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Synthesis and characterization of η^5-monocyclopentadienyl (p-nitrobenzonitrile)ruthenium(II) salts: second harmonic generation powder efficiencies

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Abstract

A new family of salts $[\mathrm{Ru}(\eta^5\text{-}C_5H_5)((+)\text{-}(\mathrm{DIOP})(p\text{-}NCC_6H_4NO_2)][X]$ ($X = p\text{-}CH_3C_6H_4SO_3^-$, Cl^-, NO_3^-, BF_4^-, PF_6^-, ClO_4^- and $CF_3SO_3^-$), has been synthesized. Variation of the counterion shows that $[\mathrm{Ru}(\eta^5\text{-}C_5H_5)((+)\text{-}(\mathrm{DIOP})(p\text{-}NCC_6H_4NO_2)]^+$ can improve by a factor of 25 the value of second harmonic generation powder efficiency. The relation between ^{1}H and ^{13}C NMR spectroscopic data and second harmonic generation values accounts for an electronic interaction between the counterions and π delocalized electronic system on the chromophore.

Key words: Ruthenium; Second harmonic generation; Non-linear optics; Cyclopentadienyl

1. Introduction

The potential applications in the area of telecommunications, new laser technology and integrated optics, of materials with large optical non-linearities, and the promising results reported in the last few years [1,2] justify the current interest in the development of new organometallic materials with high values of second harmonic generation (SHG). This effect is characterized by the bulk susceptibilities $\chi^{(2)}$ on the macroscopic level and the first hyperpolarizability β on the molecular level.

For the scientific development of new materials showing non-linear optical (NLO) properties, a firm understanding of the electronic origin of this phenomenon is required. Knowledge of the relationship between the molecular hyperpolarizability and π electron delocalization has been considered an important contribution for this understanding. However, for SHG purposes, crystallization in a non-centrosymmetric space group is crucial for an overall non-linear response of a material [3,4]. Although organic molecules containing π donor-acceptor groups can exhibit large molecular second order optical non-linearities, they mostly crystallize in centrosymmetric space groups, leading to materials with vanishing $\chi^{(2)}$ [5]. Strategies of synthesis to overcome this major obstacle include the use of chiral functional groups [6], incorporation of the chromophore in host molecules or glassy polymer matrices [7], intercalation compounds [8], the incorporation of functional groups that encourage asymmetric intermolecular hydrogen bonding [9] and creation of coulombic interactions by variation of counterions. This last effect can provide the driving force to overcome the centrosymmetry originating from dipolar interactions in organic compounds.

Some additional factors may also contribute to a better response in the solid state, these being mainly related to an adequate alignment of the chromophore

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in the bulk material leading to optimal phase matching [10].

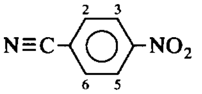
We have previously studied the SHG properties of some organometallic compounds containing *p*-substituted benzonitriles attached to η^5-monocyclopentadienyliron(II) derivatives and identified *p*-$NCC_6H_4NO_2$ as a promising ligand. This nitrile has the peculiarity of possessing both N≡C and NO_2 as acceptor groups instead of the usual donor-acceptor system. A value of SHG efficiency of 38 times that of urea was reported for the compound $[Fe(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})(p\text{-}NCC_6H_4NO_2)][PF_6]$ [11]. Our continuing studies prompted us to investigate the behaviour of *p*-$NCC_6H_4NO_2$ and other related nitriles after coordination to other organometallic fragments and we found that, contrary to the iron system, $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})(p\text{-}NCC_6H_4NO_2)][PF_6]$ was only about three times more efficient than urea in SHG response at 1.064 μm laser frequency [12].

In order to improve that value and to have a better understanding of the role of the counterion variation on the bulk material response, we prepared a family derived from the cation $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})(p\text{-}NCC_6H_4NO_2)]^+$ crystallized with a range of anions of varying size and shape. A variation of 25 times was found in the powder SHG efficiencies of the compounds studied. The experimental ^1H, ^{13}C, ^{31}P NMR and UV-vis spectroscopic data together with electrochemical studies by cyclic voltammetry were analysed in order to gain insight about any correlation between these experimental data and the SHG efficiency of the compounds.

2. Results and discussion

Compounds of general formula $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})(p\text{-}NCC_6H_4NO_2)][X]$ ($X = Cl^-$, NO_3^-, BF_4^-, *p*-$CH_3C_6H_4SO_3^-$, PF_6^-, ClO_4^- and $CF_3SO_3^-$) were prepared by chloride abstraction of the starting material $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})Cl]$ by the salt of the adequate counterion in the presence of a slight excess of *p*-nitrobenzonitrile in methanol, at room temperature. After workup, orange ($X = Cl^-$, BF_4^-, PF_6^- and $CF_3SO_3^-$), yellow greenish ($X = p\text{-}CH_3C_6H_4SO_3^-$), golden ($X = ClO_4^-$) and brown ($X = NO_3^-$) crystals of $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})(p\text{-}NCC_6H_4NO_2)][X]$ were obtained in *ca.* 60–85% yield. All compounds were fairly stable towards oxidation in air and to moisture both in the solid state and in solution. Most of the compounds crystallized with a molecule of solvent, the formulation being supported by the analytical data, IR and ^1H, ^{13}C, ^{31}P NMR spectra (see Tables 1 and 2) as discussed below. The molar conductivities of 10^{-3} M solutions of the complexes in nitromethane, in the range 60–92 Ω^{-1} cm^2 mol^{-1}, are consistent with the values reported for 1:1 electrolytes [13].

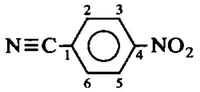
TABLE 1. ^1H NMR data for complexes $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})(p\text{-}NCC_6H_4NO_2)][X]$ [a]

Counterion X	 δ (ppm), multiplicity, relative integral, assignment
p-$CH_3C_6H_4SO_3^-$	4.67 (s, 5H, η^5-C_5H_5); 7.96 (d, 2H, H_2, H_6); 8.32 (d, 2H, H_3, H_5)
Cl^-	4.72 (s, 5H, η^5-C_5H_5); 8.07 (d, 2H, H_2, H_6); 8.39 (d, 2H, H_3, H_5)
NO_3^-	4.68 (s, 5H, η^5-C_5H_5); 7.90 (d, 2H, H_2, H_6); 8.39 (d, 2H, H_3, H_5)
BF_4^-	4.65 (s, 5H, η^5-C_5H_5); 7.77 (d, 2H, H_2, H_6); 8.40 (d, 2H, H_3, H_5)
PF_6^-	4.65 (s, 5H, η^5-C_5H_5); 7.73 (d, 2H, H_2, H_6); 8.40 (d, 2H, H_3, H_5)
ClO_4^-	4.66 (s, 5H, η^5-C_5H_5); 7.79 (d, 2H, H_2, H_6); 8.40 (d, 2H, H_3, H_5)
$CF_3SO_3^-$	4.66 (s, 5H, η^5-C_5H_5); 7.78 (d, 2H, H_2, H_6); 8.40 (d, 2H, H_3, H_5)

[a] Acetone-d_6 with TMS.

Typical IR bands confirm the presence of the cyclopentadienyl ligand (≈ 3060 cm^{-1}), and the anions *p*-$CH_3C_6H_4SO_3^-$ (1190 cm^{-1}), NO_3^- (1380 cm^{-1}), BF_4^- (1070 and 1050 cm^{-1}), PF_6^- (830 and 540 cm^{-1}), ClO_4^- (1090 cm^{-1}) and $CF_3SO_3^-$ (1260 and 630 cm^{-1}). The coordinated nitrile was identified by $\nu(CN) \approx$ 2220 cm^{-1} and characteristic bands of NO_2 (1520 and 1340 cm^{-1}).

TABLE 2. ^{13}C NMR data for complexes $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})(p\text{-}NCC_6H_4NO_2)][X]$ [a]

Counterion X	 δ (ppm), assignment
p-$CH_3C_6H_4SO_3^-$	84.55 (C_5H_5); 117.14 (C1); 124.04 (C3, C5); 127.08 (CN); 134.43 (C2, C6); 149.74 (C4)
Cl^-	84.62 (C_5H_5); 117.27 (C1); 124.14 (C3, C5); 127.11 (CN); 134.82 (C2, C6); 149.86 (C4)
NO_3^-	84.32 (C_5H_5); 116.99 (C1); 124.19 (C3, C5); 126.78 (CN); 134.03 (C2, C6); 149.79 (C4)
BF_4^-	84.44 (C_5H_5); 117.05 (C1); 124.24 (C3, C5); 126.94 (CN); 134.02 (C2, C6); 149.95 (C4)
PF_6^-	84.22 (C_5H_5); 116.75 (C1); 124.25 (C3, C5); 126.66 (CN); 134.01 (C2, C6); 149.88 (C4)
ClO_4^-	84.44 (C_5H_5); 117.02 (C1); 124.24 (C3, C5); 126.90 (CN); 134.06 (C2, C6); 149.96 (C4)
$CF_3SO_3^-$	84.42 (C_5H_5); 116.98 (C1); 124.24 (C3, C5); 126.94 (CN); 134.12 (C2, C6); 149.98 (C4)

[a] Chloroform-*d*.

No significant shifts on ν(CN) were observed upon coordination, although it has been generally reported that a normal σ coordination of a functional nitrile group to a metal centre leads to positive shifts on ν(CN). Our previous work on compounds $[MCp_2(L)(p\text{-}NCC_6H_4R']^+$ ($M = Mo^{IV}$ and W^{IV}), where $p\text{-}NCC_6H_4R'$ was an extended family of benzonitriles, was consistent with this observation and was supported by EHMO calculations showing that π back donation from the metal fragment to the coordinated nitrile would be impossible [14]. However, in compound $[Fe(\eta^5\text{-}C_5H_5)((+)\text{-DIOP}))(p\text{-}NCC_6H_4NO_2)][PF_6]$, we found experimental evidence for that type of π bonding, which would promote the extension of the π system from the metal fragment towards an NO_2 acceptor group, through the benzene ring and would explain the relatively large SHG efficiency for that compound. In the ruthenium analogue compounds $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})(NCC_6H_4NO_2)][X]$, presented in this work, we did not find the same experimental evidence for such a π-back donation, since for example, no negative shifts were observed for ν(CN). Nevertheless, as no positive shifts were observed either, it is reasonable to assume the existence of a weak π delocalization from the ruthenium fragment towards the NO_2 group. This is not surprising since ruthenium is known to be a less effective π donor than iron.

Analysis of ^1H NMR data shows that coordination of p-substituted nitriles at the organometallic Ru^{II} centre leads to a trend of shielding on H_2 and H_6 aromatic protons as found before for Fe^{II} analogue compounds [11]. Nevertheless, it was observed in the present work that the counterion might have an unexpected effect on that shielding since, differences up to 0.3 ppm were observed on signals relative to H_2 and H_6 protons depending on the varying counterion, while signals relative to H_3, H_5 and Cp remained in very narrow ranges, 8.32–8.40 and 4.65–4.72 ppm, respectively, for all the compounds studied.

A corresponding effect was found in ^{13}C NMR spectra (Table 2) where no significant changes occurred for aromatic carbons, including Cp and N≡C functional groups, except for the same trend of shielding on C2 and C6 aromatic atoms. A tentative correlation between this spectroscopic evidence and the values of SHG obtained for these compounds (Table 3) may suggest that better SHG values occur in compounds possessing relatively more shielded H_2 and H_6 protons. For example, comparison of chemical shifts for $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})(p\text{-}NCC_6H_4NO_2)][CF_3SO_3]$ (which is 10 times better than urea) and $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})(p\text{-}NCC_6H_4NO_2)][Cl]$ (only 0.5 times urea) shows values at 7.78 and 8.07 ppm, respectively.

In the light of these results, it seems reasonable to suggest that coulombic interactions of the varying counterion, besides the packing effect, may play an additional role in the electronic interaction that would contribute to a slight enhancement on charge density at crucial positions, leading to a more effective polarization of the chromophore. Obviously, this intramolecular effect would be stronger in the solid state.

Published work on systematic studies relative to the effect of the varying counterion on SHG efficiency of several organic [15] and organometallic compounds [1] reported more dramatic variation on SHG values than those found in the present work. If was found that in some cases the alignment of the molecules in the crystal lattice would lead to a non-centrosymmetric crystallization. This is clearly not the case in the compounds reported in this paper since they all crystallized in non-centrosymmetric space groups due to the presence of the chiral co-ligand ((+)-DIOP). Although in the present case additional packing effects may also be involved, since some of these compounds show different colours in solution and in the solid state, they might not be important, at least for compounds presenting the best and the lower SHG values, since both are orange either in solution or as solids.

The UV-vis absorption spectra of $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})(p\text{-}NCC_6H_4NO_2)][CF_3SO_3]$ and $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})(p\text{-}NCC_6H_4NO_2)][p\text{-}CH_3C_6H_4SO_3]$, recorded in chloroform and acetonitrile solutions exhibit two strong low-lying bands at $\lambda_{max} \approx 230$ and 363 nm with slight dependency on the solvents used (~ 10 nm). The corresponding values of ϵ ($0.4\text{–}4 \times 10^5$ cm^{-1} M^{-1}) were in good agreement with the charge-transfer transitions expected for these com-

TABLE 3. Powder SHG efficience of $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})(p\text{-}NCC_6H_4NO_2)][X]$ salts

Anion	Colour	SHG value [a]	Anion	Colour	SHG value
$p\text{-}CH_3C_6H_4SO_3^-$	Yellow greenish	0.4	PF_6^-	Orange	2.7
Cl^-	Orange	0.5	ClO_4^-	Golden	2.9
NO_3^-	Brown	1.2	$CF_3SO_3^-$	Orange	10
BF_4^-	Orange	1.9			

[a] Second-harmonic intensity measured at 1.604 μm fundamental radiation, relative to urea.

pounds. The higher energy band was attributed to the blue shifted transition that occurs at 258 nm in the uncoordinated benzonitrile.

The electrochemistry of each compound was studied by cyclic voltammetry in acetonotrile between -1.6 and 1.6 at 200 mV s^{-1}.

The electrochemical behaviour of this family of salts is characterized by two irreversible redox processes. The first at $E_{p/2} = -0.74$ V ($\Delta E = 100$ mV, $i_a/i_c \approx 0.5$) was attributed to occur on the coordinated nitrile (free $E_{p/2} = -0.86$ V). The second redox process occurs at $E_{p/2} = 1.26$ V ($\Delta E = 140$ mV, $i_a/i_c \approx 0.4$) was attributed to the oxidation $Ru^{II} \rightarrow Ru^{III}$. In the parent compound, $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})Cl]$, this oxidation occurs quasi-reversibly at $E_{p/2} = -0.56$ V ($\Delta E = 65$ mV, $i_a/i_c \approx 0.9$). There was no significant evidence for any effect of the counterion on the behaviour of both redox processes.

3. Summary

In this work, we found that even in compounds crystallizing non-centrosymmetrically, the counterion can play an important role on the values of second harmonic generation efficiency. Furthermore, ^1H and ^{13}C spectroscopic data account for an electronic interaction between the counterion and the π-delocalized system on the chromophore, which might be responsible for the observed values of SHG.

4. Experimental details

All manipulations were carried out under a vacuum or dinitrogen atmosphere by use of standard Schlenk techniques. Absolute methanol was used without further purification. Solvents for recrystallizations were dried following standard methods [16]. Solid state IR spectra were taken on a Perkin Elmer 457 spectrophotometer with KBr pellets; only significant bands are cited in the text. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Unity 300 spectrometer at probe temperature. The UV-vis spectra were taken on Shimadzu 1202 spectrophotometer. Microanalyses were performed in our laboratories.

The ^1H (acetone-d_6) and ^{13}C (chloroform-d) chemical shifts are reported in parts per million (ppm) downfield from internal Me_4Si and the ^{31}P (chloroform-d) NMR spectra are reported in ppm downfield from external standard 85% H_3PO_4.

$[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})Cl]$ was prepared following the literature [17]. Reagents salts: $Tl(p\text{-}CH_3C_6H_4SO_3)$, $TlNO_3$, $TlPF_6$, were prepared by adequate techniques; $AgBF_4$, $LiClO_4$, and $AgCF_3SO_3$ were used as purchased from Aldrich Chemical Co.

(+)-DIOP ^1H and ^{13}C NMR data are very similar for all the complexes: ^1H: 1.06 (s, 3H, CH_3); 1.26 (s, 3H, CH_3); 2.59 (m, 1H, CH); 3.00 (m, 1H, CH); 3.40 (m, 2H, CH_2); 3.80 (m, 2H, CH_2); 7.46 (m, 10H, C_6H_5); 7.65 (m, 4H, C_6H_5); 7.78 (m, 4H, C_6H_5); 8.12 (t, 2H, C_6H_5). ^{13}C: 26.75 (CH_3); 28.73 (CH_2, $^1J(C\text{-}P) = 20.49$); 30.48 (CH_2, $^1J(C\text{-}P) = 26.85$); 75.42 (CH, $^2J(C\text{-}P) = 10.40$); 78.23 (CH); 108.90 ($C(CH_3)_2$); 128.92–134.16 (*aryl* CH); 138.38 (C-*ipso*, aryl-CH); 141.27 (C-*ipso*, aryl-CH).

The ^{31}P NMR spectrum for all compounds, at room temperature, displayed two doublets at 36.1 ppm, an AB pattern with $J(P_AP_B) = 37.6$ Hz, showing two inequivalent phosphorus atoms, whereas free (+)-DIOP shows a singlet a -22.9 ppm in the same solvent.

4.1. Preparation of $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})(p\text{-}NCC_6H_4NO_2)][X]$

All the complexes were prepared by the process described below with two slight modifications for two of the compounds. To an orange solution of $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})Cl]$ (1 mmol) in degassed methanol (40 ml) was added 1.1 mmol of the nitrile ($p\text{-}NCC_6H_4NO_2$) and 1.1 mmol of the appropriate salt; then the mixture was stirred at room temperature for a period of 14–20 h. When $X = ClO_4^-$ the mixture was refluxed for 5 h. A precipitate of chloride was observed without any significant change in colours of the solutions. After filtration, the solution was evaporated to dryness under a vacuum and washed several times with ether to remove the excess of starting materials. The residue was recrystallized from dichloromethane/ether ($X = p\text{-}CH_3C_6H_4^-$, SO_3^-, Cl^-, PF_6^-, ClO_4^-) or acetone/ether ($X = NO_3^-$, BF_4^-, $CF_3SO_3^-$). In the case of $X = Cl^-$, to a solution of $[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})Cl]$ (1 mmol) was added a large excess of nitrile (7 mmol). In this case, warming up the solid residue obtained after extraction of unreacted starting materials, by ether, leads to the decomposition of the complex formed as shown by sublimation of the p-benzonitrile.

$[Ru(\eta^5\text{-}C_5H_5)((+)\text{-DIOP})(p\text{-}NCC_6H_4NO_2)][X]$

$X = CH_3C_6H_4SO_3^-$: 75% yield, m.p. 189–191°C. Anal. Found: C, 59.70; H, 5.12; N, 2.71. $C_{50}H_{48}N_2O_7P_2RuS \cdot 1/2(CH_3CH_2)_2O$ calcd.: C, 61.16; H, 5.23; N, 2.74%.

$X = Cl^-$: 60% yield, m.p. 145–150°C. Anal. Found: C, 58.30; H, 4.70; N, 3.20. $C_{43}H_{41}ClN_2O_4P_2Ru \cdot 1/2(CH_2Cl_2)$ calcd.: C, 58.66; H, 4.75; N, 3.14%.

$X = NO_3^-$: 65% yield, m.p. 187–191°C. Anal. Found: C, 57.70; H, 4.60; N, 4.00. $C_{43}H_{41}N_3O_7P_2Ru \cdot 1/2(CH_3)_2CO$ calcd.: C, 59.13; H, 4.91; N, 4.65%.

$X = BF_4^-$: 60% yield, m.p. 168–175°C. Anal. Found: C, 56.48; H, 5.01; N, 2.47. $C_{43}H_{41}BF_4N_2O_4P_2Ru \cdot (CH_3)_2CO$ calcd.: C, 57.69; H, 4.95; N, 2.92%.

X = PF_6^-: 85% yield, m.p. 193–197°C. Anal. Found: C, 53.82; H, 4.51; N, 2.90. $C_{43}H_{41}F_6N_2O_4P_3Ru$ calcd.: C, 53.92; H, 4.31; N, 2.92%.

X = ClO_4^-: 85% yield, m.p. 207–210°C. Anal. Found: C, 56.35; H, 5.05; N, 3.04. $C_{43}H_{41}ClN_2O_8P_2Ru \cdot 1/2(CH_3CH_2)_2O$ calcd.: C, 56.93; H, 4.88; N, 2.95%.

X = $CF_3SO_3^-$: 80% yield, m.p. 200–203°C. Anal. Found: C, 52.41; H, 4.29; N, 2.84. $C_{44}H_{41}F_3N_2O_7P_2RuS$ calcd.: C, 54.94; H, 4.30; N, 2.90%.

4.2. SHG technique

All compounds synthesized in this work were tested for second harmonic generation, using the Kurtz powder technique [18]. For measurements, a Nd:YAG laser operating at 1.064 μm was used, pulsed at 30 ps. The peak power of the picosecond laser was measured to be less than 0.5 mJ. The diameter of the approximately TEM_{00}mode beam was 2 mm. Repetition rates were kept below 2 Hz and filters were inserted into the incident beam path as necessary to prevent the saturation of the photomultiplier tube with second harmonic light. Samples were mulled to fine powders; grain sizes were not standardized. For this reason, signals between individual measurements were seen to vary in some cases as much as ±20%.

4.3. Electrochemical apparatus

The electrochemical instrumentation for CV consisted of a EG&G Princeton Applied Research Potenciostat Model 273A, connected to the data acquisition software (EG & G PAR Electrochemical Analysis Model 273 Version 3.0). The voltammetric experiments were performed at room temperature, in an argon atmosphere, in a standard single-compartment three-electrode design (PAR polarographic cell). A Pt wire was used as counter electrode and the working electrode was a 2-mm piece of Pt wire for voltammetry. The reference electrode, a calomel electrode containing a saturated solution of potassium chloride, was calibrated using a solution of ferrocene (1 mM) in acetonitrile containing 0.1 M $LiClO_4$ for which the ferricinium/ferrocene potential was in agreement with the literature value [19]. Solutions used were 1 mM in solute and 0.1 M in the supporting electrolyte, tetrabutylammonium hexafluorophosphate (Sigma Chemical Co.).

The acetonitrile (reagent grade material) was dried over CaH_2 and P_2O_5 and distilled under dinitrogen just before use. Solutions were degassed and kept under an argon atmosphere during each experiment.

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