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# Ferrocenyl D- $\pi$ -A chromophores containing 3-dicyanomethylidene-1-indanone and 1,3-bis(dicyanomethylidene)indane acceptor groups

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## Abstract

The nonlinear optical properties of ferrocenyl (Fc) D- $\pi$ -A chromophores containing powerful 3-dicyanomethylidene-1-indanone (**2**) and 1,3-bis(dicyanomethylidene)indane-based acceptor group (**3**) have been measured by EFISH technique at 1.907  $\mu\text{m}$  and compared with those reported for the Fc compound containing the 3-dicyanomethylidene-2,3-benzo[*b*]thiophen-1,1-dioxide group (**1**). The values of  $\mu\beta \cdot (2\omega)$  are 160 and  $280 \times 10^{-48}$  esu for **2** and **3**, respectively, whereas **1** displays a value of  $140 \times 10^{-48}$  esu [Inorg. Chim. Acta 242 (1996) 43]. The X-ray crystallographic study of **1** and **2** revealed significant distortions of the structure of the ferrocene moieties due to the contribution of a charge-separated  $\eta^6$ -fulvene mesomeric form and important steric effects. The cyclic voltammetry data showed an anodic shift of the Fe(II)/Fe(III) oxidation potentials of **2** and **3** in comparison to those of ferrocenecarboxaldehyde (**4**) and 2-(ferrocenylmethylidene)-1,3-indandione (**5**), and an approximately additive effect of the substitution of one or two carbonyl oxygens in **5** by the C(CN)<sub>2</sub> group.

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**Keywords:** NLO; Chromophores; Ferrocene; Electronic absorption spectra; Crystal structures electrochemistry

## 1. Introduction

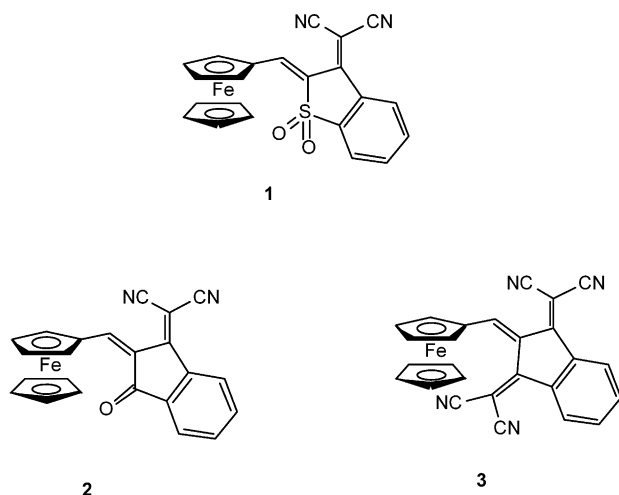
There has been considerable interest in the use of the ferrocenyl (Fc) moiety as a donor group in donor- $\pi$ -acceptor (D- $\pi$ -A) chromophores displaying enhanced second-order nonlinear optical (NLO) properties [1–6]. Electron donor ability of this group is closely similar to that of the *p*-methoxyphenyl group, but it offers a unique possibility of the redox switching of NLO properties [7–9] and allows easy introduction of chirality, important for bulk NLO properties [1]. It has been demonstrated that similarly to related purely organic

systems, quadratic nonlinear hyperpolarisability ( $\beta$ ) of Fc- $\pi$ -A molecules depends on the electron-accepting ability of A and the nature of the  $\pi$ -bridge connecting the Fc and A moieties. Usually, for a given  $\pi$ -bridge,  $\beta$  increases with stronger accepting ability of A. Although theoretical calculations predicted an “inverted region”, where an increase of the electron-accepting properties of A will lead to a decrease of  $\beta$  (maximum of  $\beta$  is expected for the bond alternation length parameter  $\pm 0.05 \text{ \AA}$  [6]), neutral Fc systems studied up to now are situated in the “normal region” [10–14]. Therefore, it is of particular interest to introduce to the Fc- $\pi$ -A systems very strong acceptor groups to approach structural conditions maximising their molecular hyperpolarisability. Molecules with short  $\pi$ -bridges are of special importance because they are usually more readily available than more extended ones and less sensitive to heat and light.

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Among the most efficient neutral acceptor groups hitherto described is the 3-dicyanomethylidene-2,3-benzo[*b*]thiophen-1,1-dioxide group present in the Fc compound **1**. This compound displays  $\mu\beta(2\omega) = 140 \times 10^{-48}$  esu at 1907 nm ( $\beta(0) = 29 \times 10^{-30}$  esu) and extension of the polyethylenic  $\pi$ -bridge resulted in the increase of  $\mu\beta(2\omega)$  up to  $11\,200 \times 10^{-48}$  esu [10,11].



Stimulated by recent reports on large quadratic hyperpolarisabilities of organic molecules containing 3-dicyanomethylidene-1-indanone and 1,3-bis(dicyanomethylidene)indane acceptor moieties [14–17], we became interested in the introduction of these potent acceptors into Fc- $\pi$ -A compounds.

Here we report synthesis, electronic absorption spectra and a second-order NLO property of **2** and **3**, second-harmonic generation efficiency,  $\mu\beta \cdot (2\omega)$ , measured by the electric-field-induced second-harmonic generation (EFISH) technique [18,19]. The latter parameter is usually considered as a “molecular factor of merit” for possible applications of NLO chromophores in poled polymeric systems because it combines first hyperpolarisability ( $\beta$ ) and the ability of the molecule to couple with a macroscopic poling field (molecular dipole moment  $\mu$ ).

We thought that it would also be of interest to determine molecular structures of **2** and **3** to gain insight into influence of very strongly electron-withdrawing groups, stabilising charge-separated mesomeric  $\eta^6$ -ful-

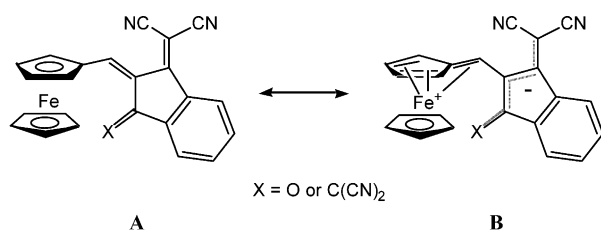


Fig. 1. Main mesomeric structures of **2** and **3**.

vene structure **B** (Fig. 1), on the geometry of Fc- $\pi$ -A compounds.

Finally, we report electrochemical properties of **2** and **3**, which shed additional light on their electronic structures.

## 2. Results and discussion

### 2.1. Syntheses of **2** and **3**

Compounds **2** and **3** were prepared by the Knoevenagel condensation of ferrocenecarboxaldehyde (**4**) with 3-dicyanomethylidene-1-indanone and 1,3-bis(dicyanomethylidene)indane, respectively (Fig. 2).

The former reaction took place smoothly, in refluxing methanol, whereas the latter under the same conditions led to a complex, intractable mixture. However, heating of ferrocenecarboxaldehyde with 1,3-bis(dicyanomethylidene)indane in acetic anhydride to 55–60 °C afforded **3** in 67% yield. Compounds **2** and **3** were characterised by spectral methods and elemental analyses. Their X-ray structures have been determined (vide infra).

### 2.2. Molecular structures of **2** and **3**

The molecular and crystal structures of **2** and **3** have been determined by the X-ray diffraction method. They are shown in Figs. 3 and 4, and the respective molecular packings are shown in Figs. 5 and 6. Crystallographic data are collected in Table 1 and selected bond lengths and angles in Table 2.

The structure of **2** reveals the (*Z*)-configuration resulting probably from the steric reasons, the dicyanomethylidene group being bulkier than the carbonyl oxygen atom.

Both structures provide evidence for significant donor–acceptor interactions in the ground state, represented in Fig. 1 by the charge-separated  $\eta^6$ -fulvene structure **B** (Fig. 1). The distances between the iron

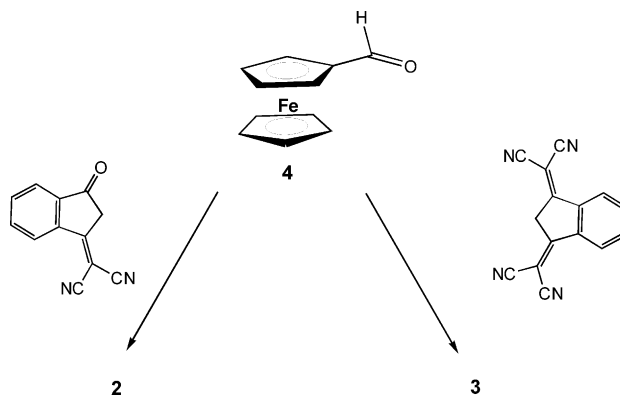


Fig. 2. Synthesis of **2** and **3**.

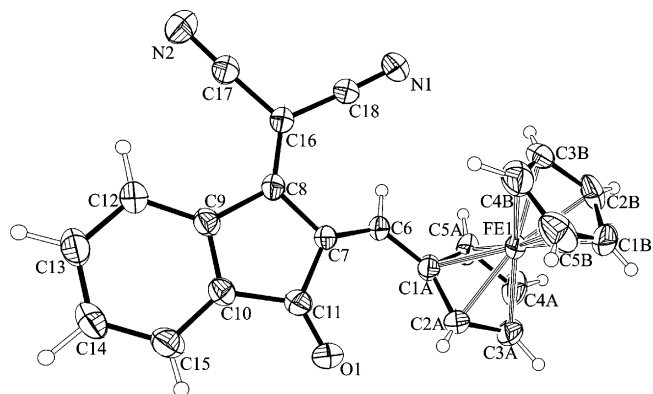


Fig. 3. The ORTEP drawing of molecule **2** with atom-numbering scheme. Displacement ellipsoids are shown at 30% probability level.

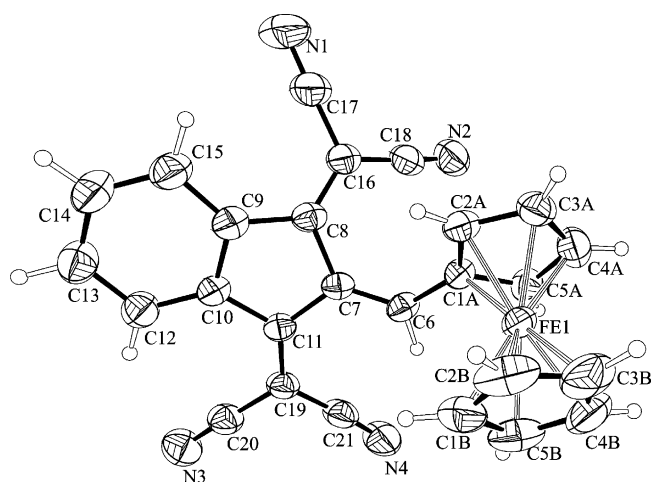


Fig. 4. The ORTEP drawing of molecule **3** with atom-numbering scheme. Displacement ellipsoids are shown at 30% probability level.

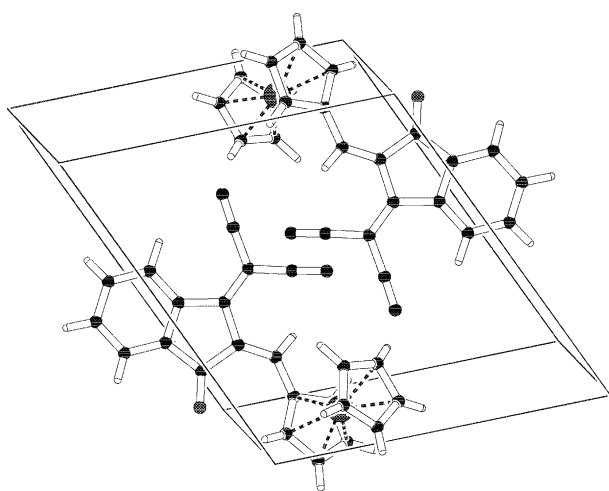


Fig. 5. View of the molecular packing in the unit cell of **2**.

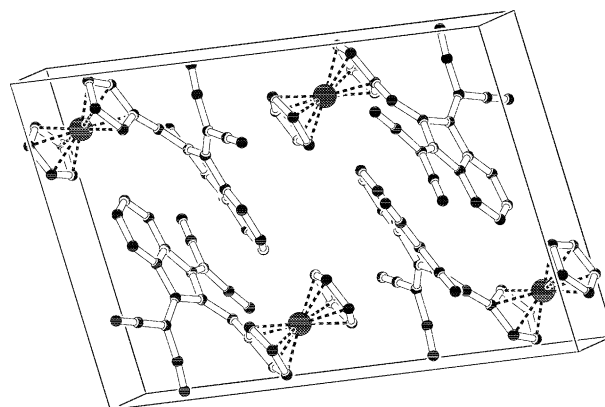


Fig. 6. View of the molecular packing in the unit cell of **3**.

than the analogous distance in ferrocene, 1.649 Å. The distances of Fe–unsubstituted Cp plane are slightly longer (1.654(1) and 1.653(7) Å). The Cp rings in **2** and **3** are not parallel to each other but form angles 4.0(2)° and 2.8(2)°. The methine carbon C6 is tilted from the substituted Cp plane ring towards iron and the angle between the C7–C6 bond and this plane is 10.2(3)° and 5.02(3)° in **3**. The distance between iron and C6 is 2.954(4) Å in **2** and 3.034(4) Å in **3**. The length of the C1A–C6 bond is 1.432(4) Å in **2** and 1.444(5) Å in **3**, whereas that of the C6–C7 bond is 1.367(4) Å in **2** and 1.362(5) Å in **3**. The bonding situation observed in **2** and **3** is to compare with that determined for the cationic  $\eta^6$ -fulvene complex **6** (Fig. 7).

It is evident that all the above-mentioned structural features can be explained assuming an important contribution of the charge-separated structure **B** (Fig. 1) in description of the structure of the ground states of **2** and **3**. Unexpectedly, the contribution of this structure seems to be higher in **2** than in **3**. This may be due to the larger distortion from the coplanarity of the  $\pi$ -system observed in **2** than in **3**. In fact, the plane of the five-membered ring in the indane moiety forms with the plane of the substituted Cp ring an angle of 35.8(2)° in **2** and 31.2(2)° in **3** (the intersection axis is approximately the C6–C7 bond). In **2**, the carbonyl oxygen is only slightly pushed away from the indane five-membered ring plane (0.168(3) Å) and the angle between this plane and the plane of the C16(C17N2)(C18N2) moiety is 15.9(2)°. In **3**, the angle between the indane five-membered ring plane and the plane of the C16(C17N2)(C18N2) moiety is 12.7(2)°, whereas the same angle for the C19(C20N3)(C21N4) moiety is 21.6(2)°. The bonds linking the C(CN)<sub>2</sub> moieties to the indane rings (1.372(5) and 1.375(5) Å) seem to be longer than the C8–C16 bond in **2** (1.361(4) Å), but unfortunately these differences are not statistically significant.

Both compounds crystallise in centrosymmetrical space groups ( $P\bar{1}$  and  $P2_1/c$ , respectively), excluding bulk second-order NLO properties.

Table 1  
Summary of crystallographic data and structure refinement details

	2	3
<i>Crystal data</i>		
Empirical formula	C <sub>23</sub> H <sub>14</sub> N <sub>2</sub> OFe	C <sub>26</sub> H <sub>14</sub> N <sub>4</sub> Fe
Formula weight	390.22	438.23
Crystal description	Green plate	Dark green needle
Crystal size (mm <sup>3</sup> )	0.32 × 0.12 × 0.6	0.1 × 0.1 × 0.6
Space group	P $\bar{1}$	P2 <sub>1</sub> /c
Unit cell dimensions		
<i>a</i> (Å)	11.180(2)	12.690(3)
<i>b</i> (Å)	12.114(2)	9.144(2)
<i>c</i> (Å)	7.354(3)	17.830(2)
$\alpha$ (°)	107.51(2)	
$\beta$ (°)	105.14(2)	99.758(8)
$\gamma$ (°)	66.458(9)	
<i>V</i> (Å <sup>3</sup> )	859.5(4)	2038.9(4)
<i>Z</i>	2	4
<i>d<sub>x</sub></i> (g cm <sup>-3</sup> )	1.508	1.428
<i>Data collection</i>		
Diffractometer	Rigaku AFC5S	Rigaku AFC5S
Radiation type	Cu–K $\alpha$ (1.54178)	Cu–K $\alpha$ (1.54178)
$\lambda$ (Å)		
$\mu$ (mm <sup>-1</sup> )	7.15	6.09
Temperature (K)	293(2)	296(2)
Data collected ( <i>h, k, l</i> )		
	–6 ≤ <i>h</i> ≤ 13	0 ≤ <i>h</i> ≤ 15
	–13 ≤ <i>k</i> ≤ 14	0 ≤ <i>k</i> ≤ 10
	–8 ≤ <i>l</i> ≤ 8	–22 ≤ <i>l</i> ≤ 21
Number of reflections measured	3435	4056
Number of independent reflections	3262	3879
<i>R</i> <sub>int</sub>	0.0362	0.0389
Number of reflections with <i>I</i> > 2σ( <i>I</i> )	2702	1972
<i>Solution and refinement</i>		
Solution	Direct methods	Direct methods
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	
H atoms treatment	Refined	Refined
Number of parameters	301	337
<i>R</i> ( <i>F</i> ) <sup>a</sup>	0.057	0.121
<i>wR</i> ( <i>F</i> <sup>2</sup> ) <sup>b</sup>	0.118 <sup>c</sup>	0.117 <sup>d</sup>
<i>R</i> ( <i>F</i> ) <sup>a</sup>	0.042 for 2702 reflections	0.046 for 1972 reflections
<i>wR</i> ( <i>F</i> <sup>2</sup> ) <sup>b</sup>	0.109 for 2702 reflections <sup>c</sup>	0.102 for 1972 reflections <sup>d</sup>
( $\Delta/\sigma$ ) <sub>max</sub>	0.000	0.003
Different peak/hole (e Å <sup>-3</sup> )	0.447/–0.513	0.348/–0.386

<sup>a</sup>  $R(F) = \Sigma(|F_o - F_c|) / \Sigma|F_o|$ .

<sup>b</sup>  $wR(F^2) = [\Sigma w(|F_o - F_c|)^2 / \Sigma|F_o|^2]^{1/2}$ .

Table 2  
Selected bond lengths (Å) and angles (°)

Parameter	2	3
<i>Bond lengths (Å)</i>		
C1A–C6	1.432(4)	1.444(2)
C7–C6	1.367(4)	1.362(5)
C16–C8	1.361(4)	1.372(5)
C16–C18	1.432(4)	1.418(6)
C16–C17	1.440(4)	1.429(6)
C7–C8	1.464(3)	1.471(5)
C7–C11	1.486(4)	1.471(5)
C9–C10	1.385(4)	1.413(5)
C9–C12	1.398(4)	1.383(6)
C9–C8	1.482(4)	1.465(5)
C10–C11	1.484(4)	1.462(5)
O1–C11	1.212(3)	–
C11–C19	–	1.375(5)
C19–C20	–	1.443(6)
C19–C21	–	1.417(6)
C17–N1	1.139(4)	1.140(5)
C18–N2	1.141(4)	1.140(5)
C20–N3	–	1.134(5)
C21–N4	–	1.145(6)
<i>Bond angles (°)</i>		
C1A–C6–C7	131.5(3)	127.9(4)
C6–C7–C8	124.5(2)	126.3(3)
C6–C7–C11	127.6(2)	126.7(4)
C8–C7–C11	106.9(2)	106.4(3)
C7–C8–C9	107.5(2)	107.1(3)
C8–C9–C12	131.7(3)	131.5(4)
C7–C11–C10	105.8(2)	106.9(4)
C7–C11–O1	128.7(3)	–
C7–C11–C19	–	125.5(4)
C10–C11–O1	125.5(3)	–
C10–C11–C19	–	126.3(4)
C7–C8–C16	126.4(2)	127.9(4)
C8–C16–C17	123.7(3)	123.2(4)
C8–C16–C18	123.4(2)	124.1(4)
C16–C17–N1	177.3(3)	177.3(5)
C16–C18–N2	176.8(3)	175.4(5)
C17–C16–C18	112.8(2)	112.7(4)
C19–C20–N3	–	178.5(6)
C19–C21–N4	–	174.6(5)
C20–C19–C21	–	112.7(4)

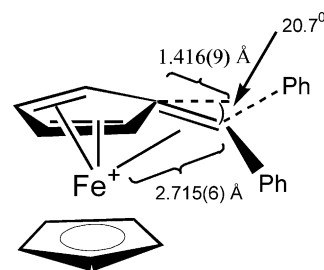


Fig. 7. Structural features of the CpFeCpCH(Ph)<sub>2</sub><sup>+</sup> (data taken from Ref. [5]).

### 2.3. Linear and nonlinear optical properties of 2 and 3

The second-order NLO properties of **2** and **3** have been investigated using EFISH generation technique

which provides information about scalar product  $\mu\beta(2\omega)$  of the vectorial part of the first hyperpolarisability tensor  $\beta$  and the dipole moment vector  $\mu$ .

Table 3  
Electronic absorption and EFISH data

Compound	$\lambda_{\max}$ ( $\epsilon_{\max} \times 10^{-4}$ ) in $\text{CHCl}_3$ (nm) ( $\text{cm}^{-1} \text{M}^{-1}$ )	$\mu\beta \cdot (2\omega)$ at 1907 nm ( $10^{-48}$ esu)	References
<b>1</b>	419 (1.3), 667 (0.7) <sup>a</sup>	140	[10]
<b>2</b>	414 (1.0), 632 (0.5)	160	This work
<b>3</b>	415 (1.9), 659 (0.6)	280	This work

<sup>a</sup> In dichloromethane; in chloroform  $\lambda_{\max}$  424 and 677 nm are reported, but the values of  $\epsilon_{\max}$  are not given.

Electronic absorption and  $\mu\beta \cdot (2\omega)$  data for **2** and **3** along with those of **1**, taken from Ref. [10], are collected in Table 3.

The electronic absorption spectra of Fc- $\pi$ -A compounds usually exhibit two absorption bands in the visible region. The lower energy band is attributed to a metal-to-ligand charge transfer (MLCT) transition, whereas its higher energy counterpart to a  $\pi$ - $\pi^*$  transition (in fact both bands have some d-d character). Both bands are red-shifted when the acceptor strength increases and display significant solvatochromism (Table 4) [10,11].

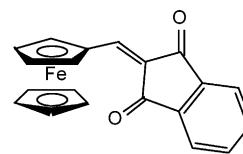
The data of Table 3 indicate that linear optical properties (i.e. energies and intensities of the absorption bands corresponding to the above-mentioned charge transfer transitions) of **2** and **3** are close to those reported for **1**. The value of  $\mu\beta \cdot (2\omega)$  of **1** and **2** are practically identical, whereas that of **3** is twice higher. The data confirm strong electron-acceptor properties of 3-dicyanomethylidene-1-indanone and 1,3-bis(dicyanomethylidene)indane acceptor groups, suggested earlier for purely organic systems [14–17].

#### 2.4. Redox properties

The cyclic voltammetry studies of compounds **2** and **3** were carried out in acetonitrile solutions. For comparison, the Fe(II)/Fe(III) oxidation potentials of ferrocenecarboxaldehyde (**4**) and 2-(ferrocenylmethylidene)-1,3-indandione (**5**) [20] were also measured under the same conditions.

Table 4  
Solvatochromism of **2** and **3** ( $\lambda_{\max}$  and  $\epsilon_{\max}$  of the lowest energy band in various solvents)

Solvent	$\lambda_{\max}$ (nm) ( $\epsilon_{\max} \times 10^{-4}$ ( $\text{cm}^{-1} \text{M}^{-1}$ ))	
	<b>2</b>	<b>3</b>
Hexane	613 (0.4)	637 (0.7)
Benzene	622 (0.4)	656 (0.7)
Chloroform	632 (0.5)	659 (0.6)



**5**

The cyclic voltammograms are shown in Fig. 8. The oxidation potentials are gathered in Table 5.

All compounds studied show a reversible single-electron oxidation wave due to the oxidation of Fe(II) to Fe(III) in the ferrocene fragment. All oxidation potentials are shifted anodically with respect to the oxidation potential of ferrocene (0.392 V vs. SCE). This means that electron density at the iron atom in **2–5** is reduced by the effect of electron-withdrawing groups. The indandione moiety in **5** seems to be weaker electron-accepting group than the formyl group in **4**. The replacement of one carbonyl oxygen in **5** by the  $\text{C}(\text{CN})_2$  moiety brings about an anodic shift of the oxidation potential of 30 mV, whereas the same substitution of the second carbonyl oxygen causes an anodic shift of 26 mV. The observed effect is therefore roughly additive. Compounds **2** and **3** also show two irreversible one-electron reduction processes at  $\sim -0.65$  V and  $-0.8$  to  $0.9$  V. We assign these waves to reduction to unstable radical anions and dianions. Similar behaviour of a Fc- $\pi$ -A system with a strong acceptor group has already been noted [21].

### 3. Conclusions

Compounds **2** and **3** are strongly polarised Fc- $\pi$ -A systems exhibiting low-lying intramolecular charge-transfer bands in their electronic absorption spectra and enhanced second-order NLO properties ( $\mu\beta$ ). The energies of the charge-transfer transitions as well as oxidation potentials of the Fc moiety suggest that separation of the charge in the ground state of **3** is more important than in **2**. However, X-ray data lead to the opposite conclusion. Deformation of the metallocene moiety, characteristic for a  $\eta^6$ -fulvene structure, is larger in **2** than in **3**. In our opinion, packing effects present in the solid state may be responsible for this discrepancy.

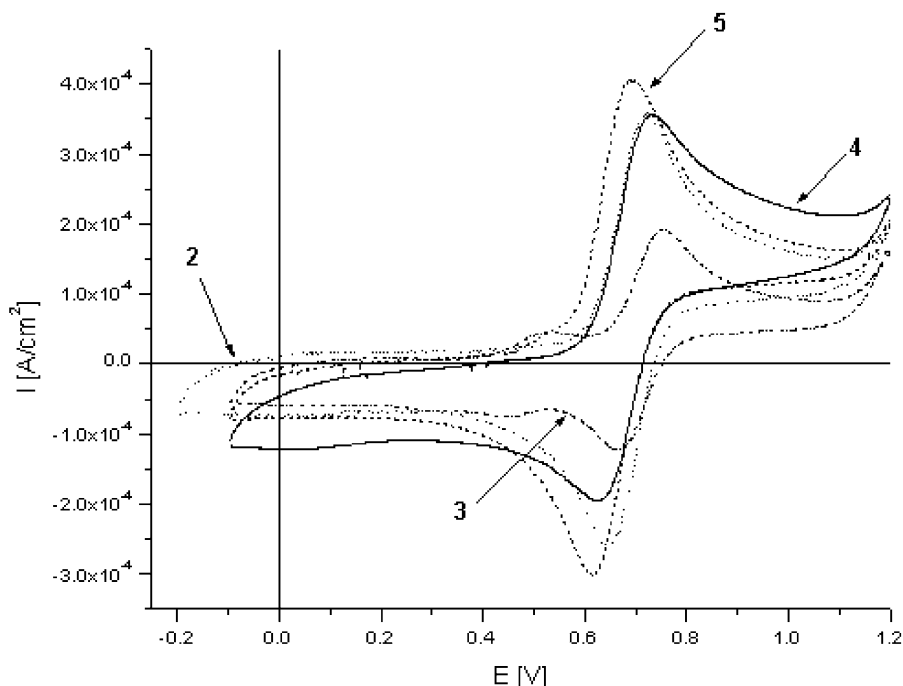


Fig. 8. The cyclic voltammety curves of the compounds **2–5** on a polycrystalline Au working electrode in acetonitrile solutions ( $c = 1 \times 10^{-3} \text{ mol dm}^{-3}$ ; supporting electrolyte:  $\text{Et}_4\text{NClO}_4$ ,  $0.1 \text{ mol dm}^{-3}$ ),  $v = 0.200 \text{ V s}^{-1}$ ; reference electrode SCE ( $\text{KCl}_{\text{sat}}$ ).

Table 5  
Cyclic voltammety data for compounds **2–5**

Compound	$E_{1/2}$ (V) vs. $\text{Fc}/\text{Fc}^+$	$\Delta E_p$ (V)
<b>2</b>	0.292	0.077
<b>3</b>	0.318	0.088
<b>4</b>	0.286	0.108
<b>5</b>	0.262	0.079

#### 4. Experimental

All operations were performed under an atmosphere of dry pure argon. Solvents were freshly distilled over the appropriate drying agents immediately prior to use. Compound **5** was prepared according to the literature method [21]. All other reagents were commercially available (Fluka, Aldrich) and were used as received. Chromatographic separations were carried out on Kieselgel 60 (230–400-mesh ASTM) purchased from Merck, using chloroform–hexane (1:1) as eluent.  $^1\text{H-NMR}$  spectra were recorded in  $\text{CDCl}_3$  solutions on a Varian Gemini 200 BB spectrometer at 200 MHz. Electronic absorption spectra were recorded on a Helios  $\alpha$  spectrometer.

##### 4.1. Synthesis of **2**

To a boiling solution of ferrocenecarboxaldehyde (40 mg, 0.19 mmol) in methanol (5 ml), 3-dicyanomethyle-

neindan-1-one (110 mg, 0.57 mmol) was added and the solution was stirred without heating for 15 min. After evaporation of the solvent, chromatography and recrystallisation from hexane, green **2** was obtained in 86% yield.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): 8.66 (d,  $J = 6.6 \text{ Hz}$ , aromatic H), 8.46 (s, 1H, vinylic H), 7.88 (d,  $J = 6.6 \text{ Hz}$ , aromatic H), 7.74 (m, 2H, aromatic H), 5.32 (bs, 2H, substituted Cp), 5.05 (bs, 2H, substituted Cp), 4.35 (s, 5H, unsubstituted Cp). VIS ( $\lambda_{\text{max}}/\text{solvent}$ ): 613 nm (hexane), 622 nm (benzene), 632 nm (chloroform). Anal. Calc. for  $\text{C}_{23}\text{H}_{14}\text{FeN}_2\text{O}$ : C, 70.79; H, 3.62; N, 7.18. Found: C, 70.57; H, 3.73; N, 7.09%.

##### 4.2. Synthesis of **3**

A solution of ferrocenecarboxaldehyde (106 mg, 0.5 mmol) and 1,3-bis(dicyanomethylene)indane (80 mg, 0.33 mmol) in acetic anhydride (12 ml) was heated to  $55\text{--}60^\circ\text{C}$  for 1.5 h. After evaporation of the solvent, chromatography ( $\text{SiO}_2/\text{chloroform}$ –hexane 1:1) and recrystallisation from hexane, dark green compound was obtained in 67% yield.  $^1\text{H-NMR}$  (acetone- $d_6$ ,  $\delta$ ): 8.71 (s, 1H, -vinylic H), 8.60 and 8.49 (ms, 1H each H-4 and H-7), 8.00 (m, 2H, H-5 and H-6), 5.18 (t,  $J = 2.1 \text{ Hz}$ , 2H, substituted Cp), 5.00 (t,  $J = 2.1 \text{ Hz}$ , 2H, substituted Cp), 4.38 (s, 5H, unsubstituted Cp). VIS ( $\lambda_{\text{max}}/\text{solvent}$ ): 637 nm (hexane), 656 nm (benzene), 659 nm (chloroform). Anal. Calc. for  $\text{C}_{26}\text{H}_{14}\text{FeN}_4$ : C, 71.23; H, 3.19; N, 12.78. Found: C, 70.95; H, 3.34; N, 12.55%.

#### 4.3. X-ray

Data were collected on a Rigaku AFC5S diffractometer using Cu–K $\alpha$  ( $\lambda = 1.54178 \text{ \AA}$ ) X-ray source and a graphite monochromator. Analytical absorption corrections were applied. Experimental details are given in Table 1. The crystal structures were solved by direct methods using SHELXS86 [22] and refined by full-matrix least-square method using SHELXL97 [23]. All hydrogen atoms except for H2 atom were refined using rigid body model. The molecular geometry was calculated by PARST [24] and PLATON [25].

#### 4.4. EFISH measurements

The principle of EFISH technique is described elsewhere [18,19]. In order to avoid reabsorption of the generated second harmonics, the data were recorded using 1.907  $\mu\text{m}$ , 10 ns incident laser pulses. The compounds were dissolved in chloroform at various concentrations (0–5 mM). The centrosymmetry of the solution was broken by dipolar orientation of the chromophores with a high-voltage pulse (around 5 kV applied on 2 mm during 5  $\mu\text{s}$ ) synchronised with the laser pulse. The compounds were dissolved in chloroform at various concentrations (0–5 mM) and put into the cell. Calibration of the cell was made by monitoring the second-harmonic signal generated by a series of solutions of 2-methyl-4-nitroaniline in chloroform ( $\mu\beta = 71 \times 10^{-48} \text{ esu}$ ).

#### 4.5. Cyclic voltammetry

The experiments were carried out using standard three-electrode system with a platinum mesh as an auxiliary electrode and the working polycrystalline gold electrode prepared by means of electrochemical cleaning in 1.0 M HClO $_4$ . As a reference electrode, the classical SCE (in water KCl $_{\text{sat}}$  solutions, connected by Luggin capillary and electrolytic bridge with acetonitrile supporting electrolyte) one was used as a reference electrode. All measurements were conducted by means of PAR 273 potentiostat–galvanostat. The CorWare and CorView 2.4 programs were used for database (with  $\pm 0.001 \text{ V}$  of measured potentials and  $\pm 1 \times 10^{-5}$  accuracy). The measurements were carried out in acetonitrile (Fluka AG, p.a.) without purification. Tetraethylammonium perchlorate (Et $_4$ NClO $_4$ , 0.1 mol dm $^{-3}$  electrolyte; FLUKA AG, p.a.) was used as a supporting electrolyte. The sweep potential rate was 0.020–0.200 V s $^{-1}$ .

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