210[c]
2c	276 [33 700] 345 (sh, vw), 475 [10 200]	−2030[c]
3	319 [11 200], 366 (sh, w)	−600
4	272 [27 300], 355 (sh, w), 474 [3300]	−1040
5	257 [104 800] 322 (sh, w), 479 [2200]	−2800
6	260 [395 800] 325 (sh, w), 482 [10 600]	−3435

[a] In DMF. [b] By using 10^{-3}M solutions, the error of EFISH measurements is ±10%. [c] Similar values are obtained working in $CHCl_3$ at the same concentration.

The second-order NLO response was determined as $\mu\beta_{1.907}$ values by means of the EFISH technique[4] working in DMF solution with a non resonant incident wavelength of 1.907 µm. As shown in Table 1, all complexes show a negative good to large value of $\mu\beta_{1.907}$ (-600 to -3435×10^{-48} esu). The negative sign of $\mu\beta_{1.907}$ is in agreement with a reduction of the dipole moment in the excited state due to MLCT transitions, which dominate the second order NLO response.[2]

It must be noticed that the second-order NLO response of complexes with 1,10-phenanthroline as the chelating ligand is much higher for complexes **2a**, **2b** and **2c**, carrying two triphenylphosphines instead of two CO (**1a**, **1b**) as ancillary ligands. It is similar in the case of complexes with 4,5-diazafluorene as the chelating ligand (compare **3** with **4** and **5** with **6**). The rather low second-order NLO response of complexes with two CO ligands, such as **1a**, **1b** and **3** ($\mu\beta_{1.907}$ from -600×10^{-48} esu to -730×10^{-48} esu), appears to be quite independent of the nature of the chelating ligand (4,5-diazafluorene or 1,10-phenanthroline).

The second-order NLO response of complexes **1a**, **1b** and **3** is reasonably attributed mainly to MLCT transitions from the metal to the π* aromatic system of the 1,10-phenathroline or of the 4,5-diazafluorene. The relevant increase (by a factor of 2–3) of the second-order NLO response observed upon substitution of the "$Ru(CO)_2Cl_2$" moiety by "$Ru(PPh_3)_2Cl_2$", as in the case of **2a**, **2b**, **4**, could be explained by an increase of $\beta_{1.907}$ due to an increase of the electronic density and consequently of the donor properties of the Ru centre involved in the MLCT transitions controlling the quadratic hyperpolarizability $\beta_{1.907}$. The determination of the dipole moment of **1b** and **2b** by the Guggenheim method[16] confirms this suggestion since $\beta_{1.907}$ increases by a factor of 3.8 moving from **1b** ($\beta_{1.907} = -77 \times 10^{-30}$ esu, $\mu = 9.4 \times 10^{-18}$ esu) to **2b** ($\beta_{1.907} = -291 \times 10^{-30}$ esu, $\mu = 7.6 \times 10^{-18}$ esu).

Differently from **1a** and **1b**, a significant enhancement of the absolute value of $\mu\beta_{1.907}$ is observed on moving from **2a** to **2b** ($\mu\beta_{1.907} = -1585 \times 10^{-48}$ and -2210×10^{-48} esu, respectively). Such a trend was previously reported for the cationic complexes of Ir(III), [Ir(phenylpyridine)$_2$(5-R-1,10-phen][PF_6][3] and was attributed to an increase of the acceptor properties of the π* orbitals of the 1,10-phenanthroline bearing the NO_2 group and therefore to a more facile MLCT transition. Moreover, as for the case of these cationic Ir(III) complexes,[3] the second-order NLO response of **2c** carrying the more polarisable 4,7-diphenyl-1,10-phen ligand ($\mu\beta_{1.907} = -2030 \times 10^{-48}$ esu) is high and comparable to that of **2b** ($\mu\beta_{1.907} = -2210 \times 10^{-48}$ esu).

It is relevant that the presence of a fullerene group on the 4,5-diazafluorene ligand leads to a huge increase of the $\mu\beta_{1.907}$ value (from -600×10^{-48} esu for **3** to -2800×10^{-48} esu for **5**). Moreover, as when comparing **1a** and **2a**, substitution of the "$Ru(CO)_2Cl_2$" (**5**) by the "$Ru(PPh_3)_2Cl_2$" (**6**) moiety affords an additional increase of the $\mu\beta_{1.907}$ value (-3435×10^{-48} esu).

Remarkably, the high absolute value of $\mu\beta_{1.907}$ of **5** and **6**, when compared to that of **3** and **4** (Table 1), clearly evidences the important role of the fullerene group in enhancing the NLO response. This effect cannot be explained by a particularly strong electron-accepting ability of the fullerene (there is only a small red shift in the MLCT band on going from **4** to **6**) but can be attributed to its large polarizability.

As pointed out, in the case of the Ru(II) complexes **2a**, **2b** and **2c** with various substituted 1,10-phenanthrolines, the strong increase of the second-order NLO response is characterized by the presence of a rather strong absorption band in the range 459–507 nm, suggesting that this latter is a MLCT transition at relatively low energy, thus producing a relevant effect on the second-order NLO response. This suggestion is supported by the evidence that the increase of the second-order NLO response moving from **2a** to **2c** occurs with a parallel red shift of this band (Table 1). This new band could be attributed to a significant red-shift of the dπ → pπ* MLCT band involving the 1,10-phenanthroline π* system due to the increased electronic density on the Ru(II) centre, produced by coordination of two phosphines. However in complexes **5** and **6**, with a fullerene substituent on the π* acceptor chelated ligand, there is always a band at about 480 nm, independent of whether the two phosphines are present, although when they are present these latter ligands increase the intensity of this band about 4–5 times (Table 1). A TD-DFT investigation is underway to give a definite answer to the electronic origin of the second-order NLO response in these interesting Ru(II) NLO chromophores.

Experimental

Synthesis and characterization of the various Ru(II) complexes

General information. All reagents and solvents were purchased from Sigma–Aldrich.

^{1}H and ^{31}P NMR spectra were obtained on a Bruker Avance DRX 400 MHz instrument. Elemental analyses were carried out in the Dipartimento di Chimica Inorganica, Metallorganica e Analitica "Lamberto Malatesta" of the Milan University. Dipole moments, μ, were measured in $CHCl_3$ using a WTW-DM01 dipole meter (dielectric constant) coupled with a RX-5000 ATAGO Digital Refractometer (refractive index) according to the Guggenheim method.[16] All reactions were carried out under a nitrogen atmosphere. $[Ru(CO)_2Cl_2]_n$ and $[Ru(PPh_3)_3Cl_2]$ were prepared as described in the literature.[9,10]

The known complexes *trans*-Cl,*cis*-CO-$[Ru(1,10\text{-phen})(CO)_2Cl_2]$ (**1a**) and *cis*-Cl,*trans*-PPh_3-$[Ru(1,10\text{-phen})(PPh_3)_2Cl_2)]$ (**2a**) were also prepared as previously reported.[8,9] The new complex *trans*-Cl,*cis*-CO-$[Ru(5\text{-}NO_2\text{-}1,10\text{-phen})(CO)_2Cl_2)]$ (**1b**) was prepared with the same procedure as described below in the case of **1a**, whereas the complexes *cis*-Cl,*trans*-PPh_3-$[Ru(5\text{-}NO_2\text{-}1,10\text{-phen})(PPh_3)_2Cl_2)]$ (**2b**) and *cis*-Cl,*trans*-PPh_3-$[Ru(4,7\text{-diphenyl-}1,10\text{-phen})(PPh_3)_2Cl_2]$ (**2c**) were prepared as described in the case of **2a**.[10,11]

The new complexes *trans*-Cl,*cis*-CO-$[Ru(4,5\text{-diaz})(CO)_2Cl_2]$ (**3**, diaz = diazafluorene), *cis*-Cl,*trans*-PPh_3-$[Ru(4,5\text{-diaz})(PPh_3)_2Cl_2]$ (**4**), *trans*-Cl,*cis*-CO-$[Ru(9\text{-fulleriden-}4,5\text{-diaz})(CO)_2Cl_2]$ (**5**) and *cis*-Cl,*trans*-PPh_3-$[Ru(9\text{-fulleriden-}4,5\text{-diaz})(PPh_3)_2Cl_2]$ (**6**) were prepared similarly using 4,5-diazafluorene[12] or 9-fulleriden-4,5-diazafluorene[13] instead of the 1,10-phenanthroline derivatives. The geometry of the complexes was given on the basis of IR and NMR spectroscopies, according to the literature.[14]

***Trans*-Cl,*cis*-CO-$[Ru(1,10\text{-phen})(CO)_2Cl_2]$ (1a).** The polymeric precursor $[Ru(CO)_2Cl_2]_n$ (76 mg, 0.33 mmol) and the 1,10-phenanthroline ligand (65 mg, 0.36 mmol) were dissolved in 20 mL of degassed CH_3OH and the mixture was heated under reflux. After 1 h the orange solution became cloudy and an orange-yellow powder appeared. The solid was filtered off, washed with hot CH_3OH and Et_2O and dried under vacuum.

Yield: 43%. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 9.96 (d, 2H), 9.02 (d, 2H), 8.39 (s, 2H), 8.20 (m, 2H). IR($CHCl_3$), νCO (cm^{-1}): 2069, 2011. Anal. calcd (found) for $RuC_{14}H_8N_2O_2Cl_2$: C 41.20 (41.33), H 1.97 (1.98), N 6.86 (6.82).

***Trans*-Cl,*cis*-CO-$[Ru(5\text{-}NO_2\text{-}1,10\text{-phen})(CO)_2Cl_2]$ (1b).** Yield: 47%. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 9.69 (dd, 1H), 9.68 (dd, 1H), 9.45 (dd, 1H), 9.02 (s, 1H), 8.82 (dd, 1H), 8.18 (m, 2H). IR($CHCl_3$), νCO (cm^{-1}): 2072, 2014. Anal. calcd (found) for $RuC_{14}H_7N_3O_4Cl_2$: C 37.11 (37.01), H 1.55 (1.56), N 9.27 (9.24).

***Cis*-Cl,*trans*-PPh_3-$[Ru(1,10\text{-phen})(PPh_3)_2Cl_2]$ (2a).** $[Ru(PPh_3)_3Cl_2]$ (328 mg, 0.34 mmol) and the 1,10-phenanthroline ligand (62 mg, 0.34 mmol) were dissolved in 20 mL of degassed CH_2Cl_2 and the mixture was heated under reflux. After 2 h the dark-red solution became cloudy and a brown powder appeared. The solid was filtered, washed with hot CH_3OH and Et_2O and dried under vacuum.

Yield: 56%. ^{1}H-NMR (400 MHz, CD_2Cl_2, 25 °C, TMS): δ (ppm) 8.90 (d, 2H), 7.79 (d, 2H), 7.74 (s, 2H), 7.31 (t, 12H), 7.15 (t, 6H), 7.02 (m, 12H), 6.86 (dd, 2H). ^{31}P-NMR (CD_2Cl_2, 25 °C, TMS): δ (ppm) 24.36 (s, 2P, *trans*-PPh_3). Anal. calcd (found) for $RuP_2C_{48}H_{38}N_2Cl_2$: C, 65.75 (65.90): H 4.37 (4.37), N 3.20 (3.25).

***Cis*-Cl,*trans*-PPh_3-$[Ru(5\text{-}NO_2\text{-}1,10\text{-phen})(PPh_3)_2Cl_2]$ (2b).** Yield: 67%. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 9.23 (d, 1H), 9.13 (d, 1H), 8.63 (s, 1H), 8.47 (d, 1H), 7.85 (d, 1H), 7.32 (m, 11H) 7.12 (t, 6H), 7.03 (m, 13H), 6.89 (m, 2H). ^{31}P-NMR ($CDCl_3$, 25 °C, TMS): δ (ppm) 23.08 (s, 2P, PPh_3). Anal. calcd (found) for $RuP_2C_{48}H_{37}N_3O_2Cl_2$: C 62.55 (62.48), H 4.05 (4.01), N 4.56 (4.58).

***Cis*-Cl,*trans*-PPh_3-$[Ru(4,7\text{-diphenyl-}1,10\text{-phen})(PPh_3)_2Cl_2]$ (2c).** Yield: 67%. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 8.99 (d, 2H), 7.78 (s, 2H), 7.67 (m, 6H), 7.39 (m, 16H), 7.12 (m, 6H), 7.02 (m, 12H) 6.75 (sbr, 2H), 1.57 (s, 2H). ^{31}P-NMR ($CDCl_3$, 25 °C, TMS): δ (ppm) 23.50 (s, 2P, PPh_3). Anal. calcd (found) for $RuC_{60}H_{46}N_2P_2Cl_2$: C 70.03 (69.97), H 4.50 (4.55), N 2.72 (2.69).

***Trans*-Cl,*cis*-CO-$[Ru(4,5\text{-diaz})(CO)_2Cl_2]$ (3).** The polymeric precursor $[Ru(CO)_2Cl_2]_n$ (0.36 mmol, 80 mg) was dissolved in hot degassed CH_3OH (20 mL) under nitrogen, affording a pale yellow solution that was cooled to room temperature. Then the ligand (0.36 mmol, 61 mg) was slowly added. The colour of the solution changed from light yellow to dark yellow. The solution was heated under stirring for 2 h. Then the resultant yellow precipitate was filtered under nitrogen, washed with CH_3OH and hexane and dried under vacuum.

Yield: 53%. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 8.90 (d, 2H), 8.16 (d, 2H), 7.65 (dd, 2H), 4.37 (s, 2H). ^{13}C-NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 195.179 (s, 2C, CO). IR($CHCl_3$), νCO (cm^{-1}): 2069, 2006. Anal. calcd (found) for $RuC_{13}H_8N_2O_2Cl_2$: C 39.41 (39.37), H 2.03 (2.01), N 7.07 (7.04).

***Cis*-Cl,*trans*-PPh$_3$-[Ru(4,5-diaz)(PPh$_3$)$_2$Cl$_2$] (4).** Yield: 57%. ^{1}H-NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ (ppm) 8.80 (d, 2H), 7.84 (d, 2H), 7.55 (dd, 2H), 7.14 (m, 12H), 7.06 (m, 6H), 6.89 (m, 12H), 4.07 (s, 2H). ^{31}P-NMR (CDCl$_3$, 25 °C, TMS): δ (ppm) 22.57 (s, 2P, PPh$_3$). Anal. calcd (found) for RuC$_{47}$H$_{38}$N$_2$P$_2$Cl$_2$: C 65.28 (65.21), H 4.40 (4.38), N 3.24 (3.22).

***Trans*-Cl,*cis*-CO-[Ru(9-fulleriden-4,5-diaz)(CO)$_2$Cl$_2$] (5).** The polymeric precursor [Ru(CO)$_2$Cl$_2$]$_n$ (0.086 mmol, 20 mg) was dissolved in hot degassed MeOH (6 mL). The pale yellow solution was cooled at room temperature. The ligand (0.086 mmol, 76 mg) was dissolved in a mixture of cold degassed CS$_2$ (10 mL) and CH$_2$Cl$_2$ (3 mL) in a Schlenk tube, affording a dark red solution that was added *via* cannula to the first one. The resultant solution, cloudy and red, was heated under reflux for 48 h affording a brown precipitate that was filtered under nitrogen and dried under vacuum.

Yield: 46%. ^{1}H-NMR (400 MHz, CDCl$_3$ + CS$_2$, 25 °C, TMS): δ (ppm) 9.19 (m, 2H), 7.86 (m, 1H). IR(CHCl$_3$), νCO (cm^{-1}): 2062, 1989. Anal. calcd (found) for RuC$_{73}$H$_6$N$_2$O$_2$Cl$_2$: C 78.65 (78.44), H 0.54 (0.53), N 2.51 (2.49).

***Cis*-Cl,*trans*-PPh$_3$-[Ru(9-fulleriden-4,5-diazafluorene)(PPh$_3$)$_2$-Cl$_2$] (6).** The precursor [Ru(PPh$_3$)$_3$Cl$_2$] (0.043 mmol, 41 mg) and the ligand (0.043 mmol, 38 mg) were dissolved under nitrogen in degassed CS$_2$ (10 mL). The dark red solution was heated under reflux. The reaction was monitored by Thin Layer Chromatography (Silica; toluene : MeOH = 9 : 1). After 18 h, the solvent was removed under vacuum and a sticky solid was formed. This precipitate was dissolved in CH$_2$Cl$_2$, filtered, dried and ground in Et$_2$O in order to obtain a dark brown powder. This powder was filtered using a Büchner funnel, dried under vacuum and further purified by column chromatography (silica gel).

Yield: 48%. ^{1}H-NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ (ppm) 8.21 (d, 2H), 7.70 (m, 20H), 7.67 (m, 6H), 7.35 (d, 2H), 7.17 (m, 14H), 6.77 (t, 2H), 5.31 (s, 2H). ^{31}P-NMR (400 MHz, CDCl$_3$, 25 °C): δ (ppm) 24.171 (s, 2P, PPh$_3$). Anal. calcd (found) for RuC$_{107}$H$_{36}$N$_2$P$_2$Cl$_2$: C 81.16 (80.95), H 2.29 (2.30), N 1.77 (1.76).

Second-order NLO properties: EFISH measurements

The molecular quadratic hyperpolarizabilities of all of the investigated complexes (Table 1) were measured by the solution-phase dc Electric Field Induced Second Harmonic (EFISH) generation method,[4] which can provide direct information on the intrinsic molecular NLO properties through eqn (1):

$$\gamma_{\mathrm{EFISH}} = (\mu\beta_\lambda/5k\mathrm{T}) + \gamma(-2\omega;\, \omega,\, \omega,\, 0) \qquad (1)$$

where $\mu\beta_\lambda/5kT$ is the dipolar orientational contribution and $\gamma(-2\omega;\, \omega,\, \omega,\, 0)$, a third order term corresponding to the mixing of two optical fields at ω and of the DC poling field at $\omega = 0$, is the electronic cubic contribution to γ_{EFISH} which is usually negligible. β_λ is the projection along the dipole moment axis of the vectorial component of the tensor of the quadratic hyperpolarizability, working with an incident wavelength λ.

All EFISH measurements were carried out at the Dipartimento di Chimica Inorganica Metallorganica e Analitica "Lamberto Malatesta" of the Università degli Studi di Milano, in DMF solutions at a concentration of 1 × 10^{-3} M, working with a non resonant incident wavelength of 1.907 µm, obtained by Raman-shifting the fundamental 1.064 µm wavelength produced by a Q-switched, mode-locked Nd^{3+}:YAG laser manufactured by Atalaser. The apparatus for the EFISH measurements was a prototype made by SOPRA (France). The $\mu\beta_{\mathrm{EFISH}}$ values reported are the mean values of 16 successive measurements performed on the same sample.

X-Ray determination of the structure of *Cis*-Cl,*trans*-PPh$_3$-[Ru(5-NO$_2$-1,10-phen)(PPh$_3$)$_2$Cl$_2$] (2b)†. Crystals of *Cis*-Cl,*trans*-PPh$_3$-[Ru(5-NO$_2$-1,10-phen)(PPh$_3$)$_2$Cl$_2$], suitable for single-crystal X-ray diffraction studies, were obtained by slow addition at room temperature of pentane to a solution of the complex in CH$_2$Cl$_2$.

Crystal data for 2b. C$_{48}$H$_{37}$Cl$_2$N$_3$O$_2$P$_2$Ru, M = 921.72, monoclinic, a = 15.502(3), b = 17.677(4), c = 15.861(3) Å, β = 105.97(3)°, U = 4178.6(16) Å^3, T = 294(2) K, space group $P2_1/n$ (no. 14), Z = 4, μ = (Mo-Kα) 0.624 mm^{-1}. 33 525 reflections (10 548 unique; R_{int} = 0.049) were collected at room temperature in the range 1.84 $< 2\theta <$ 58.32°, employing a 0.12 × 0.07 × 0.05 mm crystal mounted on a Bruker APEX II CCD diffractometer and using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). Final R_1 [wR_2] values are 0.0455 [0.2222] on $I > 2\sigma(I)$ [all data].

Datasets were corrected for Lorentz-polarization effects and for absorption (SADABS[17]). The structure was solved by direct methods (SIR-97[18]) and completed by iterative cycles of full-matrix least squares refinement on F_o^2 and ΔF synthesis using the SHELXL-97[19] program (WinGX suite)[20] Hydrogen atoms, located on the ΔF maps, were allowed to ride on their carbon atoms.

Conclusions

In conclusion, we have shown that various Ru(II) complexes with substituted 1,10- phenanthroline or 4,5- diazafluorene represent a new interesting family of highly active second-order NLO chromophores. Remarkably, the presence of a fullerene substituent produces a strong enhancement of the second-order NLO response, but maintaining a significant transparency towards the second harmonic generation, as for instance in the case of **5** and **6**. These properties make them excellent candidates for the preparation of materials characterized by high second harmonic generation properties, potentially also redox-switchable due to the presence of Ru(II).

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Notes and references

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