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Synthesis and nonlinear optical properties of a range of 1-ferrocenyl(2-(4-alkyl)pyridiniumyl)ethylene iodides

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Abstract

The preparation of a range of compounds of general formula Fc–CH=CH–$C_5H_4N^+$–X, where X = C_nH_{2n+1} (n = 1–5, 10 or 18) and O^-, was achieved via condensation of the relevant picolinium iodide with ferrocene carboxaldehyde. The spectroscopic properties of these materials were shown to be very similar, however the SHG, measured by the Kurtz powder technique, showed that increasing the alkyl chain above three carbons resulted in a dramatic loss of SHG efficiency. The O^- compound also yielded very little SHG. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nonlinear optical properties; 1-Ferrocenyl(2-(4-alkyl)pyridiniumyl)ethylene iodides; Kurtz powder technique

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1. Introduction

The nonlinear optical (NLO) properties of organometallic compounds have been thoroughly reviewed in the literature [1–4]. One area of interest within this field is the properties of the product of the condensation of acyl ferrocenes [4]. A number of NLO studies have been carried out on ferrocene derivatives, including the first on an organometallic compound in 1987 [5]. Other work followed rapidly [6–9], and among these compounds of the general formula [{η^5-C_5H_5}Fe{η^5-$C_5H_3(CH_3)CH{=}CHR$}] exhibited a Second Harmonic Generation (SHG) of 1.2–17.0 times that of urea [7].

The largest SHG so far recorded for an organometallic compound came from a series of salts [{η^5-C_5H_5}Fe{η^5-$C_5H_4CH{=}CHC_5H_4N^+{-}CH_3$}][$X^-$] where X = I^-, Br^-, Cl^-, $CF_3SO_3^-$, NO_3^-; or $B(C_6H_5)_4^-$ [8,9]. In these the value of the SHG (measured by the Kurtz Powder method) was found to be dependant on the anion, with the iodide salt giving a value 220 times that of urea. Similar findings on the dependence of the SHG on the anion have been reported for organic salts [10,11]. In a systematic study of ferrocene and ruthenocene derivatives of the form [{η^5-C_5H_5}M{η^5-$C_5H_4CH{=}CHC_6H_4X$}] where X = NO_2, COMe, CN and CHO, it was found that: (1) substitution of C_5H_5 for C_5Me_5 leads to an increase in dipole moment and NLO response; (2) the first molecular hyperpolarisability of ferrocenes are greater than those of analogous ruthenocenes; and (3) the degree of conjugation in the substituent has a great effect on the NLO response [12–14].

A series of ferrocenyl Schiff bases of the general formula [{η^5-C_5H_5}Fe{η^5-$C_5H_4CH{=}NR$}] where R = C_6H_5, C_6H_4–p-F, N=CH(C_6H_4–p-NO_2) or C_6H_4–p-CN have been prepared [15,16], and although a considerable solvatochromism was observed (a good indicator of NLO activity) crystallisation occurred in a centrosymmetric space group [15,17,18]. The ferrocenyl imine [{η^5-C_5H_5}Fe{η^5-$C_5H_4CH{=}NR{-}N{=}CH(C_6H_4$–$p$-$NO_2)$}] manifested some NLO response, but it was small (1/3 that of urea). This was due to the compound crystallising in the noncentrosymmetric space group $P2_1/n_1$ where the molecular arrangement ensures a cancelling of the dipolar nature of the molecule [16]. Moreover in these structures it was found that the C=N when attached to a ferrocenyl moiety acts as an electron sink which effectively blocks transfer of electron density to

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the acceptor; it is not a good congucator of electron density [18,19]. Also in these structures it was found that the C=N group, by its electron withdrawing nature, is the most dominant force controlling the molecular confirmation [18].

Although the effect of varying the anion in [Fc–CH=CH$C_5H_4N^+$–R][X^-], where R = CH_3, has been investigated there are no reports of the effect of variation of the quaternising groups. This is an important effect as the nature of the group could: (1) effect the electron density on the quaternary N thereby directly affecting the NLO response; and (2) effect the packing of molecules (due to the relative steric bulks of the groups used) and thus the NLO response. In this work, we report the NLO results of a systematic study of substitution of the R group in [Fc–CH=CH–$C_5H_4N^+$–R][I^-].

2. Results and discussion

The preparation of [Fc–CH=CH–$C_5H_4N^+$–R][I^-] was carried out using a slight modification of the literature procedure for R = CH_3 [9] as shown in Fig. 1. The reaction was carried out under nitrogen in ethanol. The products were purified by column chromatography on neutral alumina using acetonitrile as the eluant. Use of protic solvents such as methanol resulted in the decomposition of the product on the column. The purified products were stored in a dessicator and the vessels were flushed with dry dinitrogen prior to storage to stop hydrolysis. Since the stoichiometry of the reactants were not detailed in the literature [9], that used in this work was a twofold excess of ferrocene carboxaldehyde and was chosen to simplify the chromatographic step. The retention time of the unreacted picolimium salt was very similar to that of the product, whereas the aldehyde had a significantly lower retention time.

FABS mass spectra of all the compounds showed distinctive signals for the cations and the $FeCp^+$ fragment [20,21] confirming the formula of the compounds prepared. The FABS data for the cations are presented in Table 1. Elemental analysis showed a good agreement with the calculated values for all compounds.

2.1. Mössbauer spectroscopy

The Mössbauer spectral parameters are also presented in Table 1. They show little variation between compounds. The i.s. values are all around 0.53 mm s^{-1} and the half-widths at half-heights (Γ) around 0.14 mm s^{-1}. The fact that all the compounds show smaller quadrupole splitting (q.s.) than ferrocene (q.s. 2.37 mm s^{-1} at 80 K) [22] indicates that all the substituents are electron withdrawing, as expected. It is worth noting that the q.s. values for all the compounds other than Fc–CH=CH–$C_5H_4N^+$–O^-, which is larger, are in the range found for the ferrocenyl Schiff base compounds [22,23]. There is a noticeable trend in the q.s. data, a steady decrease for Fc–CH=CH–$C_5H_4N^+$–CH_3 to Fc–CH=CH–$C_5H_4N^+$–$C_{10}H_{21}$. Both Fc–CH=CH–$C_5H_4N^+$–$C_{18}H_{37}$ and Fc–CH=CH–$C_5H_4N^+$–O^- have q.s. values higher than Fc–CH=CH–$C_5H_4N^+$–$C_{10}H_{21}$ and that of the latter is the largest. The q.s. arises from the lattice and the valence electron density around the iron. Of these two effects the latter is known to dominate the q.s. of iron sandwich compounds [22,23]. However, the markedly different q.s. value of Fc–CH=CH–$C_5H_4N^+$–O^- is probably caused by the absence of an ionic lattice. The decreasing q.s. of Fc–CH=CH–$C_5H_4N^+$–CH_3 to Fc–CH=CH–$C_5H_4N^+$–$C_{10}H_{21}$ is indicative of a decrease in electron density in the ferrocenyl group. This is consistent with the gradual decrease in the strength of the donation from the quaternising group causing the electron deficient nitrogen to pull more electron density away from the ferrocenyl group. The higher q.s. of the other two compounds is caused by weaker electron withdrawal either due to donation from the quaternising group, or by a molecular conformation which does not allow conjugation of the π system.

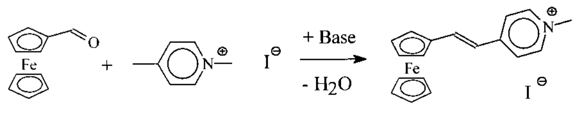

Fig. 1. Reaction scheme for synthesis of [Fc–CHCH–C_5H_5N–R][I].

2.2. Electronic absorption spectroscopy

The electronic absorption spectra of the compounds were recorded in two solvents wherever possible and the data are presented in Table 1. The compounds show a solvatochromic shift, consistent with the compounds being polarisable and some times indicative of nonlinear optical materials [5], though in the solvents used (chosen due to solubility) the shifts are small.

2.3. NMR spectroscopy

^1H- and ^{13}C-NMR spectra were recorded and the ^1H spectra are assigned by analogy to the spectra of Fc–CH=CH–$C_5H_4N^+$–CH_3 in the literature [9]. The NMR spectra of the compounds are remarkably similar for the Fc–CH=CH–$C_5H_4N^+$–alkyl derivatives and some of the ^1H spectral data are presented in Table 2 and the labelling scheme is shown in Fig. 2. The literature does not report the ^{13}C-NMR data for Fc–CH=CH–$C_5H_4N^+$–CH_3 [9], some of the ^{13}C spectral data are presented in Table 3 and the labelling scheme shown in Fig. 3. The resonances at around 70 ppm are

Table 1
Spectroscopic data

($FcCHCHC_5H_4N^+$–X), X shown below	Mass spectra (m/z)		Mössbauer		Water		Acetonitrile	
	Observed	Calculated	i.s. (mm s^{-1})	q.s. (mm s^{-1})	Band 1 — λ_{max} (nm) absorbance	Band 2 — λ_{max} (nm) absorbance	Band 1 — λ_{max} (nm) absorbance	Band 2 — λ_{max} (nm) absorbance
CH_3	304.07	304.1	0.54(1)	2.30(1)	542.8, 0.337	356.0, 1.379	542.8, 0.208	353.2, 1.179
C_2H_5	318.10	318.1	0.52(1)	2.27(1)	541.6, 0.293	356.0, 1.215	543.2, 0.287	355.2, 1.129
C_3H_7	332.11	332.2	0.53(1)	2.27(1)	542.4, 0.169	355.2, 0.687	542.4, 0.311	355.2, 1.174
C_4H_9	346.13	346.2	0.52(1)	2.25(1)	543.2, 0.322	357.6, 1.382	548.0, 0.327	357.2, 1.391
C_5H_{11}	360.15	360.2	0.51(1)	2.26(1)	543.2, 0.163	355.2, 0.586	548.8, 0.433	358.0, 1.826
$C_{10}H_{21}$	430.25	430.2	0.52(2)	2.24(1)	544.0, 0.186	356.8, 0.722	548.6, 0.517	357.6, 1.724
$C_{18}H_{37}$	542.41	542.2	0.53(1)	2.28(2)	550.4, 0.275	358.4, 1.023	548.8, 0.511	359.2, 2.149
O^-	305.3	305.1	0.54(1)	2.34(1)	471.6, 0.244	339.6, 1.964		

Table 2
^{1}H-NMR spectroscopic data

(FcCHCHC$_5$H$_4$N$^+$–X), X shown below	δ of ferrocenyl resonances H$_{2\text{ and }3}$ above H$_1$	δ of vinyl resonances H$_{\text{a and b}}$	δ of pyridiniumyl resonances H$_{1'\text{ and }2'}$	δ of quaternising group resonance. H$_{a'}$ only
CH_3 ($CDCl_3$) [18]	4.63, 1.8 Hz 4.58, 1.8 Hz 4.20	7.66, 15.6 Hz 6.66, 15.8 Hz	8.85, 6.6 Hz 6.8, 6.8 Hz	4.43
CH_3	4.79, 1.85 Hz 4.60, 1.85 Hz 4.24	8.04, 16.04 Hz 7.08, 16.04 Hz	8.89, 6.99 Hz 8.18, 6.99 Hz	4.46
C_2H_5	4.79, 1.85 Hz 4.61, 1.85 Hz 4.24	8.06, 15.84 Hz 7.09, 15.84 Hz	8.99, 6.99 Hz 8.20, 6.99 Hz	4.74, 7.40 Hz
C_3H_7	4.82, 1.86 Hz 4.58, 1.86 Hz 4.25	8.08, 16.04 Hz 7.11, 16.04 Hz	9.01, 7.00 Hz 8.20, 7.00 Hz	4.68, 7.43 Hz
C_4H_9	4.78, 1.85 Hz 4.61, 1.85 Hz 4.24	8.05, 16.04 Hz 7.09, 16.04 Hz	8.98, 7.00 Hz 8.20, 7.00 Hz	4.71, 7.40 Hz
C_5H_{11}	4.78, 1.85 Hz 4.60, 1.85 Hz 4.24	8.08, 16.04 Hz 7.11, 16.04 Hz	9.02, 6.78 Hz 8.21, 6.78 Hz	4.71, 7.40 Hz
$C_{10}H_{21}$	4.81, † Hz 4.60, † Hz 4.24	8.10, 15.64 Hz 7.12, 15.64 Hz	9.01, 6.60 Hz 8.22, 6.60 Hz	4.73, 7.41 Hz
$C_{18}H_{37}$	4.80, 1.98 Hz 4.60, 1.98 Hz 4.24	8.09, 16.50 Hz 7.11, 16.50 Hz	9.03, 6.60 Hz 8.22, 6.60 Hz	4.72, 7.26 Hz
O^-	4.58, 1.99 Hz 4.37, 1.99 Hz 4.16	7.19, 16.25 Hz 6.77, 16.25 Hz	8.06, 6.38 Hz 7.49, 6.38 Hz	

^{1}H-NMR data recorded in d^6-acetone, referenced to TMS. Chemical shifts in ppm. †, resonance not observed.

typical of the ferrocenyl group [24]. No resonance which could be assigned to the quaternary carbon C_4 was observed in any of the compounds. The ^{13}C chemical shift of ethene is 123 ppm, the two resonances in this area of the spectra for Fc–CH=CH–$C_5H_4N^+$–X were therefore assigned to the vinyl carbons [25], and the higher field resonances were assigned to the pyridiniumyl carbons [25]. The coupling constants of the vinyl protons is similar for all compounds showing that all the compounds are in the *E* configuration across the C=C.

2.4. Nonlinear optical properties

The products both ground and unground were examined by scanning electron microscopy and by the Kurtz powder technique for SHG measurement. Table 4 shows the results of these studies. Particle sizes are approximate and are measured from the electron micrographs shown in Fig. 4.

The first point which must be addressed is that the SHGs of Fc–CH=CH–$C_5H_4N^+$–CH_3 are much lower than that reported in the literature (220 times the SHG of urea) [9]. This disparity could be caused by either a difference in the particle morphology or by slight differences in the measurement technique. Differences in particle size could also explain the change in the order of the SHG of the ground and unground samples [4]. We note that Marder et al. [9] reported that their samples were ground to microcrystalline powders; particles were estimated to span 40–150 μm. The authors also state that "given the typically broad range of sizes and the possibility of preferential orientation of particles, the uncertainty in the measured efficiencies can be quite large, perhaps a factor of two or more." However, the SHG results suggest that the CH_3, C_2H_5 and C_3H_7 derivatives show a noticeable SHG for both ground and unground samples. The results show that

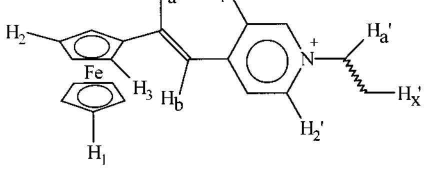

Fig. 2. ^{1}H-NMR assignment scheme.

Table 3
^{13}C-NMR spectroscopic data

($FcCHCHC_5H_4N^+$–X), X shown below	δ of ferrocenyl resonances			δ of vinyl resonances	δ of pyridiniumyl resonances		δ of alkyl group resonances
	C_1	$C_{2 \text{ and } 3}$	C_4	$C_{a \text{ and } b}$	$C_{1'}$	$C_{2'}$ and $C_{3'}$	$C_{a'}$ only
CH_3	68.92, 5	70.90, 2; 68.07, 2	†	118.58, 121.79	154.63, 1	145.38, 2; 143.91, 2	67.55
C_2H_5	70.73, 5	72.70, 2; 69.88, 2	†	123.90, 120.38	154.80, 1	145.26, 2; 144.59, 2	56.60
C_3H_7	70.72, 5	72.65, 2; 69.90, 2	†	123.83, 120.41	154.73, 1	145.22, 2; 144.82, 2	60.80
C_4H_9	70.68, 5	72.61, 2; 69.86, 2	†	123.80, 120.36	154.71, 1	145.21, 2; 144.76, 2	60.79
C_5H_{11}	70.74, 5	72.68, 2; 69.90, 2	†	123.84, 120.43	154.78, 1	145.27, 2; 144.83, 2	61.06
$C_{10}H_{21}$	70.74, 5	72.65, 2; 69.92, 2	†	123.83, 120.44	154.77, 1	145.25, 2; 144.83, 2	61.04
$C_{18}H_{37}$	70.74, 5	72.65, 2; 69.95, 2	†	123.76, 120.35	154.72, 1	145.20, 2; 144.76. 2	61.02
O^-	7.060, 5	70.49, 2; 68.18, 2	69.31, 1	123.32, 122.50	135.85, 1	132.25, 2; 127.81, 2	69.86

^{13}C-NMR data recorded in d^6-acetone, referenced to TMS. Chemical shifts in ppm. †, resonance not observed.

the SHG is affected by the particle size of the material and that this affect cannot readily be predicted, additionally the first molecular hyperpolarisability vectors combined with the packing of the powder will affect how the frequency doubled emission interferes constructively and destructively with itself altering the measured bulk SHG. Thus the results of Kurts powder SHG measurements are best used as an indicator of SHG activity and this suggests that for comparison the SHG measured on the ground samples is a better comparative measure of the bulk SHG. It appears that as the chain length of the R groups increases the SHG decreases. The low values as the chain length increases may be caused by a change in the molecular packing of the crystal (not necessarily causing a change in the crystallographic space group and not resulting in a centrosymmetric space group) or leading to the molecules becoming increasingly amorphous with increasing chain length. The NMR studies of the materials in solution suggest that the structure and electronic environment of the materials vary only very slightly in solution and this would be relevant to any study of the molecular hyperpolarisabilities; however, it is difficult to make any comment on the solid state structure and packing as no high quality powder X-ray diffraction patterns could be recorded during this work. The compounds could not be crystallised without significant decomposition occurring. The Mössbauer spectra show that there is little variation in the electron density around the ferrocenyl group in these compounds indicating that there is little chance of a dramatic conformational change having occurred across the series of materials.

Although, the SHGs of the compounds do not show a direct relationship between the length of the chain (R) and the SHG, the results show that such changes dramatically affect the SHG and that the compounds with the shorter R chains, the stronger electron donors, have the largest SHG values in this system.

3. Experimental

UV spectra were recorded using a Perkin–Elmer λ3 spectrometer. IR spectra were recorded using a Perkin–Elmer 1600 FTIR spectrometer, NMR spectra were recorded using a JEOL EX 270 spectrometer. Mass spectra were recorded by M-Scan, all at room temperature. Electron microscopy was carried out using a Cambridge Instruments, Stereoscan 360. Kurtz powder SHG measurements were made at 1.907 μm using 0.1 mJ pulses at 3 Hz with a pulse width of 8 ns. Mössbauer spectra were recorded at 80 K with the previously reported methodology [26]. All chemicals were of at least Analar grade and were used as purchased unless otherwise stated.

Preparation of 1-alkyl-4-picolinium iodides was achieved by simple methods [27]. 4-Picoline-*N*-oxides were prepared according to the literature procedure using H_2O_2 [28]. The experimental method used was the

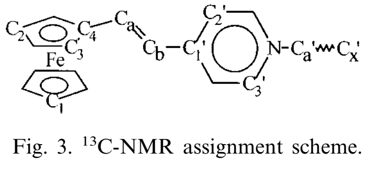

Fig. 3. ^{13}C-NMR assignment scheme.

Table 4
SHG by Kurtz powder technique

($FcCHCHC_5H_4N^+$–X), X shown below	Particle size (μm)	SHG vs. urea	Particle size (μm)	SHG vs. urea
CH_3	200	9.2	20	11.7
C_2H_5	300	14.6	20	0.4
C_3H_7	150	0.5	20	2.9
C_4H_9	500	0.3	20	0.2
C_5H_{11}	160	0.4	20	0.3
$C_{10}H_{21}$	125	0.5	20	0.4
$C_{18}11_{37}$	250	0.6	20	0.3
O^-			20	0.3

same for all compounds, except for Fc–CH=CH–$C_5H_4N^+$–O^- for which K^tBuO was used instead of Et_3N.

3.1. Preparation of *E-1-ferrocenyl-2-(4-methyl pyridiniumyl)ethylene iodide*

Ferrocene carboxaldehyde (5 g, 0.02 mol), methyl-4-picolinium iodide (2.35 g, 0.01 mol) and Et_3N (5 ml) were dissolved in dry EtOH (50 ml), over 3 Å molecular sieves, in a reflux apparatus under dry dinitrogen. The reaction mixture was then heated under reflux for 8 h, then allowed to cool and the EtOH evaporated off. Portions of the crude reaction mixture were then purified on a neutral alumina column using MeCN as the eluant.

Figs. 1 and 2 present the labelling system used to assign the NMR resonances.

3.1.1. *Fc–CH=CH–$C_5H_4N^+$–CH_3I^-*

^{1}H-NMR (($(CD_3)_2CO$, 270 MHz): $\delta = 8.89$ (d, $J=6.99$ Hz, 2H, H'_2), 8.18 (d, $J=6.99$ Hz, 2H, H'_1), 8.04 (d, $J=16.04$ Hz, 1H, H_a), 7.08 (d, $J=16.04$ Hz, 1H, H_b), 4.79 (t, $J=1.85$ Hz, 2H, $H_{2\text{ or }3}$), 4.60 (t, $J=1.85$ Hz, 2H, $H_{2\text{ or }3}$), 4.46 (s, 3H, H'_a), 4.20 (s, 5H, H_1). ^{13}C-NMR (($(CD_3)_2CO$, 270 MHz), $\delta = 154.63$ (1C, $C_{1'}$), 145.38 (2C, $C_{2'\text{ or }3'}$), 143.91 (2C, $C_{2'\text{ or }3'}$), 121.79 (1C, C_a or b), 118.58 (1C, $C_{a\text{ or }b}$), 70.90 (2C, $C_{2\text{ or }3}$), 68.92 (5C, C_1), 68.07 (2C, $C_{2\text{ or }3}$), 67.55 (1C, $C_{a'}$). ^{57}Fe Mössbauer (relative to iron foil): i.s. 0.54(1), q.s. 2.30(1); Γ, 0.14(1). Anal. Found: C, 50.05; H, 4.21; N, 3.27. Calc.: C, 50.15, H, 4.21, N, 3.25%.

3.1.2. *Fc–CH=CH–$C_5H_4N^+$–$C_2H_5I^-$*

^{1}H-NMR (($(CD_3)_2CO$, 270 MHz): $\delta = 8.99$ (d, $J=6.99$ Hz, 2H, H'_2), 8.20 (d, $J=6.99$ Hz, 2H, H'_1), 8.06 (d, $J=15.84$ Hz, 1H, H_a), 7.09 (d, $J=15.84$ Hz, 1H, H_b), 4.79 (t, $J=1.85$ Hz, 2H, $H_{2\text{ or }3}$), 4.74 (qu, $J=7.40$ Hz, 2H, H_a), 4.61 (t, $J=1.85$ Hz, 2H, $H_{2\text{ or }3}$), 4.24 (s, 5H, H_1), 1.70 (t, $J=7.40$ Hz, 3H, H'_b). ^{13}C-NMR (($(CD_3)_2CO$, 270 MHz): $\delta = 154.80$ (1C, $C_{1'}$), 145.26 (2C, $C_{2'\text{ or }3'}$), 144.59 (2C, $C_{2'\text{ or }3'}$), 123.90 (1C, $C_{a\text{ or }b}$), 120.38 (1C, $C_{a\text{ or }b}$), 72.70 (2C, $C_{2\text{ or }3}$), 70.72 (5C, C_1), 69.88 (2C, $C_{2\text{ or }3}$), 56.60 (1C, C_a), 16.73 (1C, C_b). ^{57}Fe Mössbauer (relative to iron foil): i.s. 0.52(1), q.s. 2.27(1); Γ, 0.13(1). Anal. Found: C, 51.15; H, 4.53; N, 3.17. Calc.: C, 51.27; H, 4.53; N, 3.17%.

3.1.3. *Fc–CH=CH–$C_5H_4N^+$–$C_3H_7I^-$*

^{1}H-NMR (($(CD_3)_2CO$, 270 MHz): $\delta = 9.01$ (d, $J=7.00$ Hz, 2H, H'_2), 8.22 (d, $J=7.00$ Hz, 2H, H'_1), 8.08 (d, $J=16.04$ Hz, 1H, H_a), 7.11 (d, $J=16.04$ Hz, 1H, H_b), 4.82 (t, $J=1.86$ Hz, 2H, $H_{2\text{ or }3}$), 4.68 (t, $J=4.73$ Hz, 2H, H'_a), 4.58 (t, $J=1.86$ Hz, 2H, $H_{2\text{ or }3}$), 4.25 (s, 5H,

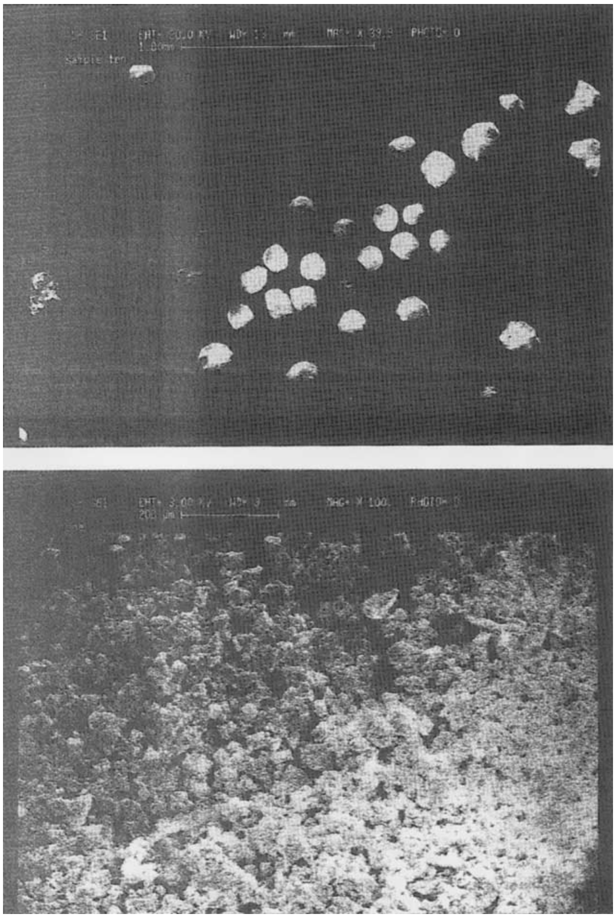

Fig. 4. SEM images of unground (top) and ground (bottom) [Fc–CHCH–C_5H_5N–CH_3][I].

H_1)), 1.44 (se, $J = 3.22$ Hz, 2H, H'_b), 0.98 (t, $J = 3.29$ Hz, 3H, H_c). ^{13}C-NMR ((CD_3)$_2$CO, 270 MHz;), $\delta =$ 154.73 (1C, $C_{1'}$), 145.22 (2C, $C_{2'\text{ or }3'}$), 144.82 (2C, $C_{2'\text{ or}}$ 3'), 123.83 (1C, $C_{a\text{ or }b}$), 120.41 (1C, $C_{a\text{ or }b}$), 72.65 (2C, $C_{2\text{ or }3}$), 70.72 (5C, C_1), 69.90 (2C, $C_{2\text{ or }3}$), 60.80 (1C, C_a), 33.93 (1C, C_b), 13.81 (1C, C_c). ^{57}Fe Mössbauer (relative to iron foil): i.s. 0.53(1), q.s. 2.27(1); Γ, 0.15(1). Anal. Found: C, 52.24; H, 4.83; N, 3.06. Calc.: C, 52.32; H, 4.83; N, 3.05%.

3.1.4. Fc–CH=CH–$C_5H_4N^+$–$C_4H_9I^-$

^{1}H-NMR ((CD_3)$_2$CO, 270 MHz): $\delta = 8.98$ (d, $J = 7.0$ Hz, 2H, H'_2), 8.20 (d, $J = 7.0$ Hz, 2H, H'_1), 8.05 (d, $J = 16.04$ Hz, 1H, H_a), 7.09 (d, $J = 16.04$ Hz, 1H, H_b), 4.78 (t, $J = 1.85$ Hz, 2H, $H_{2\text{ or }3}$), 4.71 (t, $J = 7.40$ Hz, 2H, H'_a), 4.61 (t, $J = 1.85$ Hz, 2H, $H_{2\text{ or }3}$), 4.24 (s, 5H, H_1), 1.46 (q, $J = 7.82$ Hz, 2H, H'_c), 0.98 (t, $J = 7.82$ Hz, 3H, H'_d). [Hb resonance obscured by solvent.] ^{13}C-NMR ((CD_3)$_2$CO, 270 MHz): $\delta = 154.71$ (1C, $C_{1'}$), 145.21(2C, $C_{2'\text{ or }3'}$), 144.76 (2C, $C_{2'\text{ or }3'}$), 123.80 (1C, C_a or b), 120.36 (1C, $C_{a\text{ or }b}$), 72.61 (2C, $C_{2\text{ or }3}$), 70.68 (5C, C_1), 69.86 (2C, $C_{2\text{ or }3}$), 60.79 (1C, C_a), 33.34 (1C, C_b), 18.47 (1C, C_c), 13.16 (1C, C_d). ^{57}Fe Mössbauer (relative to iron foil): i.s. 0.52(1), q.s. 2.25(1); Γ, 0.14(1). Anal. Found: C, 53.22; H, 5.12; N, 2.98. Calc.: C, 53.31; H, 5.11; N, 2.69%.

3.1.5. Fc–CH=CH–$C_5H_4N^+$–$C_5H_{11}I^-$

^{1}H-NMR ((CD_3)$_2$CO, 270 MHz): $\delta = 9.02$ (d, $J =$ 6.78 Hz, 2H, H'_2), 8.21 (d, $J = 6.78$ Hz, 2H, H'_1), 8.08 (d, $J = 16.04$ Hz, 1H, H_a), 7.11 (d, $J = 16.04$ Hz, 1H, H_b), 4.78 (t, $J = 1.85$ Hz, 2H, $H_{2\text{ or }3}$), 4.71 (t, $J = 7.40$ Hz, 2H, H'_a), 4.60 (t, $J = 1.85$ Hz, 2H, $H_{2\text{ or }3}$), 4.24 (s, 5H, H_1), 2.12 (multiplet, 2H, H_b), 1.42 (m, 4H, $H_{c\text{ and }d}$), 0.91 (t, $J = 6.99$ Hz, 3H, H'_e). ^{13}C-NMR ((CD_3)$_2$CO, 270 MHz): $\delta = 154.78$ (1C, $C_{1'}$), 145.27 (2C, $C_{2'\text{ or }3'}$), 144.83 (2C, $C_{2'\text{ or }3'}$), 123.84 (1C, $C_{a\text{ or }b}$), 120.43 (1C, C_a or b), 72.68 (2C, $C_{2\text{ or }3}$), 70.74 (5C, C_1), 69.90 (2C, C_2 or 3), 61.06 (1C, C_a), 31.67 (1C, C_b), 22.78 (1C, C_d), 14.13 (1C, C_e). [C_c probably obscured by solvent.] ^{57}Fe Mössbauer (relative to iron foil): i.s. 0.51(1), q.s. 2.26(1); Γ, 0.13(1). Anal. Found: C, 54.17; H, 5.39; N, 2.89. Calc.: C, 54.24; H, 5.38; N, 2.87%.

3.1.6. Fc–CH=CH–$C_5H_4N^+$–$C_{10}H_{21}I^-$

^{1}H-NMR ((CD_3)$_2$CO, 270 MHz): $\delta = 9.01$ (d, $J =$ 6.60 Hz, 2H, H'_2), 8.22 (d, $J = 6.60$ Hz, 2H, H'_1), 8.10 (d, $J = 15.64$ Hz, 1H, H_a), 7.12 (d, $J = 15.84$ Hz, 1H, H_b), 4.81 (multiplet, 2H, $H_{2\text{ or }3}$), 4.73 (t, $J = 7.41$ Hz, 2H, H'_a), 4.60 (t, $J = 7.41$ Hz, 2H, $H_{2\text{ or }3}$), 4.24 (s, 5H, H_1), 1.41 and 1.28 (m, 14H, $H'_{b\text{ to }h}$), 0.867 (m, 5H, $H'_{i\text{ and }j}$). ^{13}C-NMR ((CD_3)$_2$CO, 270 MHz): $\delta = 154.77$ (1C, $C_{1'}$), 145.25 (2C, $C_{2'\text{ or }3'}$), 144.83 (2C, $C_{2'\text{ or }3'}$), 123.83 (1C, C_a or b), 120.44 (1C, $C_{a\text{ or }b}$), 72.65 (2C, $C_{2\text{ or }3}$), 70.74 (5 C, C_1), 69.92 (2C, $C_{2\text{ or }3}$), 61.04 (1C, C_a), 32.60 (1C, C_b), 30.63 (2C, $C_{c\text{ and }d}$), 30.01 (3C, $C_{e\text{ to }g}$), 26.74 (1C, C_h), 23.33 (1C, C_i) 14.37 (1C, C_j). ^{57}Fe Mössbauer (relative to iron foil): i.s. 0.52(2), 2.24(1); Γ, 0.16(1). Anal. Found: C, 58.15; H, 6.52; N, 2.52. Calc.: C, 58.19; H, 6.51; N, 2.51%.

3.1.7. Fc–CH=CH–$C_5H_4N^+$–$C_{18}H_{37}I^-$

^{1}H-NMR ((CD_3)$_2$CO, 270 MHz): $\delta = 9.03$ (d, $J =$ 6.60 Hz, 2H, H'_2), 8.22 (d, $J = 6.60$ Hz, 2H, H'_1), 8.09 (d, $J = 16.50$ Hz, 1H, H_a), 7.11 (d, $J = 16.50$ Hz, 1H, H_b), 4.80 (t, $J = 1.98$ Hz, 2H, $H_{2\text{ or }3}$), 4.722 (t, $J = 7.26$ Hz, 2H, H'_a), 4.60 (t, $J = 1.98$ Hz, 2H, $H_{2\text{ or }3}$), 4.244 (s, 5H, H_1), 1.28 (multiplet, 32H, $H'_{b\text{ to }q}$), 0.88 (t, $J = 7.05$ Hz, 3H, H'_r). ^{13}C-NMR ((CD_3)$_2$CO, 270 MHz): $\delta = 154.72$ (1C, $C_{1'}$), 145.20 (2C, $C_{2'\text{ or }3'}$), 144.76 (2C, $C_{2'\text{ or }3'}$), 123.76 (1C, $C_{a\text{ or }b}$), 120.35 (1C, $C_{a\text{ or }b}$), 72.65 (2C, C_2 or 3), 70.74 (5C, C_1), 69.95 (2C, $C_{2\text{ or }3}$), 61.02 (1C, C_a), 32.60 (1C, C_b), 31.95 (2C, C_c), 31.65 (1C, C_d), 31.38 (1C, C_e), 31.10 (1C, C_f), 30.95 (1C, C_g), 30.88 (2C, C_h), 30.81 (1C, C_i), 30.20 (4C, $C_{j\text{ to }m}$), 28.82 (1C, C_n), 28.52 (1C, C_o), 26.69 (1C, C_p), 23.28 (1C, C_q), 14.31 (1C, C_r). ^{57}Fe Mössbauer (relative to iron foil): i.s. 0.53(1), q.s. 2.28(2); Γ, 0.14(2). Anal. Found: C, 62.76; H, 7.85; N, 2.10. Calc.: C, 62.79; H, 7.83; N, 2.09%.

3.1.8. Fc–CH=CH–$C_5H_4N^+$–O^-

^{1}H-NMR ((CD_3)$_2$CO, 270 MHz): $\delta = 8.06$ (d, $J =$ 6.38 Hz, 2H, H'_2), 7.49 (d, $J = 6.38$ Hz, 2H, H'_1), 7.19 (d, $J = 16.25$ Hz, 1H, H_a), 6.77 (d, $J = 16.25$ Hz, 1H, H_b), 4.58 (t, $J = 1.99$ Hz, 2H, $H_{2\text{ or }3}$), 4.37 (t, $J = 1.99$ Hz, 2H, $H_{2\text{ or }3}$), 4.16 (s, 5H, H_1). ^{13}C-NMR ((CD_3)$_2$CO, 270 MHz): $\delta = 135.85$ (1C, $C_{1'}$), 132.25 (2C, $C_{2'\text{ or }3'}$), 127.81(2C, $C_{2'\text{ or }3'}$), 123.32 (1C, $C_{a\text{ or }b}$), 122.50 (1C, C_a or b), 70.49 (2C, $C_{2\text{ or }3}$), 70.06 (5C, C_1), 69.31, 154.72 (1C, $C_{1'}$), 145.20 (2C, $C_{2'\text{ or }3'}$), 144.76 (2C, $C_{2'\text{ or }3'}$), 123.76 (1C, $C_{a\text{ or }b}$), 120.35 (1C, $C_{a\text{ or }b}$), 72.65 (2C, C_2 or 3), 70.74 (5C, C_1), 69.95 (1C, C_4) 69.18 (2C, $C_{2\text{ or }3}$). ^{57}Fe Mössbauer (relative to iron foil): i.s. 0.54(1), q.s. 2.34(1); Γ, 0.13(1). Anal. Found: C, 66.89; H, 4.96; N, 4.63. Calc.: C, 66.91; H, 4.95; N, 4.59%.

4. Conclusions

Condensation of ferrocene carboxaldehyde with an 1-alkyl-4-picolinium iodide offers a suitable method for the preparation of the compounds detailed above. The Me-, Et- and Pr-derivatives exhibit a significant SHG measured by the Kurtz powder technique. The results of this study indicate that changing the chain length of the quatenising group dramatically influences the SHG with the highest SHGs being measured for the strongest electron donating, short chain R groups (Me $\approx$ Et $\geq$ Pr). These compounds are however probably unsuited to industrial applications due to their decomposition in a wet atmosphere.

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