A Novel and Perfectly Aligned Crystal of a Ferrocenyl Chromophore Displaying High Quadratic Nonlinear Optical Bulk Efficiency

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The highest nonlinear optical bulk efficiency for a 2-(4-nitrophenyl)ethenylferrocene (140 times that of urea) has been achieved for ***E*-4** owing to a favourable noncentrosymmetrical packing in which all molecules are perfectly aligned (*P*1 space group).

Introduction

Molecular nonlinear optical materials has been recognised for many years as a promising field because of their potential applications in emerging photonic technologies.[1] Most efforts have been devoted to organic molecules in which electron donor/acceptors are linked through conjugated backbones. More recently organometallic molecules have attracted attention because metal complexes are capable of strong electron acceptor/donor effects depending upon the nature of the metal, its oxidation states and coordination spheres. These new characteristics may allow a subtle tuning of the NLO properties and make organometallic species very attractive.[2] In any case, two prerequisites are needed for quadratic NLO activity: first, the constituting chromophores have to possess a molecular hyperpolarizability (β) as large as possible, and secondly they must be arranged in a noncentrosymmetrical fashion. A dramatic illustration of such requirements can be found in organometallic chemistry.[3] The (*Z*)-2-(4-nitrophenyl)ethenylferrocene isomer **Z-1** has a β value of 13×10^{-30} esu, and the *E* isomer ***E*-1** possesses a larger hyperpolarizability at the molecular level ($\beta = 31 \times 10^{-30}$ esu; see Table 1). However, whereas the *Z* isomer exhibits a large second harmonic generation (SHG) efficiency in the solid state (62 times that of urea), the *E* isomer is completely inactive in the solid state due to its centrosymmetrical crystal packing.[4] We have been able to overcome this tendency for centrosymmetric crystallisation of ***E*-1** by using chiral enantiomerically pure analogues of this molecule that furnished noncentrosymmetrical crystals, sometimes with high bulk efficiencies (up to 100 times that of urea).[5] More recently, we became interested in analogues of ***E*-1** bearing substituents on the second cyclopentadienyl ring (see Scheme 1) in order to modulate crystal packing or to incorporate chromophores into polymers. In the next section we will disclose our first results with a particular emphasis on ***E*-4**, which possesses a high NLO efficiency because of a very unusual crystal packing.

Results and Discussion

To obtain our target molecules, we developed a new procedure to prepare 1,1′-disubstituted ferrocenes involving the monoacetal **2** (see Scheme 1). The free aldehyde function was used to build the first substituent. Hydrolysis of the acetal function could then furnish a new formyl group in order to build up the second substituent. During our studies, we were able to isolate compound ***E*-4** and to obtain single crystals suitable for X-ray diffraction analysis. ***E*-4** crystallises in the *P*1 space group. Each unit cell contains one single molecule (Figure 1). The crystal has no symmetry elements so all the molecules of ***E*-4** are strictly identical and absolutely parallel to each other (see Figure 2). This packing is unique and very favourable for the NLO efficiency because each chromophore will add its contribution to the overall property. The *P*1 space group is very rare for NLO active chromophores. Only few examples of such crystal packings have been disclosed, usually for merocyanine- or 4-nitrophenol-based materials.[6] However, to the best of our knowledge, only one such crystal where the NLO chromophore is alone and perfectly aligned, has already been described.[6a]

The NLO properties of these materials has been measured by a Kurtz−Perry powder test.[7] An SHG efficiency of 140 times that of urea has been recorded at 1.906 μ. This efficiency is the highest value recorded so far in this series of 2-(4-nitrophenyl)ethenylferrocenes and one of the highest for organometallic compounds in general.[2,8] The optical properties of ***E*-4** are very close to those of the related compound ***E*-1**.[9] Furthermore, the molecular hyperpolarizability β of ***E*-4** has been calculated by ZINDO (see Table1).[10] The calculated β value is only slightly higher for ***E*-4** than for ***E*-1**, so the high NLO bulk efficiency of ***E*-4**

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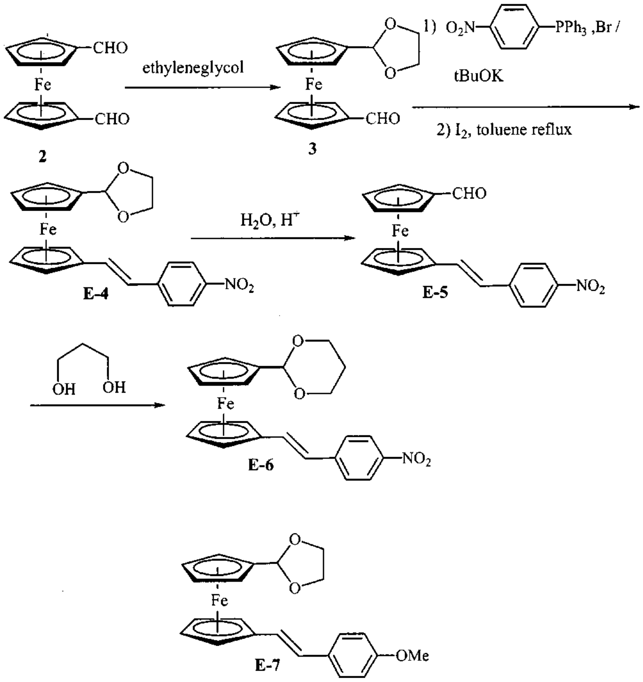
Table 1. ZINDO calculated absorption maxima (in nm), experimental absorption maxima (in nm in an ethanol solution), oscillator strengths (*f*), dipole moment changes between ground and excited states (in D), composition of the excited state in the configuration interaction and β_0 (in 10^{-30} $cm^3 \cdot esu^{-1}$) for ***E*-4** and ***E*-1**

	λ_{max}(calcd.)	λ_{max}(expt.)	*f*	$\Delta\mu$	Composition of CI expansion[a]	β_0
***E*-4**	360	364	0.84	16.7	$-0.780\ \chi 70 \rightarrow 71\ -0.462\ \chi 68 \rightarrow 71$	26.3
***E*-1**	343	362	0.80	17.6	$-0.729\ \chi 56 \rightarrow 57\ -0.538\ \chi 54 \rightarrow 57$	20.9

[a] Orbital 70 and 56 are the HOMOs for ***E*-4** and ***E*-1**, respectively.



Scheme 1

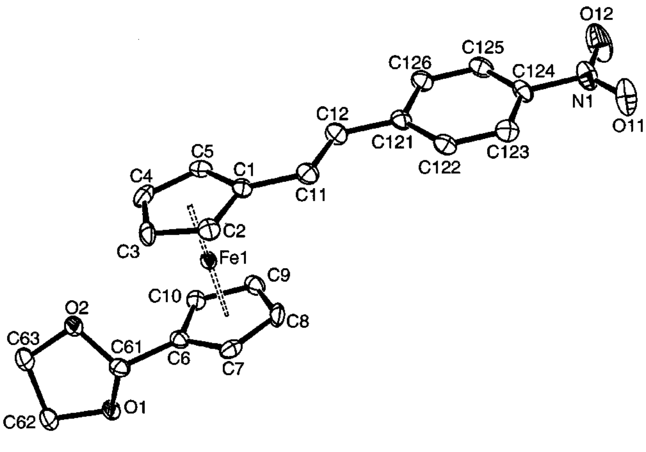


Figure 1. Molecular view of ***E*-4** with atom labelling scheme; ellipsoids represent 30% probability

crystals is probably due to the very favourable crystal packing.

The nonlinear optical properties of 2-(4-nitrophenyl)ethenylferrocenes have been extensively studied,[2] but only a few types of crystal packing for such compounds have been reported. These compounds have a clear tendency for head-to-tail crystallisation.[4,5,11] Why, then, does ***E*-4** crystallise with such a completely different packing? The still common opinion about a tendency of molecules with a large dipole moment for head-to-tail crystallisation has been ruled out by a thorough study.[12] It therefore seems clear to us that the noncentrosymmetrical crystallisation of ***E*-4** is not due to a lower dipole moment compared to ***E*-1**.[13] The crystal structure of ***E*-4** arises from infinite ribbons of molecules with short nitro−dioxane distances. A close study of the distances within the crystal reveals six relatively short H−O contacts that cannot be explained by geometrical constraints within the molecule (see Table 2 and Figure 3). These contacts may be described as C−H···O hydrogen bonds, as defined in the literature, between slightly acidic protons and oxygen acceptors.[14] Indeed, all C−O distances and all C−H···O angles fall into the expected range for such bonds (3−4 Å and 90−180°, respectively).[14b] The six short H−O contacts correspond to two unsymmetrically bifurcated interactions between one hydrogen atom and the two oxygen atoms of the nitro group, and two interactions between one hydrogen atom and only one oxygen atom of the nitro group (see Figure 3).[14d] In the absence of stronger intermolecular forces, such as OH···O hydrogen bonds, π-π stacking or donor−acceptor interactions, we believe that these C−H···O interactions are responsible for the unique crystal packing of ***E*-4**. Furthermore, this proposal is

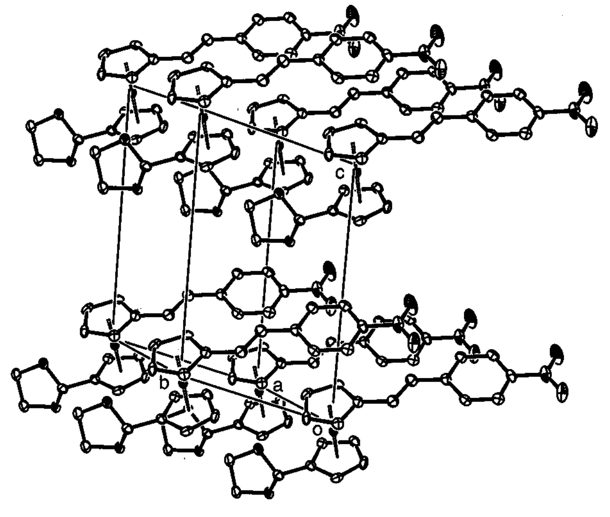


Figure 2. View of the packing in ***E*-4** showing the perfect alignment of the chromophores

Table 2. Distances and angles for C−H···O contacts

Contact[a]	O−C distance (Å)	O−H distance (Å)	O−H−C angle (°)
O(11)−H(62b)−C(62)	3.204(3)	2.99	93.7
O(11)−H(62a)−C(62)	3.204(3)	2.80	106.1
O(11)−H(63b)−C(63)	3.542(3)	3.16	105.4
O(12)−H(62b)−C(62)	3.477(3)	2.97	113.8
O(12)−H(63a)−C(63)	3.329(4)	2.90	107.9
O(12)−H(63b)−C(63)	3.329(4)	3.23	87.3

[a] The symmetry transformations used to generate the dioxane fragment [C(62), C(63), H···] are $x - 1$, $y - 2$, $z + 1$.

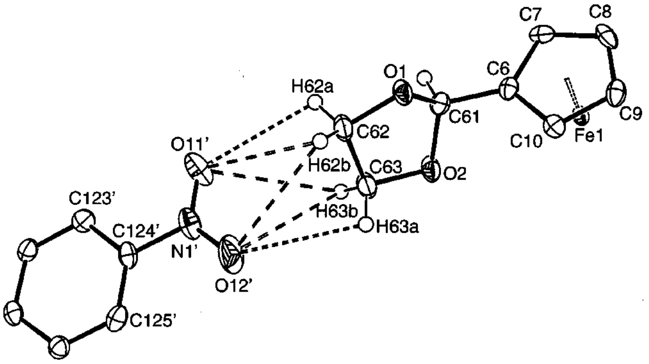


Figure 3. View showing the hydrogen interactions C−H···O between the hydrogen atoms of the dioxane moiety and the O atoms of the nitro group in ***E*-4**

strengthened by the study of a closely related molecule ***E*-7**, obtained by formally replacing the acceptor nitro group of ***E*-4** by a methoxy group. ***E*-7** lacks a good acceptor, such as a nitro group, able to form C−H···O hydrogen bonds and crystallises in the centrosymmetric space group $P2_1/c$.[15]

We also decided to study a close analogue of ***E*-4** where the five-membered dioxane ring has been replaced by the six-membered dioxolane ring, namely compound ***E*-6**. Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a dichloromethane solution of ***E*-6** (Figure 4). In this case, we observed a centrosymmetrical packing and, of course, no NLO bulk efficiency. If the nitrostyryl fragments of ***E*-4** and ***E*-6** are identical within experimental errors as shown in Table 2, the relative geometry of the dioxane or dioxolane with respect to the Cp ring to which they are attached is different. The dioxane ring is twisted with respect to the Cp by a dihedral angle of 73.9°, whereas the dioxolane moiety is nearly parallel to the Cp with a dihedral angle of 13.5°. The twist observed for the dioxane in ***E*-4** allows the four hydrogens of the two CH_2 groups to form hydrogen bonds with the nitro fragment of the symmetry related molecule, as shown in Figure 3. In ***E*-6**, however, the presence of a third CH_2 group prevents the interaction of the four acidic hydrogens close to the oxygen atoms with the nitro group, the tendency for centrosymmetrical packing cannot therefore be overcome, and it packs in a more common centrosymmetrical way. However, the intermolecular packing is still stabilised by C−H···O interactions between the oxygen of the nitro group and two hydrogens H(8′) and H(9′) of the unsubstituted Cp ring of the symmetry related molecule. Such C−H···O interactions between a Cp ring of a ferrocene moiety and the O atoms of a nitro group seems to be rather common and many examples can be found in the literature.[16] These interactions lead to the head-to-tail packing of two molecules arranged around the inversion centre shown in Figure 5.

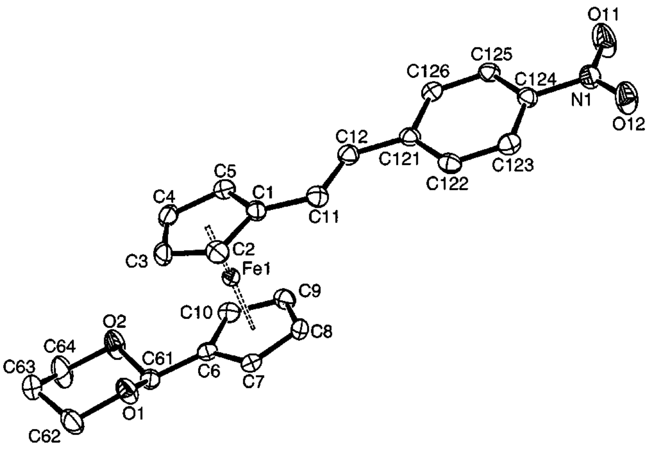


Figure 4. Molecular view of ***E*-6** with atom labelling scheme; ellipsoids represent 30% probability

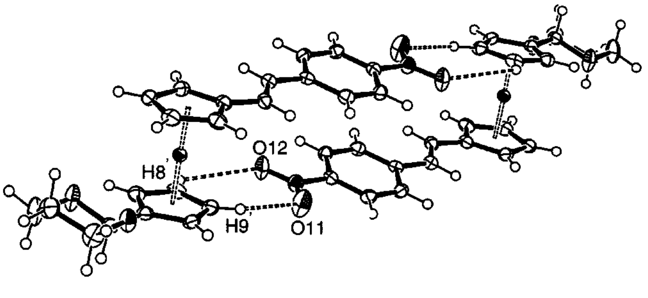


Figure 5. View showing the hydrogen interactions between the oxygen of the nitro group and some hydrogen atoms of the Cp ring in ***E*-6** [O(11)···C(9′) 3.627(3), O(11)···H(9′) 2.99 Å and O(11)···H(9′)−C(9′) 124.7(2)°; O(12)···C(8′) 3.744(3), O(12)···H(8′) 2.44 Å and O(12)···H(8′)−C(8′) 156.3(2)°]

In conclusion, we have reported a rare example of a highly efficient NLO materials (SHG efficiency 140 times the value for urea!) where the crystal contains only perfectly aligned chromophores. Furthermore, we have discovered specific interactions between a dioxane ring and a nitro group which, if they can be generalised in other systems, might be a new and useful example of a supramolecular building block for crystal engineering.[17]

Experimental Section

All reactions were carried out in the absence of air using standard Schlenk techniques and vacuum line manipulations. Thin layer chromatography was carried out on Merck 60F254 precoated silica gel plates. Preparative flash chromatography was performed on Merck Kieselgel. Instrumentation: Bruker AM250 (^{1}H, ^{13}C NMR), Hewlett−Packard HP MSD 7590 (GC-MS), Stoe IPDS (X-ray). Elemental analyses were performed by the Service d′Analyse du Laboratoire de Chimie de Coordination, Toulouse (France).

1,1′-Ferrocenedicarboxaldehyde was synthesised according to ref.[18] 4-(Nitrobenzyl)triphenylphosphonium bromide was synthesised by a similar procedure to that described in ref.[19] for the synthesis of 4-(nitrobenzyl)triphenylphosphonium chloride.

2-(1′-Formylferrocenyl)-1,3-dioxolane (3): 1,1′-Ferrocenedicarboxaldehyde (5 g, 20.6 mmol) was added to a round-bottomed flask equipped with a Dean−Stark apparatus. The system was purged with argon and the red solid was dissolved in 80 mL of dry toluene. Ethylene glycol (1.15 mL, 20.6 mmol) and *p*-toluenesulfonic acid (300 mg, 1.58 mmol) were then added successively to the reaction mixture. After heating for 2 h at 170 °C, the reaction mixture was cooled back to room temp. and diluted with 100 mL of dichloromethane. Anhydrous potassium carbonate was then added and the mixture was stirred for 1 h. After filtration through celite and evaporation of the solvents, the crude materials was purified by flash chromatography on silica gel with a pentane/ether mixture (1:2, v/v) as eluent to yield 3.54 g of **3** as a brown solid (yield = 60%). − ^{1}H NMR ($CDCl_3$): δ = 9.90 (s, 1 H, CHO), 5.55 (s, 1 H, O−CH−O), 4.76 (t, *J* = 1.9 Hz, 2 H, Cp), 4.57 (t, *J* = 1.9 Hz, 2 H, Cp), 4.36 (t, *J* = 1.9 Hz, 2 H, Cp), 4.21 (t, *J* = 1.9 Hz, 2 H, Cp), 3.93 (m, 4 H, CH_2-CH_2). − ^{13}C NMR ($CDCl_3$): δ = 193.9 (CHO), 101.8 (O−CH−O), 86.2 (quat. Cp), 80.1 (quat. Cp), 80.0 (Cp), 73.9 (Cp), 70.4 (Cp), 69.9 (Cp), 65.4 (CH_2-CH_2). − MS (DCI, NH_3): *m*/*z* (%) = 287 (32) [M + 1]. − $C_{14}H_{14}FeO_3$ (286.11): calcd. C 58.77, H 4.93; found C 58.73, H 4.75.

(*E*)-2-[1′-(4-Nitrostyryl)ferrocenyl]-1,3-dioxolane (*E*-4): *t*BuOK (2.10 g, 18.7 mmol, 3.1 equiv.) and 50 mL of dry toluene were added to a distillation apparatus. The system was purged with argon. 4-(Nitrobenzyl)triphenylphosphonium bromide (7.20 g, 15.1 mmol, 2.5 equiv.) was then added and the mixture was warmed up to reflux. After one hour, 30 mL of toluene was removed by distillation and the solution was kept at reflux for another two hours. After cooling back to room temp., a solution of **3** (1.70 g, 5.94 mmol) dissolved in 40 mL of dry toluene was added and the solution was warmed again to reflux. 20 mL of toluene was removed by distillation over a period of one hour and the solution was kept at reflux for another two hours. After cooling to room temperature, the organic phase was extracted with dichloromethane, washed with brine, dried over sodium sulfate and the solvents evaporated under reduced pressure. The crude material was purified by flash chromatography with a pentane/ether mixture (3:1, v/v) on silica gel to yield 2.38 g of **4** (yield 99%) as a mixture of Z and *E* isomers (*Z*/*E* = 1:3).

A mixture of **4** (***Z***+***E***) (1.45 g, 3.58 mmol) and I_2 (90 mg, 0.1 equiv.) dissolved in 40 mL of dry toluene was added to a one-necked round bottomed flask equipped with a condenser. The system was purged with argon and the mixture was then refluxed for 15 minutes. After cooling back to room temperature, the mixture was extracted with dichloromethane, washed with a sodium thiosulfate solution (2 M) then with brine, dried over sodium sulfate and the solvents were evaporated. After flash chromatography on silica gel, 1.40 g (97%) of pure ***E*-4** was isolated. − ^{1}H NMR ($CDCl_3$): δ = 8.21 (d, *J* = 8.8 Hz, 2 H, Ph), 7.75 (d, *J* = 8.8 Hz, 2 H, Ph), 7.34 (d, AB, *J* = 16.2 Hz, 1 H, vinyl), 6.95 (d, AB, *J* = 16.2 Hz, 1 H, vinyl), 5.66 (s, 1 H, O−CH−O), 4.66 (t, *J* = 1.8 Hz, 2 H, Cp), 4.44 (t, *J* = 1.8 Hz, 2 H, Cp), 4.31 (t, *J* = 1.9 Hz, 2 H, Cp), 4.19 (t, *J* = 1.9 Hz, 2 H, Cp), 3.84−4.01 (m, 4 H, CH_2-CH_2). − ^{13}C NMR ($CDCl_3$): δ = 146.3 (quat. Ph), 145.4 (quat. Ph), 133.4 (vinyl), 126.2 (Ph), 124.4 (Ph), 124.0 (vinyl), 102.4 (O−CH−O), 86.5 (quat. Cp), 83.1 (quat. Cp), 71.0 (Cp), 69.8 (Cp), 68.7 (Cp), 68.6 (Cp), 65.3 (CH_2-CH_2). − MS (DCI, NH_3): *m*/*z* (%) = 406 (100) [M + 1]. − $C_{21}H_{19}FeNO_4$ (405.23): calcd. C 62.24, H 4.73, N 3.46; found C 61.97, H 4.34, N 3.68.

(*E*)-1′-(4-Nitrostyryl)ferrocenecarboxaldehyde (*E*-5): A solution of ***E*-4** (1.40 g) in 30 mL of dichloromethane was added to 15 mL of a solution containing 150 mg of *p*-toluenesulfonic acid monohydrate in deoxygenated water in a Schlenk tube. The mixture was stirred for 3 h at 60 °C. After cooling, the solution was diluted with diethyl ether, washed with water, dried with sodium sulfate, evaporated and purified by flash chromatography with a pentane/ether mixture (1:2, v/v) on silica gel to yield 1.10 g of pure ***E*-5** (yield 88%). − ^{1}H NMR ($CDCl_3$): δ = 9.88 (s, 1 H, CHO), 8.19 (d, *J* = 8.9 Hz, 2 H, Ph), 7.55 (d, *J* = 8.9 Hz, 2 H, Ph), 6.94 (d, AB, *J* = 16.3 Hz, 1 H, vinyl), 6.75 (d, AB, *J* = 16.3 Hz, 1 H, vinyl), 4.78 (t, *J* = 2.0 Hz, 2 H, Cp), 4.60 (t, *J* = 1.9 Hz, 2 H, Cp), 4.58 (t, *J* = 2.0 Hz, 2 H, Cp), 4.44 (t, *J* = 1.9 Hz, 2 H, Cp). − ^{13}C NMR ($CDCl_3$): δ = 193.5 (CHO), 146.4 (quat. Ph), 143.7 (quat. Ph), 130.6 (vinyl), 126.3 (Ph), 125.6 (Ph), 124.2 (vinyl), 83.7 (quat. Cp), 80.1 (quat. Cp), 74.3 (Cp), 71.2 (Cp), 70.8 (Cp), 68.7 (Cp). − MS (DCI, NH3): *m*/*z* (%) = 379 (100) [M + 18], 362 (32) [M + 1]. − $C_{19}H_{15}FeNO_3$ (361.18): calcd. C 63.20, H 4.20, N 3.88; found C 63.01, H 4.47, N 3.64.

(*E*)-2-[1′-(4-nitrostyryl)ferrocenyl]-1,3-dioxane (*E*-6): ***E*-5** (1.0 g, 2.64 mmol) dissolved in 30 mL of dry toluene was added to a round-bottomed flask equipped with a Dean−Stark apparatus. The system was purged with argon and 1,3-propanediol (0.265 mL, 3.66 mmol) and *p*-toluenesulfonic acid (53 mg, 0.27 mmol) were added successively to the reaction mixture. After 2 h heating at 110 °C, the reaction mixture was cooled back to room temp. and diluted with 100 mL of dichloromethane. Anhydrous potassium carbonate was then added and the mixture was stirred for 1 h. After filtration through celite and evaporation of the solvents, the crude material was purified by flash chromatography on silica gel with a pentane/ether mixture (3:1, v/v) as eluent to yield 0.85 g of ***E*-6** as a red solid (yield 79%). − ^{1}H NMR ($CDCl_3$): δ = 8.18 (d, *J* = 8.8 Hz, 2 H, Ph), 7.52 (d, *J* = 8.8 Hz, 2 H, Ph), 7.08 (d, AB, *J* = 16.1 Hz, 1 H, vinyl), 6.70 (d, AB, *J* = 16.1 Hz, 1 H, vinyl), 5.25 (s, 1 H, O−CH−O), 4.51 (t, *J* = 1.8 Hz, 2 H, Cp), 4.39 (t, *J* = 1.8 Hz, 2 H, Cp), 4.29 (t, *J* = 1.8 Hz, 2 H, Cp), 4.14 (m, 2 H, OCH_2), 4.11 (t, *J* = 1.8 Hz, 2 H, Cp), 3.79 (td, *J* = 12.3 Hz and 2.3 Hz, 2 H, OCH_2), 2.2−1.9 (m, 1 H, $CH_2\mathit{CH_2}CH_2$), 1.34 (br. d, *J* = 13 Hz, 1 H, $CH_2\mathit{CH_2}CH_2$). − ^{13}C NMR ($CDCl_3$): δ = 145.8 (quat. Ph), 144.4 (quat. Ph), 132.7 (vinyl), 125.8 (Ph), 124.2 (Ph), 123.4 (vinyl), 99.6 (O−CH−O), 87.1 (quat. Cp), 82.2 (quat. Cp), 70.8 (Cp), 69.2 (Cp), 68.3 (Cp), 67.7 (Cp), 67.1 (OCH_2), 25.7 ($CH_2CH_2CH_2$). − MS (DCI, NH3): *m*/*z* (%) = 420 (100) [M + 1]. − $C_{22}H_{21}FeNO_4$ (419.26): calcd. C 62.21, H 4.73, N 3.46; found C 63.24, H 4.94, N 3.10.

Table 3. Crystal data of ***E*-4** and ***E*-6**

	***E*-4**	***E*-6**
Empirical formula	$C_{21}H_{19}FeNO_4$	$C_{22}H_{21}FeNO_4$
Formula mass	405.23	419.26
Crystal shape	Box (dark red)	Flattened needle (orange red)
Crystal size, mm	0.46 × 0.32 × 0.30	0.57 × 0.12 × 0.05
Temperature, K	180(2)	180(2)
Crystal system	Triclinic	Triclinic
space group	$P1$	$P1$
a, Å	6.0102(8)	6.1214(7)
b, Å	7.0127(9)	8.5527(9)
c, Å	11.264(2)	17.532(2)
α, °	73.39(1)	93.37(1)
β, °	88.28(2)	94.66(1)
γ, °	70.17(1)	95.59(1)
U, Å^3	426.8(1)	908.4(2)
Z	1	2
ρ(calcd), g·cm^{-3}	1.576	1.533
μ(Mo-K_α), cm^{-1}	9.082	8.599
Diffractometer used	Stoe IPDS	Stoe IPDS
Radiation used	Mo-K_α (0.71073)	Mo-K_α (0.71073)
Scan mode		
Reflections measured	3148	9123
θ range, °	$5.68 < \theta < 24.0$	$2.34 < \theta < 26.02$
Independent reflections (R_{int})	2302(0.0461)	3353(0.0403)
Reflections used [$I > 2\sigma(I)$]	2298	2550
Refinement	F	F
R	0.0226	0.0279
R_w	0.0257	0.0322
$(\Delta/\sigma)_{max}$	0.06	0.04
$\Delta\rho_{min}/\Delta\rho_{max}$	−0.37/0.38	−0.34/0.31
Flack's parameter	0.00(1)	
GOF	1.077	1.032
No of parameters	246	254

NLO Measurements: The measurements of second harmonic generation (SHG) intensity were carried out by the Kurtz−Perry powder technique[7] with 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 effects 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 as 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.

X-ray Crystallographic Study: Data for ***E*-4** and ***E*-6** were collected on a Stoe IPDS diffractometer. The final unit cell parameters were obtained by the least-squares refinement of 8000 reflections. Only statistical fluctuations were observed in the intensities monitored over the course of the data collections.

Both structures were solved by direct methods (SIR97[20]) and refined by least-squares procedures on F. All H atoms were introduced in the calculation in idealised 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 minimising the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The absolute configuration for ***E*-4** was determined by refining the Flack enantiopole parameter.[21] The weighting scheme used in the last refinement cycles was $w = w'[1 - \{\Delta F/6\sigma(F_o)\}^2]^2$, where $w' = 1/\Sigma_1^n A_r T_r(x)$ with three coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$ where x is $F_c/F_c(\max)$.[22] The models reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$, with the values listed in Table 3.

The calculations were carried out with the CRYSTALS package programs.[22] Molecular views were produced with the help of ORTEP32.[23]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-160780 (***E*-4**) and -160781 (***E*-6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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