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New chiral ferrocenyl-pyridinium salts for non-linear optics

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Abstract

Three enantiomerically pure chiral analogues of 4-[(*E*)-2-ferrocenyl-ethenyl]pyridinium iodide have been synthesized. Their bulk efficiencies in second harmonic generation (SHG) have been measured (from 0 to 0.25 times that of urea). Furthermore, the crystal structures for two of them and for the parent 4-[(*E*)-2-ferrocenyl-ethenyl]pyridinium iodide have been determined by X-ray diffraction studies. Crystal packing could explain the very different SHG bulk efficiencies in this family of materials. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Iron; Ferrocene; Chirality; Pyridinium; Non-linear optics; Crystal packing

1. Introduction

The search for materials with highly nonlinear optical (NLO) responses is currently of great scientific and technological interest [1]. These efforts have been made first on inorganic solids but are now focused on organic materials [2]. Nevertheless, organometallic compounds have recently received growing attention because of the large variety of structures available by changing the metals, their oxidation states but also by tuning the electronic or steric properties of the ligands in the coordination sphere [3]. Two characteristics are required for materials to possess quadratic NLO properties: first each chromophore has to possess a molecular hyperpolarizability as large as possible and secondly the different chromophores have to be arranged in a non-centrosymmetrical environment. This non-centrosymmetrical arrangement can essentially be obtained by two ways: poling of polymers or crystallization [1]. An established strategy to avoid centrosymmetry in the crystals is to use enantiomerically pure chiral chromophores [4]. We recently used this strategy with different *E*-4-nitrostyrylferrocenes [5]. The achiral parent molecule possesses a large molecular hyperpolarizability ($\beta = 31 \times 10^{-30}$ esu) [6] but is inactive in the solid state because of a probable centrosymmetrical crystal packing [7]. By introducing, in a stereocontrolled manner, different substituents, we obtained a series of enantiomerically pure chiral analogues of *E*-4-nitrostyrylferrocene with a substituent in the 2 position of the ferrocene moiety. With small substituents like methyl, the planar chirality, even if it ensured a non-centrosymmetrical packing, was not sufficient to overcome efficiently the strong tendency for head-to-tail arrangement of the chromophores. So a pseudo-centrosymmetrical crystal packing associated with a low bulk efficiency (eight times that of urea) was observed. But with larger substituents like trimethylsilyl, chromophores packed in a completely different manner, clearly far away from centrosymmetrical arrangement and therefore high bulk efficiency (up to 100 times that of urea) have been obtained [5].

(*E*)-1-Ferrocenyl-2-(1-methyl-4-pyridinium)ethylene salts, developed by Marder et al., possess very variable bulk efficiencies according to the counterion (from 0 to 220 times that of urea) [8]. We were interested to know if our previous strategy of using chiral analogues by introducing substituents in the 2 position of the ferrocene could be successfully applied to this set of chromophores which seemed very attractive because of the high level of bulk efficiency already reached and because of the high sensitivity to small variations (counterions) on crystal packing.

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2. Experimental

2.1. Synthesis of the chiral chromophores

Compound **5a** was synthesized following Ref. [8]. The enantiomerically pure acetals **1** and the aldehydes **2** were obtained by literature procedure [9]. Physical data for **1b**, **1c**, **2b**, **2c**, **2d** are identical to those of the literature [9,10].

2.2. General procedure for the synthesis of the pyridines 4: synthesis of (E)-1-[(R)-2-methyl-ferrocenyl]-2-(4-pyridinyl)ethylene (4b)

A solution of 0.4 ml (4.1 mmol, 1.3 equivalents) of distilled 4-picoline and of 9.6 ml of dry THF was cooled down to −78 °C in a Schlenk tube under argon; 2.2 ml (3.5 mmol, 1.1 equiv.) of a 1.5 M solution of butyllithium in hexane was slowly added: the solution turned yellow The mixture was stirred for 1 h at −78 °C. A solution containing 0.74 g (3.2 mmol) of **2b** in 9.6 ml of dry THF was then added. The mixture was stirred for 1 h at −78 °C and then allowed to slowly come back to room temperature (r.t.) overnight. The mixture was hydrolyzed by adding few milliliters of methanol then water. The organic phase was extracted by ether, washed by brine, dried on sodium sulfate and then evaporated. The crude material was purified by flash chromatography on silicagel with ether as eluent to yield 730 mg of pure **3b** as a yellow–orange oil (yield = 68%).

In a round-bottomed flask equipped with a Dean–Stark apparatus placed under argon, 230 mg (1.2 mmol, 0.6 equiv.) of *p*-toluenesulfonic acid monohydrate and 0.63 g (1.90 mmol) of **3b** were dissolved in 230 ml of toluene. The solution was heated up during 5 h in order to distil the water/toluene azeotrope: a strong red color appeared after 20 min heating. After cooling back to r.t., 5 ml of 2 M solution of sodium hydroxide was added. The organic phase was extracted by dichloromethane, washed by brine, dried on sodium sulfate and then evaporated. The crude material was first filtered on a silicagel column and then more thoroughly purified by flash chromatography on silicagel with a ether/triethylamine mixture as eluent; 570 mg of **4b** as a orange powder was isolated (yield = 58%).

^{1}H-NMR (CDCl$_3$): δ (ppm): 8.51 (m, 2H, Py), 7.29 (m, 2H, Py), 7.22 (d, $J = 16.1$ Hz, 1H, vinyl), 6.60 (d, $J = 16.1$ Hz, 1H, vinyl), 4.52 (m, 1H, subst Cp), 4.28 (m, 1H, subst Cp), 4.26 (m, 1H, subst Cp), 4.06 (s, 5H, Cp), 2.13 (s, 3H, CH$_3$). ^{13}C-NMR (CDCl$_3$): δ (ppm): 150.1 (Py), 145.2 (quat., Py), 131.2 (vinyl), 123.3 (vinyl), 120.2 (Py), 84.1 (quat., Cp), 80.4 (quat., Cp), 71.6 (Cp subst.), 70.0 (Cp), 67.8 (subst Cp), 65.0 (subst Cp), 13.7 (CH$_3$). Anal. calc. for $C_{18}H_{17}FeN$: C, 71.31, H, 5.65, N, 4.62. Found: C, 69.97, H, 5.83, N, 4.38. $[\alpha]_D = +1028$ ($c = 0.015$, CHCl$_3$). UV–vis: $\lambda_{max} = 472$ nm ($\varepsilon = 4005$, CHCl$_3$).

2.3. Synthesis of (E)-1-[(S)-2-trimethylsilyl-ferrocenyl]-2-(4-pyridinyl)-ethylene (4c): yield = 32%

^{1}H-NMR (CDCl$_3$): δ (ppm): 8.51 (m, 2H, Py), 7.25–7.20 (m, 2H Py + 1H vinyl), 6.59 (d, $J = 16.0$ Hz, 1H, vinyl), 4.78 (m, 1H, subst Cp), 4.52 (m, 1H, subst Cp), 4.26 (dd, $J = 2.4$ and 1.2 Hz, 1H, subst Cp), 4.13 (s, 5H, Cp), 0.35 (s, 9H, SiMe$_3$). ^{13}C-NMR (CDCl$_3$): δ (ppm): 150.1 (Py), 145.1 (quat., Py), 132.9 (vinyl), 123.6 (vinyl), 120.1 (Py), 86.1 (quat., Cp), 75.9 (subst Cp), 73.3 (quat., Cp), 71.8 (subst Cp), 69.4 (Cp), 68.1 (subst Cp), 0.7 (SiMe$_3$). Anal. calc. for $C_{20}H_{23}FeNSi$: C, 66.48, H, 6.42, N, 3.88. Found: C, 69.97, H, 5.83, N, 3.90. $[\alpha]_D = +610$ ($c = 0.015$, CHCl$_3$). UV–vis: $\lambda_{max} = 464$ nm ($\varepsilon = 1705$, CHCl$_3$).

2.4. Synthesis of (E)-1-[(S)-2-formyl-ferrocenyl]-2-(4-pyridinyl)ethylene (4e)

Same procedure as for **4b** but at the end of the reaction, water was added and the mixture was heated up to 60 °C during 1 h. Compound **4e** was obtained as a purple oil (yield = 27%) which have been immediately reduced to **4f**.

^{1}H-NMR (CDCl$_3$): δ (ppm): 10.17 (1H, s, CHO), 8.55 (m, 2H, Py), 7.34 (m, 2H, Py), 7.33 (d, $J = 16.1$ Hz, 1H, vinyl), 6.78 (d, $J = 16.1$ Hz, 1H, vinyl), 5.05 (m, 1H, subst Cp), 4.89 (m, 1H, subst Cp), 4.74 (m, 1H, subst Cp), 4.27 (s, 5H, Cp).

2.5. Synthesis of (E)-1-[(S)-2-hydroxymethyl-ferrocenyl]-2-(4-pyridinyl)-ethylene (4f)

Compound **4b** (140 mg, 0.4 mmol) was dissolved in 9 ml of methanol under argon. To this solution cooled down to 0 °C , was slowly added a solution of 250 mg (6.5 mmol, 15 equiv.) of sodium borohydride in 9 ml of a 2 M aqueous solution of sodium hydroxide. The mixture is stirred overnight at r.t. then extracted with dichloromethane washed with brine and dried on sodium sulfate. After evaporation of the solvent, the crude material was purified by flash chromatography on silicagel with an ethyl acetate/methanol mixture as eluant to yield 4 g as an orange oil (110 mg, yield = 79%).

^{1}H-NMR (CDCl$_3$): δ (ppm): 8.41 (m, 2H, Py), 7.20 (m, 2H, Py), 7.16 (d, $J = 16.1$ Hz, 1H, vinyl), 6.60 (d, $J = 16.1$ Hz, 1H, vinyl), 4.58 (s, 2H, CH$_2$), 4.46 (m, 1H, subst Cp), 4.41 (m, 1H, subst Cp), 4.35 (m, 1H, subst Cp), 4.10 (s, 5H, Cp), 3.32 (s, 1H, OH). ^{13}C-NMR (CDCl$_3$): δ (ppm): 149.7 (Py), 145.1 (quat., Py), 130.5 (vinyl), 124.0 (vinyl), 120.3 (Py), 87.0 (quat., Cp), 80.9 (quat., Cp), 71.2 (subst. Cp), 69.6 (Cp), 68.8 (subst Cp), 66.5 ppm (subst Cp), 59.0 (CH_2OH). Anal. calc. for $C_{18}H_{17}FeNO$: C, 67.73, H, 5.37, N, 4.39. Found: C, 66.26, H, 5.34, N, 4.04. $[\alpha]_D = -827$, ($c = 0.03$, $CHCl_3$). UV–vis: $\lambda_{max} = 462$ nm ($\varepsilon = 1360$, $CHCl_3$).

*2.6. General procedure for the synthesis of the pyridiniums **5**: synthesis of 4-[(E)-2-[(R)-2′-methylferrocenyl]-ethenyl]pyridinium iodide (**5b**)*

Compound **4b** (520 mg, 1.7 mmol) was dissolved in 15 ml of dry ether in a Schlenk tube under argon. To the solution was added 0.35 ml (5.6 mmol, 3 equiv.) of iodomethane. The mixture was stirred overnight at r.t.: a dark purple precipitate appeared steadily. The solid was filtered on a sintered glass funnel and washed with ether to yield 310 mg of a dark purple powder (yield = 40%).

^{1}H-NMR ($CDCl_3$): δ (ppm): 8.97 (m, 2H, Py), 7.84 (m, 3H, 2H Py + 1H vinyl), 6.73 (d, $J = 16$ Hz, 1H, vinyl), 4.66 (m, 1H, subst Cp), 4.56 (s, 3H, N–CH_3), 4.45 (m, 2H, subst Cp), 4.13 (s, 5H, Cp), 2.16 (s, 3H, CH_3). ^{13}C-NMR (CD_3OD): δ (ppm): 155.6 (quat., Py), 145.9 (Py), 144.8 (vinyl), 124.0 (Py), 120.7 (vinyl), 88.1 (quat., Cp), 80.2 (quat., Cp.), 75.0 (subst Cp), 71.9 (Cp), 71.5 (subst Cp), 67.3 (subst Cp), 47.7 (N–CH_3), 13.8 (CH_3). Anal. calc. for $C_{19}H_{20}FeNI$: C, 51.27, H, 4.53, N, 3.15. Found: C, 50.75, H, 3.96, N, 3.18. MS (FAB): 318 (M-127, 100%), 157 (27%), 136 (50%). $[\alpha]_{436} = -7255$ ($c = 0.002$, $CHCl_3$). UV–vis: $\lambda_{max} = 596$ nm ($\varepsilon = 9095$, $CHCl_3$).

*2.7. Synthesis of 4-[(E)-2-[(S)-2′-trimethylsilylferrocenyl]-ethenyl]-pyridinium iodide (**5c**): yield = 85%*

^{1}H-NMR (CD_3OD): δ (ppm): 10.28 (d, $J = 6.8$ Hz, 2H, Py), 9.51 (d, $J = 6.8$ Hz, 2H, Py), 9.24 (d, $J = 15.8$ Hz, 1H, vinyl), 8.52 (d, $J = 15.8$ Hz, 1H, vinyl), 6.51 (m, 1H, subst Cp), 6.14 (t, $J = 2.3$ Hz, 1H, subst Cp), 5.88 (d, $J = 2.3$ Hz and 1.2 Hz, subst Cp), 5.81 (s, 3H, CH_3), 5.61 (5H, s, Cp) 1.74 (s, 9H, $Si(CH_3)_3$). ^{13}C-NMR (CD_3OD): δ (ppm): 155.2 (quat., Py), 146.1 (Py), 145.8 (vinyl), 124.0 (Py), 121.3 (vinyl), 85.9 (quat., Cp), 79.7 (subst Cp), 77.3 (quat., Cp.), 75.6 (subst Cp), 71.4 (Cp), 70.9 (subst Cp), 47.8 (CH_3), 1.2 ($Si(CH_3)_3$). Anal. calc. for $C_{21}H_{29}FeNISi$: C, 50.12, H, 5.21, N, 2.78. Found: C, 50.31, H, 5.01, N, 2.68. MS (FAB): 376 (M-127, 100%), 304 (9%), 259 (18%). $[\alpha]_{436} = -741$ ($c = 0.03$, $CHCl_3$). UV–vis: $\lambda_{max} = 584$ nm ($\varepsilon = 5130$, $CHCl_3$).

*2.8. Synthesis of 4-[(E)-2-[(S)-2′-hydroxymethylferrocenyl]-ethenyl]-pyridinium iodide (**5f**): yield = 40%*

^{1}H-NMR (CD_3OD): δ (ppm): 8.70 (d, $J = 6.8$ Hz, 2H, Py), 8.14 (d, $J = 6.8$ Hz, 2H, Py), 8.07 (d, $J = 15.9$ Hz, 1H, vinyl), 7.10 (d, $J = 15.9$ Hz, 1H, vinyl), 4.98 (m, 1H, subst Cp), 4.81 (d, AB system, $J = 12$ Hz, 1H, CH_2), 4.76 (m, 1H, subst Cp), 4.70 (t, $J = 2.5$ Hz, 1H, subst Cp), 4.62 (d, AB system, $J = 12$ Hz, 1H, CH_2), 4.33 (s, 3H, CH_3), 4.29 (5H, s, Cp). ^{13}C-NMR (CD_3OD): d (ppm): 155.5 (quat., Py), 146.0 (Py), 144.2 (vinyl), 124.2 (Py), 121.3 (vinyl), 89.7 (quat., Cp), 80.7 (quat., Cp), 75.0 (subst. Cp), 72.3 (subst. Cp), 71.7 (Cp), 69.1 (subst. Cp), 59.7 (CH_2), 147.8 (CH_3). Anal. calc. for $C_{19}H_{20}FeONI$: C, 49.49, H, 4.37, N, 3.04. Found: C, 45.76, H, 3.63, N, 2.93. MS (FAB): 334 (M-127, 100%), 157 (93%), 136 (99%), 107 (67%). $[\alpha]_D = -679$ ($c = 0.002$, $CHCl_3$). UV–vis: $\lambda_{max} = 552$ nm ($\varepsilon = 6300$, $CHCl_3$).

2.9. SHG measurements

The measurements of second harmonic generation (SHG) intensity were carried out by the Kurtz–Perry powder technique [11], using a nanosecond Nd-YAG pulsed (10 Hz) laser operating at $\lambda = 1.064$ μm. The outcoming Stokes-shifted radiation at 1.907 μm, generated by Raman effect in a hydrogen cell, was used as the fundamental beam for second harmonic generation. The SHG signal was detected by a photomultiplier and read on an ultrafast Tektronic 7834 oscilloscope. Samples were calibrated microcrystalline powders obtained by grinding in the range 50–80 μm and put between two glass plates. The recorded efficiencies were expressed versus that of powdered (50–80 μm) urea.

2.10. X-Ray crystallographic study

Data for **5a**, **5b** and **5c** were collected on a Stoe IPDS diffractometer. The final unit cell parameters were obtained by the least-squares refinement of 2000 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collections.

All the structure were solved by direct methods (SIR92 [12]) and refined by least-squares procedures on F^2. All H atoms were introduced in calculation in idealized positions [d(CH) = 0.96 Å] and treated as riding models with isotropic thermal parameters related to the carbon to which they are attached. Least-squares refinements were carried out by minimizing the function $\Sigma w(F_o^2 - F_c^2)^2$, where F_o and F_c are the observed and calculated structure factors. The absolute structure for **5a** and the absolute configuration for **5b** and **5c** were determined by refining the Flack's enantiopole parameter [13]. The weighting scheme used in the last refinement cycles was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Models reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$ and $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$, having values listed in Table 1.

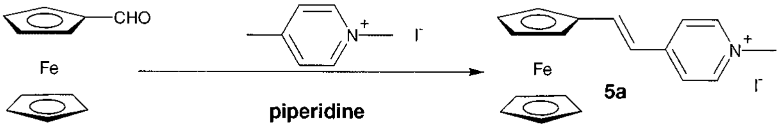
The calculations were carried out with the SHELXL-97 program [14] running on a PC. The molecular view was realized with the help of ORTEP32 [15].

3. Results and discussion

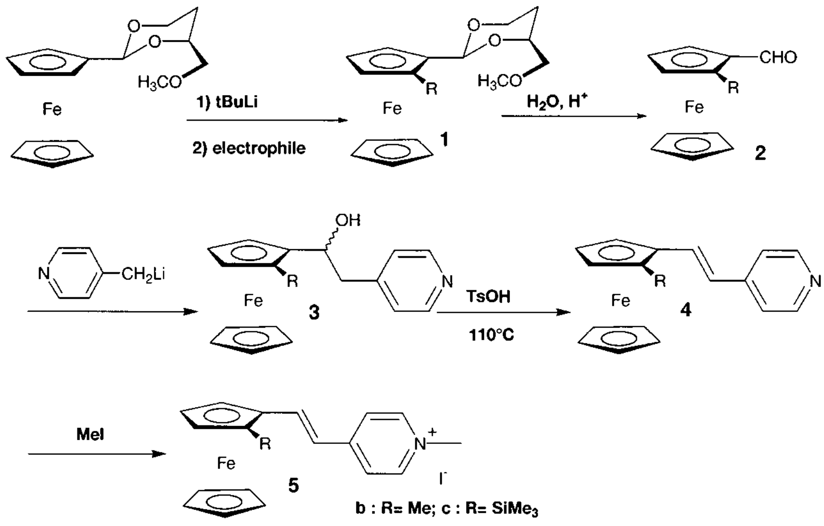
The parent molecule of the series of chromophores we proposed to study is (*E*)-1-ferrocenyl-2-(1-methyl-4-pyridinium)ethylene iodide. Unfortunately, the crystal structure of this salt (which possess the highest bulk efficiency: 220 times that of urea) was still unknown. So, our first goal was to obtain it in order to be able to compare the parent materials with the chiral analogues. (*E*)-1-Ferrocenyl-2-(1-methyl-4-pyridinium)ethylene iodide **5a** was synthesized by reaction of ferrocenecarboxaldehyde with 1-methylpyridinium iodide in the presence of piperidine following a known procedure (Scheme 1) [8]. Single crystals for X-ray diffraction structure were obtained by slow diffusion of hexane in a dichloromethane solution of **5a**. We decided to apply this method to different chiral aldehydes **2b** or **2c** with substituents of growing steric hindrance (Scheme 2). Furthermore, we wanted to obtain an analogue of **5a** with a hydroxymethyl group, which seemed of interest because of its possibility of making hydrogen bonds (Scheme 3). To obtain our target, we tried to use an acetal group as in **2d** which normally should be transformed to a formyl group by acidic hydrolysis [9]. This formyl group should be easily transformed into the desired hydroxymethyl group by simple reduction. But when the reaction was tested on different aldehydes, the reaction did not occur probably because of their larger steric hindrance compared with ferrocenecarboxaldehyde. So, a new method was tested (Schemes 2 and 3). First the 4-picoline was quantitatively deprotonated by action of a strong base (*n*-BuLi). Then, the picolinate anion reacted with the different aldehydes **2** to yield alcohol **3** as a mixture of diastereoisomers. The different alcohols **3** have been efficiently dehydrated to corresponding alkenes **4** in the presence of *p*-toluenesulfonic acid with continuous distillation of the water/toluene azeotrope. In each case, only one diastereoisomer was

Table 1
Crystal data for compounds

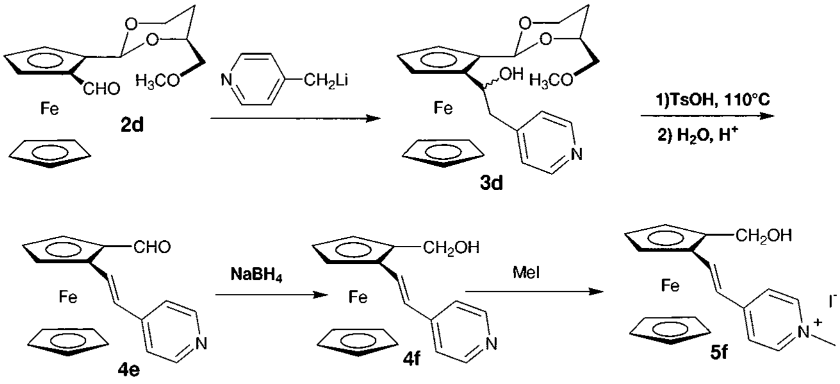
	5a	**5b**	**5c**
Formula	$[C_{18}H_{18}NFe]I$	$[C_{19}H_{20}NFe]I$	$[C_{21}H_{26}FeNSi]I$
Formula weight	431.08	445.11	503.27
Temperature (K)	293(2)	180(2)	293(2)
Shape (color)	flat (dark purple)	flat (dark purple)	flat (dark purple)
Size (mm)	0.28 × 0.27 × 0.13	0.8 × 0.4 × 0.1	0.24 × 0.24 × 0.03
Crystal system	monoclinic	monoclinic	monoclinic
Space group	Ia	$C2$	$P2_1$
a (Å)	12.426(3)	14.672(3)	6.4103(14)
b (Å)	11.038(3)	7.5156(8)	8.4597(19)
c (Å)	12.781(3)	15.984(3)	19.655(5)
β (°)	90.25(2)	97.005(18)	97.26(2)
V (Å$^{3)}$	1753.0(8)	1749.4(5)	1057.3(4)
Z	4	4	2
$F(000)$	848	880	504
ρ_{calc} (g cm^{-3})	1.633	1.690	1.581
μ (Mo–K$_\alpha$) (cm^{-1})	26.144	26.23	22.33
2θ range (°)	$4.9<2\theta<48.4$	$5.1<2\theta<48.2$	$4.2<2\theta<48.5$
Absorption correction	empirical (DIFABS)	empirical (DIFABS)	empirical (DIFABS)
Min/max transmission	0.3520/0.7703	0.3693/0.7796	0.2941/0.7364
Reflections measured	6687	6494	7283
Unique reflections (R_{int})	2603(0.0462)	2590(0.0331)	3211(0.0518)
Reflections used ($I>2\sigma(I)$)	2149	2507	2789
R_1, wR_2 ($I>2\sigma(I)$)	0.0420, 0.0953	0.0215, 0.0571	0.0408, 0.1014
R$_1$, wR_2 (all data)	0.0595, 0.1095	0.0226, 0.0578	0.0510, 0.1086
Flack's parameter	−0.05(6)	0.03(3)	0.01(4)
$\Delta\rho_{min}/\Delta\rho_{max}$	−0.757/0.637	−0.669/0.656	−0.711/0.608
Goodness-of-fit on F^2	1.031	1.052	1.094
Variable parameters	191	201	230



Scheme 1.



Scheme 2.



Scheme 3.

observed: the more stable *E* diastereoisomer. In the case of the compound **3d**, the presence of acid and water during the dehydration step was responsible for the partial deprotection of the acetal group to a formyl group to yield compound **4e** (Scheme 3). Simply by adding water to the reaction mixture and heating at 60 °C during 1 h, the complete deprotection of the acetal has been achieved. Compound **4e** is poorly stable and was quickly reduced by sodium borohydride to yield the desired compound **4g**. Action of iodomethane yielded the different pyridiniums as purple crystalline powders.

The bulk efficiency of the different chromophores **5** have been measured by a Kurtz–Perry test at $\lambda = 1.907$ mm. The results are recorded in Table 2. As expected, the presence of substituents in the 2 position of ferrocene in the different chromophores **5** has a large influence on the bulk efficiency but unfortunately not in the way we thought. In our previous study on 4-nitrostyrylferrocenes, calculations indicated that the variations on the molecular hyperpolarizability β were small and that the bulk efficiencies were essentially controlled by the crystal packing [5a]. It seems reasonable to make similar hypothesis for (*E*)-1-ferrocenyl-2-(1-methyl-4-pyridinium)ethylene salts.

For compounds **5b** and **5c**, crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane in a dichloromethane solution of the chromophore. Furthermore, the crystal structures of (*E*)-1-ferrocenyl-2-(1-methyl-4-pyridinium)ethylene nitrate (**5g**) [8] and of (*E*)-1-ferrocenyl-2-(1-methyl-4-pyridinium)ethylene hexafluorophosphate (**5h**) [16], have already been disclosed. So five crystal packings in this family are available to try to understand the correla-

Table 2
Powder test efficiencies at $\lambda = 1.907$ μm

	5a	**5b**	**5c**	**5f**
Efficiency [a]	220 [b]	0	0.25	0.1

[a] Relative to urea on microcrystalline powder ground in the 50–80 μm range.

[b] From Ref. [8] (87 times that of urea in our study).

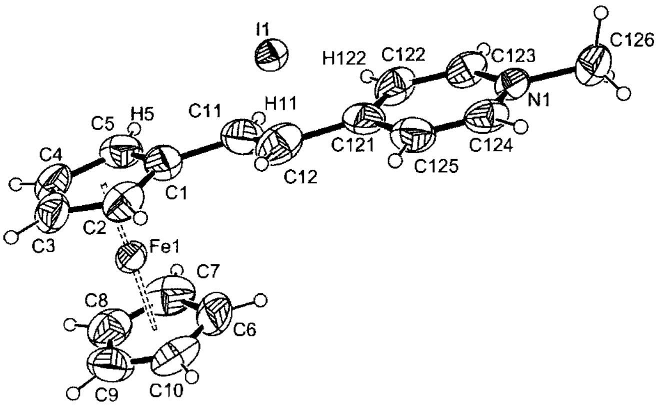


Fig. 1. Molecular view of **5a** with atom labeling scheme illustrating the I–H interactions. Ellipsoids represent 30% probability.

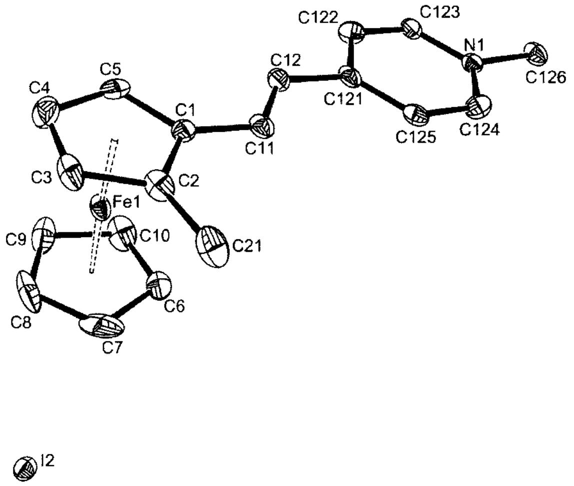


Fig. 2. Molecular view of **5b** with atom labeling scheme. Ellipsoids are drawn at 30% probability.

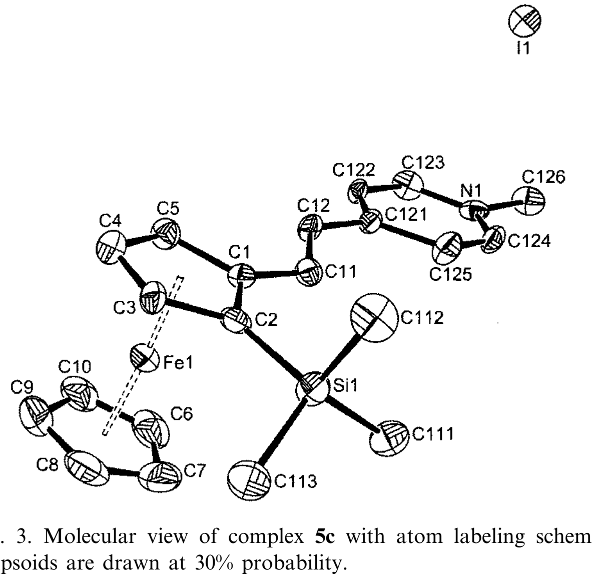


Fig. 3. Molecular view of complex **5c** with atom labeling scheme. Ellipsoids are drawn at 30% probability.

tions between bulk efficiencies and crystal arrangements.

The molecular structures of molecules **5a**, **5b** and **5c** as determined by X-ray analysis are shown with their atoms labeling schemes in Figs. 1–3. For all three compounds, the asymmetric unit is built up from one ferrocenyl-pyridinium cation and one iodine anion. As shown in Table 3, the presence of a substituent in the 2 position on the ferrocene does not drastically modify the geometry of the ferrocenyl moiety; the distances from iron to the Cp centroids of the cyclopentadienyl rings as well as the angle Cp1–Fe–Cp2 are roughly identical within experimental error. However, some discrepancies may be observed in the vinyl moieties, indeed the C=C double bond is 1.337 Å for **5b** and **5c** compared to 1.234(16) Å in **5g** and 1.161(17) Å in **5a**. The values observed for **5g** and **5a** are really too short to be realistic. These short C=C bonds might be related to the occurrence of a disorder as was recently reported in the PF_6 salt (**5h**) where the vinyl group is disordered around a mirror plane [16]. However, although there is some residual electron density in the vicinity of the C=C double bond for **5a**, it is weak and no disordered model could be properly refined. The ellipsoids for the carbon of the double bond are rather large and might reflect some dynamic disorder or fluxionality which would explain the short C=C bond.

Although the geometry of the non-substituted and substituted ferrocenyl-pyridinium molecules appears to be roughly similar except for the C–C bonds in the vinyl fragment, the packing is rather different. Indeed,

Table 3
Comparison of important bond lengths Å, bond angles (°) and other geometry parameters (°)

	5a	**5b**	**5c**	**5g**
Bond lengths				
Fe–Cp1	1.632	1.644	1.661	1.639
Fe–Cp2	1.638	1.650	1.664	1.638
C(1)–C(11)	1.567(15)	1.461(5)	1.466(11)	1.493(16)
C(11)–C(12)	1.161(16)	1.337(5)	1.337(10)	1.234(17)
C(12)–C(121)	1.625(16)	1.459(5)	1.467(11)	1.580(16)
N(1)–C(126)	1.493(15)	1.478(4)	1.473(9)	1.476(14)
Bond angles				
Cp1–Fe–Cp2	177.6	177.1	176.4	178.7
C(2)–C(1)–C(11)	134.7(15)	125.1(4)	128.6(7)	129.2(10)
C(5)–C(1)–C(11)	114.2(14)	126.7(4)	108.6(7)	121.4(10)
C(1)–C(11)–C(12)	113.3(16)	124.3(4)	125.2(7)	121.3(11)
C(11)–C(12)–C(121)	116.4(15)	125.4(5)	127.6(7)	120.6(11)
C(12)–C(121)–C(122)	130.6(14)	116.7(6)	120.7(8)	128.3(10)
C(12)–C(121)–C(125)	114.8(14)	125.4(6)	121.9(9)	116.1(10)
C(122)–C(121)–C(125)	114.6(13)	117.9(3)	117.4(7)	115.6(11)
α	21.47	178.58	177.20	18.55
θ	3.81	3.33	3.79	1.61
Δ	4.47	5.15	9.48	4.90

α (°) is the angle between the Cp1–N(1) vectors related to symmetry; θ (°) is the dihedral angle between the two Cp rings; Δ (°) is the dihedral angle between the Cp1 and the pyridine rings.

for **5g** and **5a**, the cations pack in the cell with, respectively, an angle of 18.6 and 21.5° (Table 3) between the Cp1–N1 vectors related by symmetry, leading roughly to a parallel arrangement. Whereas in the chiral salts **5b** and **5c**, the molecules were related by symmetrical packing in a nearly antiparallel arrangement. Indeed the Cp1–N1 vectors related by symmetry make an angle of 178.6 and 177.2° for **5b** and **5c,** respectively. This head-to-tail packing results in a pseudo centrosymmetric distribution of the chromophores. A perfect centrosymmetric packing was observed in the related **5h** salt. These particular packings would explain the very low SHG bulk efficiency observed for **5b**, **5c** and **5h**. Similar packing should be present in the other chiral salt **5f**.

It is worth pointing out that the relative positions of the anions with respect to the cations are also very different. In the **5a** salt, a layer of iodine anions alternate with the ferrocene-pyridinium network, whereas in **5b** and **5c**, two layers of ferrocene alternate with one layer of iodine. Moreover, in **5a**, the iodine is located in the mean plane defined by the Cp and the pyridine rings and it is rather close to H(11) of the C=C double bond, 3.09 Å and H(122) of the pyridinium ring, 3.16 Å (Fig. 1). However, why compounds **5b** and **5c** would pack so differently from their analogues **5a** and **5g**, despite the fact that, to a first approximation, they are geometrically very similar, remains an unanswered question.

4. Conclusion

The synthesis of enantiomerically pure chiral analogues of 4-[(*E*)-2-ferrocenyl-ethenyl]pyridinium iodide bearing various substituents (methyl, trimethylsilyl, hydroxymethyl) in the 2 position of the ferrocene has been achieved. Contrary to our expectations, these new compounds have very low SHG bulk efficiencies (from 0 to 0.25 times that of urea) when compared to the efficiency of the parent molecule 4-[(*E*)-2-ferrocenyl-ethenyl]pyridinium iodide (220 times that of urea). X-Ray structural analysis of **5b**, **5c** and of the achiral **5a** shows that crystal packing could explain the huge difference in SHG efficiency.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC-157002, CCDC-157003 and CCDC-157004. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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