Synthesis and Liquid Crystalline Properties of Some [3]Ferrocenophane-containing Schiff's Bases and β-Enaminoketone

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A novel series of mono-substituted [3ferrocenophane-containing Schiff's bases was synthesized by condensing the isomeric 3- and 2- p-aminophenyl[3]ferrocenophanes with aldehydes of the common formulas $p\text{-}C_{12}H_{25}O(C_6H_4)COO(C_6H_3)(X)CHO$ and $p\text{-}C_{12}H_{25}O\text{-}(C_6H_3)(X)\text{-}CHO$, (X=H or OH). Condensation of these aldehydes with the disubstituted isomers, 3,4-di- and 3,4'-bis- p-aminophenyl[3ferrocenophanes, yielded an another series of [3]ferrocenophane-containing azomethines. Besides, a β-enaminoketone derived from the 3-(p-aminophenyl)[3]ferrocenophane and $p\text{-}C_{12}H_{25}O\text{-}(C_6H_4)\text{-}(CO)\text{-}CH_2\text{-}CHO$ was prepared. Structures of the synthesized compounds were determined by means of mass, IR, UV, and ^1H NMR spectroscopies. Mono-substituted derivatives obtained from the 3-aminophenyl[3]ferocenophane and $p\text{-}C_{12}H_{25}O(C_6H_4)COO(C_6H_3)(X)CHO$ (X=H or OH) exhibited thermotropic mesomorphism of the nematic type identified by characteristic schliren textures under a polarizing optical microscope. The 3,4-disubstituted [3]ferrocenophane imines are non-mesogenic, while their isomeric 3,4'-bis-substituted analogues showed smectogenic properties. The [3]ferrocenophane-containing β-enaminoketone showed complex mesomorphic behavior apparently connected with occurrence of the keto-enamine and imino-enol tautomeric equilibrium in this compound.

Keywords: Liquid crystal, metallomesogen, ferrocene, [3]ferrocenophane, Schiff's base, aminovinylketone

I.   Introduction

Ferrocene-containing liquid crystals attract the continuous interest of many researchers all over the world [1, 2]. Three-dimensional core of a ferrocene molecule and its ability to involve in many organic reactions create extended possibilities for the syntheses of liquid crystals with widely varied molecular shapes. Among liquid crystalline ferrocene compounds those containing [3]ferrocenophane units showed broader mesophases in comparison with their unbridged analogues [3]. Furthermore, the possibility of various isomers in derivatives of rotationally fixed ferrocenophanes results in wide diversity of different molecular geometries occurring in their liquid crystalline derivatives. Thus, certain advantages of the ferrocenophane moiety over its

unbridged ferrocene counterpart in liquid crystalline systems make the former a valuable unit for incorporation into promesogenic building blocks. Recently we reported [4] inclusion of the aryl substituents to a [3]ferrocenophane molecule, which gave rise to isolation of several *p*-nitrophenylated isomers. Further efforts to obtain mesogenic materials from these arylated products afforded a series of new [3]ferrocenophane-containing liquid crystals which are described in the present article. Some of the synthesized compounds are designed specially for coordinating transition metal ions and obtaining heteronuclear metallomesogenic systems [4], which are of special interest due to their unique magnetic and optical properties.
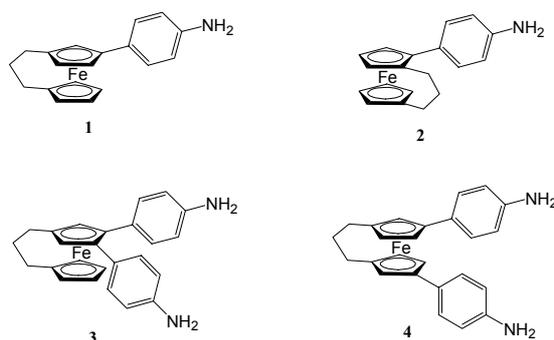

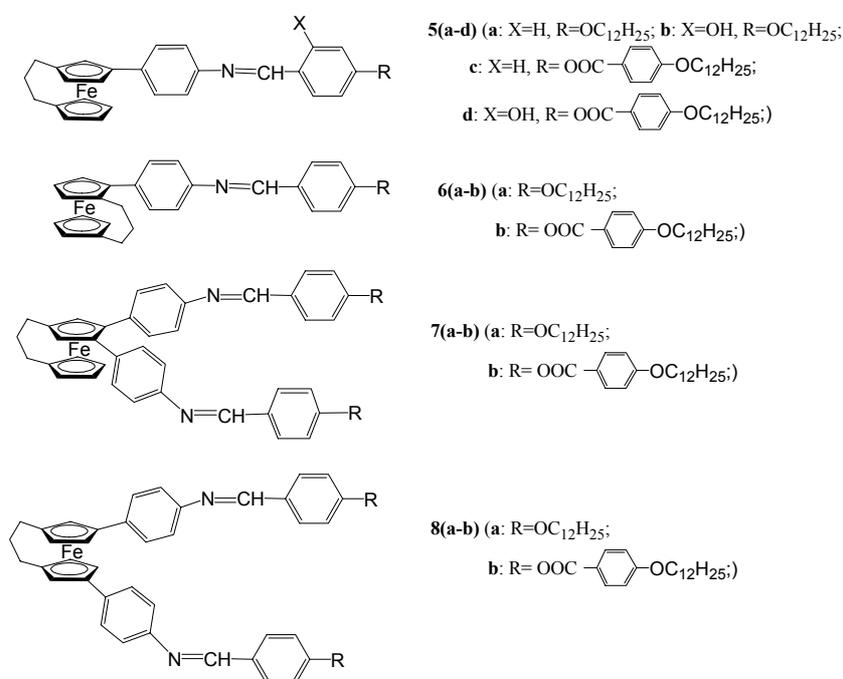**Figure 1: Structures of [3]ferrocenophane containing amines 1-4.**

Figure 2: Structures of [3]ferrocenophane containing Schiff's bases 5-8.

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II.   Results and Discussion

1. *Syntheses and Spectral Properties*

The ferrocenophane containing amines **1–4** (Fig.1) were obtained by reduction of the respective p-nitrophenyl[3]ferrocenophanes [4] with stannous(II) chloride. The imines **5–8** (Fig.2) were obtained by the Schiff's condensation of amines **1–4** with corresponding aldehydes **10** and **19**. Synthetic routes towards the ferrocenophane containing Schiff's bases **5–8** are outlined in the Figure 3.
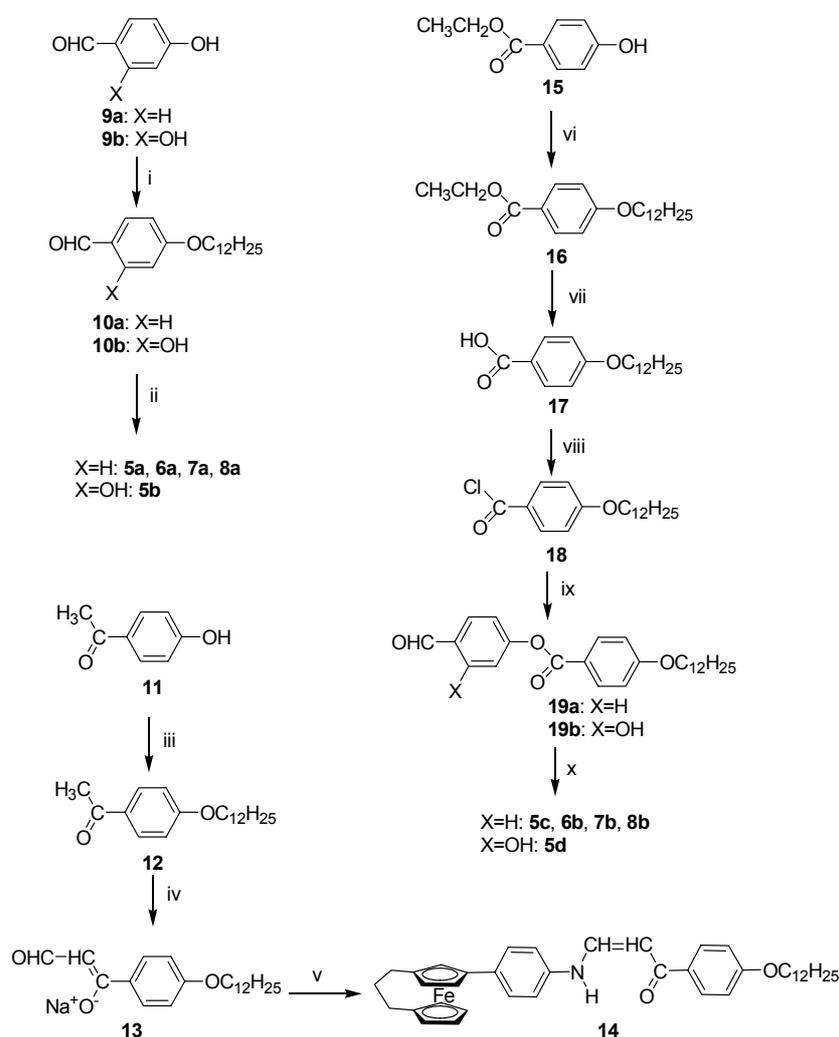
Figure 3: Synthesis of the [3]ferrocenophane-containing Schiff's bases and b-aminovinylketone. Reagents and conditions: (i, iii, vi) BrC$_{12}$H$_{25}$, K$_2$CO$_3$, in acetone, reflux; (ii, x) relevant amines 1-4, EtOH, reflux; (iv) ethylformiate, Na, abs. benzene, reflux; (v) amine 1, equimolar HCl, EtOH, reflux; vii) KOH, water/ethanol, reflux; (viii) SOCl$_2$, reflux; (ix) aldehyde 9a or 9b, pyridine/benzene, reflux.

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All the alkoxylated products were prepared using the Williamson reaction: 4-dodecyloxybenzaldehyde **10a** and 2-hydroxy-4-dodecyloxybenzaldehyde **10b** were prepared by etherification correspondingly of 4-hydroxybenzaldehyde **9a** and 2,4-dihydroxybenzaldehyde **9b** with dodecyl bromide and potassium carbonate in acetone; similar procedure was used to prepare 4-dodecyloxyacetophenone **12** from 4-hydroxyacetophenon **11**; 4-dodecyloxybenzoic acid **17** was obtained via hydrolysis of ethyl-(4-dodecyloxy)benzoate **16**, where the latter was prepared by an etherification reaction between ethyl-(4-hydroxy)benzoate **15** and 1-bromododecane. An esterification reaction between 4-hydroxybenzaldehyde **9a** and 4-dodecyloxybenzoyl chloride **18** afforded 4-(4'-dodecyloxybenzoyloxy)benzaldehyde **19a**. 2,4-Dihydroxybenzaldehyde **9b** reacts in the same conditions yielding 2-hydroxy-4-(4'-dodecyloxybenzoyloxy)benzaldehyde **19b**. β-Aminovinylketone **14** was synthesized using a reaction of 4-dodecyloxybenzoylacetaldehyde sodium salt **13** with hydrochloride of 3-(4'-aminophenyl)[3]ferrocenophane **1**. Mass-spectroscopic, IR and ^{1}H NMR data of the synthesized compounds are in a full agreement with the proposed structures. The compounds **5b**, **5d** and **14** are able to form complexes with various transition metals due to inclusion of appropriate coordinating groups into their molecules.

The figured configurations of the amines **1-4** are based on the X-ray structural studies of their nitro-precursors [4]. A propylene bridge of [3]ferrocenophane appears as three groups of signals in the areas of $1.85 – 2.00$, $2.00 – 2.10$ and $2.30 – 2.45$ ppm in ^{1}H NMR spectrum of the amine **2**, while in the amine **1** all relevant signals appear in the region of $1.85 – 2.05$ ppm. This conforms to a less symmetric structure of the amine **2** in comparison with the amine **1** and consequently more varied distances between a benzene mojety and different protons of an alkylene bridge. It is remarkable that in a ^{1}H NMR spectrum of the amine **3** two protons assigned to a diphenylated cyclopentadiene ring appear as a singlet at 3.24 ppm. The chemical and magnetic equivalency of these protons is a consequence of their equal surrounding in respect to the aromatic substituents and other parts of the [3]ferrocenophane fragment.

A ferrocene moiety is revealed in the UV spectra of all the synthesized compounds (Table 1) by two intensive maxima owing to $n-\pi^*$ and $\pi-\pi^*$ electronic transitions in the regions of $277 – 297$ and $330 – 339$ nm, and non-intensive absorption at $430 – 450$ nm assigned to d-d transitions of the iron atom [6]. An azomethine chromophore appears in the Schiff's bases **5-8** and β-aminovinilketone **14** with intensive maxima in the area of 380-390 nm which is absent in the spectra of the amines **1** and **2**. It is noticeable fact that the compounds **5b** and **5d** containing a hydroxyl in the *orto*-position to an azomethine group have an additional intensive maximum at ~ 350 nm. This additional band connected with the absorption of carbonyl groups emerged as a consequence of the imino-enol – keto-enamine tautomerism in these compounds [7,8].
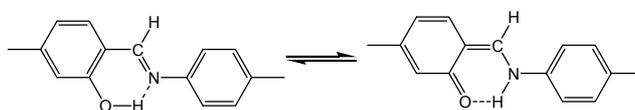
The intramolecular hydrogen bond provides the necessary stability to the corresponding keto-enamine tautomers.

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Table 1: UV/vis Spectra of the Compounds **1, 2, 5(a-d), 6(a,b), 7b, 8(a,b),** and **14** (CH_2Cl_2)

Comp.	λ_{max}, nm (log ε, l cm^{-1}·M^{-1})				
1	288 (4.303)	330 (sh) (3.511)	-	-	447 (2.698)
2	285 (4.079)	-*	-	-	440 (2.661)
5a	292 (4.461)	330 (4.377)	-	380 (sh) (4.136)	455 (sh) (3.507)
5b	286 (4.169)	326 (sh) (4.169)	347 (4.220)	385 (sh) (4.022)	440 (sh) (3.500)
5c	279 (4.639)	338 (sh) (4.236)	-	389 (sh) (3.909)	450 (sh) (3.483)
5d	277 (4.561)	330 (sh) (4.308)	350 (4.404)	382 (sh) (3.643)	460 (3.722)
6a	293 (4.401)	332 (4.338)	-	380 (sh) (3.968)	430 (sh) (3.293)
6b	277 (4.673)	329 (4.277)	-	385 (sh) (3.845)	425 (sh) (3.355)
7b	276 (5.058)	333 (4.644)	-	390 (sh) (4.228)	446 (sh) (3.820)
8a	297 (4.794)	335 (4.716)	-	387 (sh) (4.356)	455 (sh) (3.886)
8b	278 (4.931)	339 (4.520)	-	390 (sh) (4.165)	455 (3.918)
14	286 (4.224)	-*	-	390 (4.499)	450 (sh) (3.983)

*the absorption appears as inflexion and can not be defined

2. *Liquid crystalline properties*

Thermal behavior of the synthesized compounds was investigated under a polarizing microscope with a heating stage. The mono-substituted [3]ferrocenophane Schiff's bases **5a**, **5b**, and **6a** containing two benzene rings in a rigid core are non-mesomorphic (Table 2). As a matter of fact there are no evidenced examples of mono-substituted unbridged ferrocenes with two benzene rings showing liquid crystalline properties [1]. In a case of the compounds **5c** and **5d**, where a rigid core was extended by a third ring, thermotropic nematic phases were observed in a polarizing optical microscope. It is remarkable that the compound **6b**, which is isomeric to **5c**, is non-mesomorphic. A possible explanation of this fact is that the [3]ferrocenophane derivative **5c** has more extended geometry in comparison with the related 2-substituted isomer **6b**. At the same time a cyclopentadien ring of the [3]ferrocenophane fragment in the compound **6b** is very likely tilted in respect to the conjugated plane of an adjacent benzene ring because of sterical hindrance from a closely positioned propylene bridge. The characteristic UV absorption maxima of a ferrocene core at ~430 - 450 (Table 1) in the compounds **6a** and **6b** are significantly blue-shifted regarding to the related bands for their isomeric counterparts **5a** and **5c**, and this confirms additionally a previously made assumption. Thus, the conformational configuration where cyclopentadienyl rings are tilted from conjugation planes of the remaining promesogenic rigid core seems unfavorable for appearance of liquid crystalline properties in [3]ferrocenophane-containing systems.

It is interesting to compare the liquid crystalline behaviour of the [3]ferrocenophane compounds **5c**, **5d** and their ferrocene analogues [9]. The presence of a propylene bridge in the ferrocene moiety has a significant effect on the temperature range of a nematic phase in a case of the [3] ferrocenophane compound **5c**, which shows a broader mesophase (138 – 172 ºC) than its corresponding ferrocene analogue (154 – 165 ºC [9]). The nematic phase in the [3]ferrocenophane compound **5d** has almost the same width as in the related ferrocene-

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containing Schiff's base (130 – 163 ºC vs. 135 -171 ºC [9]). In general, addition of an alkylene bridge to the ferrocene fragment in a β-position to a promesogenic substituent enhances liquid crystalline properties of the mono-substituted ferrocenyl mesogens.

The disubstituted [3]ferrocenophane derivatives **7a** and **7b** do not exhibit mesomorphism. The compound **8a** shows unidentified smectic type of mesophase in a short temperature range 109 – 116 ºC. Optical texture was not defined clearly in this case, however the observed mesophase can be ascribed to a smectic type on account of its limited fluidity. The compound **8b** with a higher melting point (178 ºC) shows only a thermodynamically unstable mesophase upon cooling from an isotropic state. The optical textures under a polarizing microscope in this case were in many respects similar to those displayed by the compound **8a**.

Table 2: Phase behavior of the compounds **5(a-d)**, **6(a,b)**, **7(a,b)**, **8(a,b)** and **14**.

Compound	Transition	Temperatures, ºC
5a	Cr – I	116
5b	Cr – I	52
5c	Cr – N	138
	N – I	172
5d	Cr – N	130
	N – I	163
6a	Cr – I	105
6b	Cr – I	153
7a	Cr – I	60
7b	Cr – I	121
8a	Cr – S_x	109
	S_x – I	116
8b	Cr – I	178
	I – [S_x]	[155]
14	Complex mesomorphic behaviour*	

* 1. Fast heating (15 ºC/min): Cr_1 – I (152 ºC)/Cr2 (~ 5%). Fast cooling: I – [N] (124 ºC) – [S_A] (118 ºC) – Cr_1 (110 ºC) (Cr_1 is melting at 152 ºC in a second heating cycle).

2. Slow cooling from an isotrop between 152 – 125 ºC: I – Cr_2. Second heating: Cr_2 – I (192 ºC).

3. Cooling I (192 ºC) at 15 ºC/min: I – [N] (124 ºC) – [S_A] (118 ºC) – Cr_1 (110 ºC)

In order to compare stereometrical appearance of the isomeric pairs **5c** - **6b** and **7b** - **8b** their conformational models were obtained using HYPERCHEM 7 program for molecular simulation (Fig. 4). MM[+] mode calculation by steepest descent method was used for accomplishing initial geometries, and then further optimization was made using semi-empirical PM3 calculations by Fletcher – Reeves method. A propylene bridge in the mesogenic [3]ferrocenophane compound **5c** extends the long axis of the molecule, while in the [3]ferrocenophane compound **6b** it increases overall bulkiness of the ferrocene group in perpendicular direction to the molecular long axis. As a result of the unfavorable geometry the compound **6b** is non-mesogenic.

Commonly, both the di-substituted [3]ferrocenophanes **7b** and **8b** have undesirable stereometrical shapes for appearance of liquid crystalline properties. However, the heteroannular

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di-substituted compound **8b** showed a thermodynamically unstable mesophase (monotropic). In comparison with the homoannular di-substituted [3]ferrocenophane **7b** the compound **8b** has no restrictions for effective conjugation of all aromatic rings including cyclopentadiene rings of the ferrocene fragment, while in the former compound two adjacent benzene rings attached to the ferrocene moiety constrain each other, and, as consequence, their alignment in one plane with a cyclopentadien ring is hindered. Over again this confirmed by hypsochromic shift of the UV absorption maximum of the central iron atom at 446 nm in the compound **7b** in comparison with the analogous band for the isomer **8b** (Table 1). Hence, the [3]ferrocenophane derivatives **7a** and **7b** do not exhibit liquid crystalline properties, whereas the compounds **8a** and **8b** showed smectic phases. Though, mesomorphism of the latter compounds is merely poor due to their still not enough favorable molecular shapes.
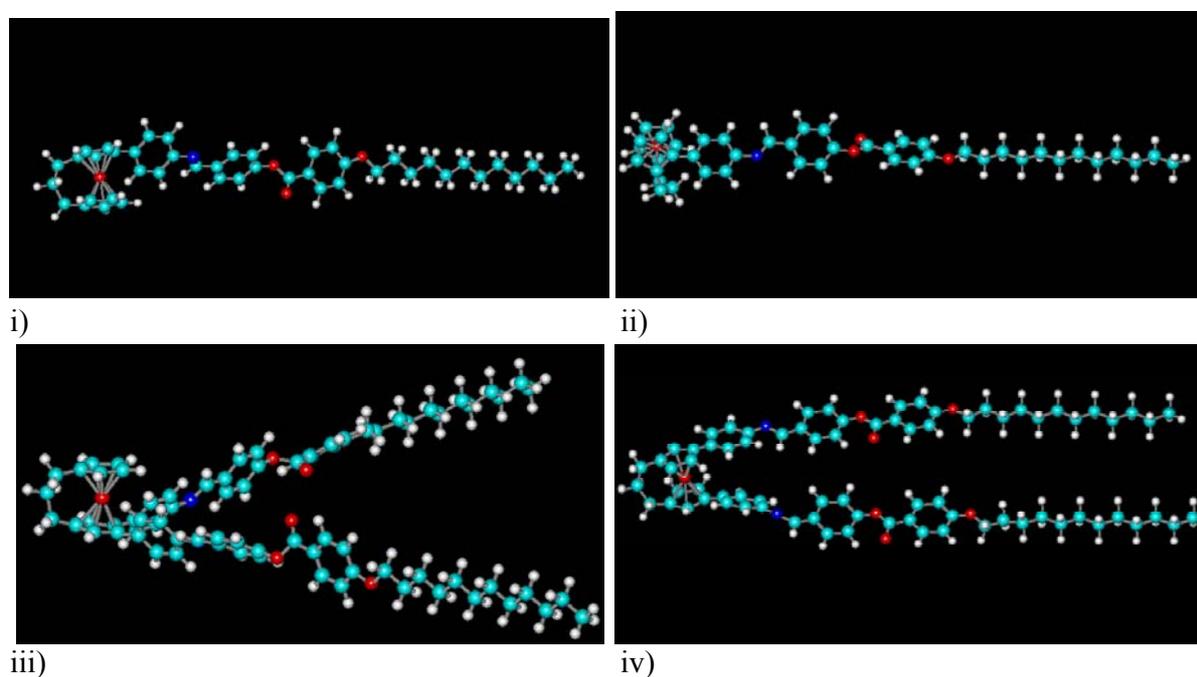

i)   ii)

iii)   iv)

Figure 4: Molecular simulation by the HYPERCHEM-7 program (Hipercube, Inc.) of the compounds 5c (i), 6b (ii), 7b (iii) and 8b (iv).

The β-aminovinyl ketone **14** showed complex behavior upon subsequent heating and cooling processes (Table 2). When a sample of the compound was heated fast, it melted to an isotropic state near 150 ºC. On the immediate rapid cooling there is a monotropic nematic phase appears at 124 ºC, then smectic A at 118 ºC which crystallizes upon further cooling below 110 ºC. This cycle can be repeated if the heating and cooling processes are performed fast enough. When cooling from an isotropic phase is carried out slowly the [3]ferrocenophane-containing β-aminovinyl ketone **14** crystallizes in the temperature range of 150 – 125 ºC into another crystal form. This second crystal form is rather high-melting (192º C) in comparison with the first crystal form. The first crystal form develops only upon fast cooling from the clearing point down to 124ºC, and further cooling from a liquid crystalline state. Generally, a sample of the

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compound **14** after the first heating-cooling cycle comprises a mixture of both crystal forms in different ratios depending on its thermal prehistory.

Obviously, the observed phase transformations in the β-aminovinyl ketone **14** are connected with the equilibrium of its keto-enamine and imino-enol tautomers.
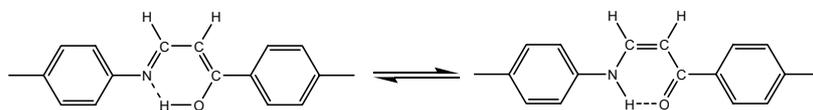
We believe that the initial low-melting keto-enamine tautomer after the first melt transforms into the more plane, and, consequently, higher-melting imino-enol tautomer. If further cooling is performed slowly enough, the latter tautomer starts to crystallize and leave a liquid zone of the tautomeric equilibrium. Eventually all the sample crystallizes mainly into the imino-enol tautomer on condition that it kept at the temperatures 125 – 140 ºC. If the cooling from an isotropic liquid is carried out rapidly the first tautomer still represented in a mixture of the tautomers by considerable amounts and can be crystallized from the intermediate liquid crystalline phases.

III. Conclusion

A series of Schiff's bases derived from 2- and 3- *p*-aminophenyl[3]ferrocenophanes has been synthesized. The 3-*p*-aminophenyl[3]ferrocenophane is a superior building block for the syntheses of ferrocenyl liquid crystals, that has been shown by comparison of the obtained nematogenic Schiff's bases containing three benzene rings in a rigid core with their unbridged analogues. Generally, inclusion of an alkylene bridge to the ferrocene fragment in a β-position to a promesogenic substituent stabilizes a liquid crystalline state of the mono-substituted ferrocenyl mesogens due to extension of their molecular long axis. The corresponding 2-substituted isomers do not exhibit liquid crystalline properties, because an alkylene bridge in this case increases an overall bulkiness of the ferrocene fragment in a perpendicular direction to the molecular long axis. Another series of azomethine compounds has been synthesized on the base of an isomeric pair of homoannular 3,4-di- and heteroannular 3,4'-bis- *p*-aminophenyl [3]ferrocenophanes. The homoannular di-substituted isomers are non-mesogenic, while their heteroannular counterparts show smectogenic behavior. Interference of two adjacent benzene rings in the homoannular isomer turns them out of the conjugation plane of a cyclopentadiene ring and makes molecular shape unfavorable for mesomorphism. Besides, a β-aminovinylketone containing two benzene rings has been synthesized from the 3-*p*-aminophenyl[3]ferrocenophane. In consequence of the keto-enamine and imino-enol tautomeric equilibrium this compound shows complex thermal behavior. Monotropic nematic and smectic A phases were observed upon rapid cooling of the [3]ferrocenophane-containing β-aminovinylketone, whereas slow cooling in a condition that only the higher melting tautomer crystallizes from a liquid phase leads to almost complete conversion of the compound into the high-melting imino-enol form.

IV. Experimental

Melting points were determined by the capillary method. Liquid crystalline properties were studied using a polarizing optical microscope "Olympus BH-2" equipped with a heating stage HS1 (INSTEC) and remote temperature controller RTC1 (INSTEC). IR spectra were recorded by using a Perkin-Elmer Paragon 1000 instrument. Mass spectra were obtained with a spectrometer MAT 8200 (Finnigan) by electron and chemical ionisation methods at 70 eV. UV and visible spectra in the region of 250 – 600 nm were recorded on a spectrophotometer Lambda-14 (Perkin-Elmer) in CH_2Cl_2. ^{1}H NMR spectra were measured on spectrometers ARX 300 and ARX 200 (Bruker) with TMS as an internal standard. Dried and distilled solvents were used in all cases.

3-(4-Aminophenyl)[3]ferrocenophane (1): 1.00 g (2.880 mmol) of 3-(p-nitrophenyl)[3]ferrocenophane, 2.60 g (11,522 mmol) of $SnCl_2 \cdot 2H_2O$ and 5 mL of aqueous HCl (conc.) were refluxed during 2 hrs in 50 mL of mixture i-PrOH/H_2O (1:1). A solution changes color from purple to yellow at the end of reaction. An obtained mixture was treated with Na_2CO_3 until obtaining pH=7. Iso-propanol was evaporated in a rotary evaporator, and the obtained yellow suspension was extracted with CH_2Cl_2. A separated aqueous layer was extracted again with dichloromethane, and combined organic layers were dried over an anhydrous Na_2SO_4. A sodium sulfate was filtered off, and dichloromethane was evaporated to dryness. The obtained residue was recrystallized from EtOH. Yield 0.86 g (94.1%). Yellowish orange powder, m.p. 95ºC. IR (KBr, cm[-1]): 3458.3 (N-H), 3368.3 (N-H), 2906.1 (C-H), 2835.5 (C-H), 1620.9, 1531.5, 1469.4, 1430.5, 1276.3, 1043.4, 829.0, 801.8. ^{1}H NMR (CDCl$_3$, δ, ppm): 1.85 – 2.05 (6H, m, Fc-CH$_2$), 3.41 (1H, m, Cp), 3.20 – 3.70 (2H, br. s, NH$_2$), 3.87 (1H, m, Cp), 4.03 (1H, m, Cp), 4.18 (2H, m, Cp), 4.38 (2H, m, Cp), 6.57 (2H, m, C$_6$H$_4$), 7.22 (2H, m, C$_6$H$_4$).

2-(4-Aminoophenyl)[3]ferrocenophane (2): 0.15 g (0.432 mmol) of 3-(p-nitrophenyl)[3]ferrocenophane was reduced with 0.6 g (2.659 mmol) of $SnCl_2 \cdot 2H_2O$ in a previous manner. 0.13 g of the obtained yellow oil was purified in a Al_2O_3 column (eluent CH_2Cl_2). Yield 0.07 g (51.1%). Yellow oil. IR (KBr, cm[-1]): 3451.4 (N-H), 3369.1 (N-H), 2915.0 (C-H), 2844.3 (C-H), 1620.0, 1524.2, 1437.3, 1277.3, 1044.0, 830.0, 800.8. ^{1}H NMR (CDCl$_3$, δ, ppm): 1.85 – 2.00 (4H, m, Fc-CH$_2$), 2.00-2.10 (1H, m, Fc-CH$_2$) 2.30-2.45 (1H, m, Fc-CH$_2$), 3.24 (1H, m, Cp), 3.40 – 3.80 (2H, br. s, NH$_2$), 3.93 (1H, m, Cp), 4.00 (1H, m, Cp), 4.06 (2H, m, Cp), 4.25 (2H, m, Cp), 6.63 (2H, m, C$_6$H$_4$), 7.23 (2H, m, C$_6$H$_4$).

3,4-Di(4-aminophenyl)[3]ferrocenophane (3): 0.0792 g (0.169 mmole) of 3,4-bis(p-nitrophenyl)[3]ferrocenophane, 0.2891 g (1.281 mmol) of $SnCl_2 \cdot 2H_2O$ and 0.4 mL of aqueous HCl (conc.) were refluxed during 4 hrs in 20 mL of a mixture i-PrOH/H_2O (2:1). Initial purple color of the reaction mixture turns to yellow at the end. An obtained mixture was neutralized with Na_2CO_3 until pH=7. Isopropanol was evaporated, and the obtained yellow suspension was extracted with CH_2Cl_2. A separated aqueous layer was extracted again with dichloromethane, and combined organic layers were dried over an anhydrous Na_2SO_4. The product was crystallized from dichloromethane solution by adding EtOH and evaporating CH_2Cl_2. Yield 0.0681 g (98.6%). Yellowish orange powder, m.p. 112ºC. Mass spectrum (m/e): 408 (M[+], 100). IR (KBr, cm[-1]): 3428.2 (N-H), 3361.0 (N-H), 1917.3 (C-H), 2845.7 (C-H), 1618.3, 1522.6, 1279.2, 1176.2, 830.6. 1H NMR (CDCl$_3$, δ, ppm): 1.80 – 2.15 (6H, m, Fc-CH$_2$), 2.50 – 3.50 (4H, br. s, NH$_2$), 3.74 (2H, m, Cp), 4.15 (2H, m, Cp), 4.29 (2H, s, Cp), 6.52 (2H, m, C6H4), 7.15 (2H, m, C$_6$H$_4$). $C_{25}H_{24}FeN_2$: Calc. 408.3240, Found 408.1278.

3,4'-Bis(4-aminophenyl)[3]ferrocenophane (4): 0.1203 g (0.257 mmole) of 3,4-bis(p-nitrophenyl)[3]ferrocenophane was reduced with 0.4535 g (2.010 mmol) of $SnCl_2 \cdot 2H_2O$ and 0.62

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mL of aqueous HCl (conc.) in 25 mL of a mixture i-PrOH/H2O (2:1). The reaction mixture was treated in a previous manner. Yield 0.1001 g (95.4%). Yellowish orange powder, m.p. 91ºC. Mass spectrum (m/e): 408 (M^+, 100). IR (KBr, cm^{-1}): 3428.2 (N-H), 3359.2 (N-H), 2907.3 (C-H), 2837.4 (C-H), 1618.2, 1528.3, 1275.5, 1179.1, 829.0. ^{1}H NMR (CDCl$_3$, δ, ppm): 1.85 – 2.10 (6H, m, Fc-CH$_2$), 2.70 – 4.10 (4H, br. s, NH$_2$), 3.78 (2H, m, Cp), 4.25 (2H, m, Cp), 4.32 (2H, m, Cp), 6.59 (2H, m, C$_6$H4), 7.16 (2H, m, C$_6$H$_4$). C$_{25}$H$_{24}$FeN$_2$: Calc. 408.3240, Found 408.1449.

4-Dodecyloxybenzaldehyde (10a): 6.9783 g (0.0571 mol) of 4-hydroxybenzaldehyde **9a**, 14.2423 g (0.0571 mol) of 1-bromododecane and 15 g of anhydrous potassium carbonate were refluxed for 40 hrs in 50 mL of acetone. Inorganic salts were filtered off, and acetone was evaporated to dryness. The residue was distilled under vacuum (165-170ºC / 0.007 mm Hg). Yield 12.3764 g (74.8%). Light yellow oil, which crystallize in a refrigerator forming paraffin-like solid. ^{1}H NMR (CDCl$_3$, δ, ppm): 0.87 (3H, t, CH$_3$), 1.29 (18H, m, CH$_2$), 1.77 (2H, m, C$\underline{H}_2$CH$_2$O), 4.05 (2H, t, CH$_2$O), 6.92 (2H, m, C$_6$H$_4$), 7.77 (2H, m, C$_6$H$_4$), 9.79 (1H, s, CHO).

2-Hydroxy-4-dodecyloxybenzaldehyde (10b): 7.8143 g (0.0566 mol) of 2,4-dihydroxybenzaldehyde **9b**, 14.1010 g (0.0566 mol) of 1-bromododecane and 40 g of anhydrous potassium carbonate were refluxed for 48 hrs in 100 mL of acetone. The obtained mixture was filtered, and a filtrate was evaporated to dryness. A residue was recrystallized from ethanol. Yield 13.1856 g (76.0%). White powder with m.p. 49 – 50ºC. ^{1}H NMR (CDCl$_3$, δ, ppm): 0.87 (3H, t, CH$_3$), 1.30 (18H, m, CH$_2$), 1.75 (2H, m, C$\underline{H}_2$CH$_2$O), 4.00 (2H, t, CH$_2$O), 6.39 (1H, m, C$_6$H$_3$), 6.51 (1H, m, C$_6$H$_3$), 7.40 (1H, m, C$_6$H$_3$), 9.71 (1H, s, CHO), 11.45 (1H, s, OH).

4-Dodecyloxyacetophenone (12): 16.51 g (0.1212 mol) of 4-hydroxyacetophenone **11**, 30.20 g (0.1212 mol) of dodecylbromide and 35 g of dry potassium carbonate were refluxed for 50 hrs in 100 mL of acetone. Inorganic salts were filtered off, and a precipitate on the filter was treated with 500 mL of water. Insoluble organics were filtered off and added to the first acetone filtrate. Acetone was evaporated to dryness, a residue was dissolved in chloroform, and a chloroform solution washed twice with water. A separated chloroform layer was dried over Na$_2$SO$_4$, and CH$_3$Cl was evaporated to dryness in a rotary evaporator. The product was recrysallized from ethanol. Yield 35 g (95%). White crystals, m.p. 58 – 59ºC. ^{1}H NMR (CDCl$_3$, δ, ppm): 0.85 (3H, t, CH$_3$), 1.28 (18H, m, CH$_2$), 1.75 (2H, m, C$\underline{H}_2$CH$_2$O), 1.49 (3H, s, CH$_3$CO), 3.97 (2H, t, CH$_2$O), 6.80 (2H, m, C$_6$H$_4$), 7.81 (2H, m, C$_6$H$_4$).

4-Dodecyloxybenzoic acid (17): 25.0 g (0.150 mol) of ethyl 4-hydroxy benzoate **15**, 37.5 g (0.150 mol) of 1-bromododecane and 130 g of potassium carbonate were refluxed in 250 mL of acetone during 50 hrs. A precipitate was filtered off, and a filtrate was evaporated to dryness. A solution of 8.4165 g (0.150 mol) of KOH in 200 mL of water/ethanol (1:1) was added to the residue of crude ester **16**, and the mixture was refluxed 24 hrs. Then 6 mL of aqueous HCl (conc.) was added, and refluxing continued for 2 hrs. The obtained white precipitate was filtered off and washed several times with water, and 2 times with ethanol. 44.3 g (96.4%) of the dry product was obtained. White powder, Cr – S$_A$ 94ºC, S$_A$ – N 131ºC, N – I 139ºC. ^{1}H NMR (CDCl$_3$, δ, ppm): 0.87 (3H, t, CH$_3$), 1.30 (18H, m, CH$_2$), 1.76 (2H, m, C$\underline{H}_2$CH$_2$O), 3.98 (2H, t, CH$_2$O), 6.84 (2H, m, C$_6$H$_4$), 7.90 (2H, m, C$_6$H$_4$), 9 – 10 (1H, very br. s, COOH).

4-(4-Dodecyloxybenzoyloxy)benzaldehyde (19a): 6.21 g (0.0203 mol) of 4-dodecyloxybenzoic acid **17** was refluxed for 5 hrs with 20 mL SOCl$_2$, and excess of thionyl chloride was distilled off. The traces of SOCl$_2$ were removed by applying vacuum during 1 hr. The obtained chloridic anhydride **18** without further characterization was dissolved in 20 mL of dry benzene and added dropwise during 45 min to a stirred solution of 2.48 g (0.0203 mol) of 4-hydroxybenzaldehyde **9a** in 20 mL of a mixture pyridine/benzene. The reaction mixture was

refluxed 4 hrs and stirred at room temperature overnight. Then mixture poured into 100 mL of water, an organic layer was separated in a separating funnel and washed with diluted aqueous HCl. Separated benzene solution was dried over sodium sulfate, filtered, and the filtrate evaporated to dryness. Recrystallization was performed in ethanol. Yield 7.69 g (92.3 %). White powder, Cr – N 66ºC, N – I 77ºC. ^{1}H NMR (CDCl$_3$, δ, ppm): 0.90 (3H, t, CH$_3$), 1.26 (18H, m, CH$_2$), 1.79 (2H, m, CH$_2$CH$_2$O), 3.98 (2H, t, CH$_2$O), 6.86 (2H, m, C$_6$H$_4$), 7.27 (2H, m, C$_6$H$_4$), 7.82 (2H, m, C$_6$H$_4$), 8.04 (2H, m, C$_6$H$_4$), 9.83 (1H, s, CHO).

2-Hydroxy-4-(4-dodecyloxybenzoyloxy)benzaldehyde (19b): The compound was prepared in a previous manner by esterification reaction of 3.5231 g (0.0255 mol) of 4-hydroxysalicylaldehyde **9b** with 7.8168 g (0.0255 mol) of 4-dodecyloxybenzoic acid **17**. Yield 5.5407 g (50.9%). White cotton-like substance, m.p. 73 – 74ºC.

A typical procedure for obtaining Schiff's bases (**5 – 8**): Equimolar amounts of the appropriate amine and aldehyde in ethanol were refluxed during of 0.5 – 1 hr. A precipitate obtained after cooling of the reaction mixture was filtered, and either recrystallized from ethanol, or precipitated from a CH$_2$Cl$_2$ solution by adding ethanol. Yields varied from 70 to 95%.

3-[4-(4-Dodecyloxybenzaldimino)phenyl][3]ferrocenophane (5a): Yield 87.0%. Light orange powder. Mass spectrum (m/e): 589 (M$^+$, 100), 420 ([M-C$_{12}$H$_{25}$]$^+$, 11.58. IR (KBr, cm^{-1}): 2919.4 (C-H), 2846.5 (C-H), 1607.9, 1568.9, 1519.6, 1465.5, 1421.6, 1304.1, 1247.2, 1162.4, 848.2. ^{1}H NMR (CDCl$_3$, δ, ppm): 0.88 (3H, t, CH$_3$), 1.27 (18H, m, CH$_2$), 1.81 (2H, m, CH$_2$CH$_2$O), 1.90 – 2.15 (6H, m, Fc-CH$_2$), 3.43 (1H, m, Cp), 3.90 (1H, m, Cp), 4.01 (2H, t, CH$_2$O), 4.12 (1H, m, Cp), 4.23 (2H, m, Cp), 4.50 (2H, m, Cp), 6.96 (2H, m, C$_6$H$_4$), 7.10 (2H, m, C$_6$H$_4$), 7.42 (2H, m, C$_6$H$_4$), 7.83 (2H, m, C$_6$H$_4$), 8.42 (1H, s, CH=N). C$_{38}$H$_{47}$FeNO: Calc. 589.6423, Found 589.3024.

3-[4-(2-Hydroxy-4-dodecyloxybenzaldimino)phenyl][3]ferrocenophane (5b): Yield 87.3%. Yellowish orange powder. Mass spectrum (m/e): 605 (M$^+$, 100). IR (KBr, cm^{-1}): 2918.8 (C-H), 2848.8 (C-H), 1608.1, 1592.5, 1519.2, 1466.9, 1431.7, 1316.2, 1279.4, 1185.6, 1102.0, 816.5. ^{1}H NMR (CDCl$_3$, δ, ppm): 0.88 (3H, t, CH$_3$), 1.27 (18H, m, CH$_2$), 1.79 (2H, m, CH$_2$CH$_2$O), 1.90 – 2.15 (6H, m, Fc-CH$_2$), 3.44 (1H, m, Cp), 3.89 (1H, m, Cp), 4.00 (2H, t, CH$_2$O), 4.11 (1H, m, Cp), 4.22 (2H, m, Cp), 4.49 (2H, m, Cp), 6.44 (1H, m, C$_6$H$_3$), 6.55 (1H, m, C$_6$H$_3$), 7.10 (2H, m, C$_6$H$_4$), 7.42 (2H, m, C$_6$H$_4$), 8.08 (1H, m, C$_6$H$_3$), 8.86 (1H, s, CH=N).

3-{4-[4-(4-Dodecyloxybenzoyloxy)benzaldimino]phenyl}[3]ferrocenophane (5c): Yield 69.7%. Yellowish orange powder. Mass spectrum (m/e): 709 (M$^+$, 100), 420 ([M-C$_{12}$H$_{25}$OC$_6$H$_4$CO]$^+$, 15.04), 289 ([C$_{12}$H$_{25}$OC$_6$H$_4$CO]$^+$, 17.66), 120 ([OC$_6$H$_4$CO]$^+$, 64.02). IR (KBr, cm^{-1}): 2920.4 (C-H), 2849.9 (C-H), 1720.8, 1610.0, 1514.5, 1466.1, 1320.2, 1267.6, 1206.9, 1173.7, 1161.0, 1079.9, 845.6. ^{1}H NMR (CDCl$_3$, δ, ppm): 0.88 (3H, t, CH$_3$), 1.24 – 1.35 (18H, m, CH$_2$), 1.82 (2H, m, CH$_2$CH$_2$O), 1.90 – 2.10 (6H, m, Fc-CH$_2$), 3.44 (1H, m, Cp), 3.90 (1H, m, Cp), 4.04 (2H, t, CH$_2$O), 4.13 (1H, m, Cp), 4.23 (2H, m, Cp), 4.52 (2H, m, Cp), 6.97 (2H, m, C$_6$H$_4$), 7.14 (2H, m, C$_6$H$_4$), 7.33 (2H, m, C$_6$H$_4$), 7.44 (2H, m, C$_6$H$_4$), 7.96 (2H, m, C$_6$H$_4$), 8.15 (2H, m, C$_6$H$_4$), 8.51 (1H, s, CH=N). C$_{45}$H$_{51}$FeNO$_3$: Calc. 709.7498, Found 709.7062.

3-{4-[2-Hydroxy-4-(4-dodecyloxybenzoyloxy)benzaldimino]phenyl}[3]ferrocenophane (5d): Yield 77.5%. Yellowish orange powder. 725 (M$^+$, 100), 436 ([M-C$_{12}$H$_{25}$OC$_6$H$_4$CO]$^+$, 87.53), 289 ([C$_{12}$H$_{25}$OC$_6$H$_4$CO]$^+$, 7.68), 120 ([OC$_6$H$_4$CO]$^+$, 50.76). IR (KBr, cm^{-1}): 2918.5 (C-H), 2848.0 (C-H), 1724.1, 1601.9, 1522.2, 1466.8, 1251.9, 1167.4, 1149.3, 1117.9, 1064.2, 837.9. ^{1}H NMR (CDCl$_3$, δ, ppm): 0.88 (3H, t, CH3), 1.24 – 1.35 (18H, m, CH$_2$), 1.82 (2H, m, CH$_2$CH$_2$O), 1.90 – 2.10 (6H, m, Fc-CH$_2$), 3.44 (1H, m, Cp), 3.90 (1H, m, Cp), 4.04 (2H, t, CH2O), 4.15 (1H, m, Cp), 4.24 (2H, m, Cp), 4.52 (2H, m, Cp), 6.82 (1H, dd, J1 = 2.24 Hz, J2 = 8.37 Hz, C$_6$H$_3$), 6.88

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(1H, d , J1 = 2.24 Hz, C_6H_3), 6.97 (2H, m, C_6H_4), 7.19 (2H, m, C_6H_4), 7.42 (1H, d, J2 = 8.37 Hz, C_6H_3), 7.46 (2H, m, C_6H_4), 8.14 (2H, m, C_6H_4), 8.66 (1H, s, CH=N). $C_{45}H_{51}FeNO_4$: Calc. 725.7492, Found 725.5511.

*2-[4-(4-Dodecyloxybenzaldimino)phenyl][3]ferrocenophane **(6a)***: Yield 93.2 %. Yellowish orange powder. Mass spectrum (m/e): 589 (M^+, 100), 420 ([M-$C_{12}H_{25}]^+$, 7.67. IR (KBr, cm^{-1}): 2917.7 (C-H), 2849.2 (C-H), 1602.1, 1584.7, 1510.1, 1466.1, 1248.8, 1160.2, 848.3. ^1H NMR (CDCl$_3$, δ, ppm): 0.88 (3H, t, CH_3), 1.25 – 1.35 (18H, m, CH_2), 1.81 (2H, m, C$\underline{H}_2$CH$_2$O), 1.88 – 2.00 (4H, m, Fc-CH_2), 2.09 (1H, m, Fc-CH_2), 2.44 (1H, m, Fc-CH_2), 3.25 (1H, m, Cp), 3.95 (1H, m, Cp), 4.02 (2H, t, CH_2O), 4.02 (1H, m, Cp), 4.13 (2H, m, Cp), 4.31 (1H, m, Cp), 4.36 (1H, m, Cp), 6.97 (2H, m, C_6H_4), 7.14 (2H, m, C_6H_4), 7.44 (2H, m, C_6H_4), 7.84 (2H, m, C_6H_4), 8.44 (1H, s, CH=N). $C_{38}H_{47}FeNO$: Calc. 589.6423, Found 589.4709.

*2-{4-[4-(4-Dodecyloxybenzoyloxy)benzaldimino]phenyl}[3]ferrocenophane **(6b)***: Yield 69.7%. Yellowish orange powder. Mass spectrum (m/e): 709 (M^+, 100), 420 ([M-$C_{12}H_{25}OC_6H_4CO]^+$, 7.79), 289 ([$C_{12}H_{25}OC_6H_4CO]^+$, 40.50), 120 ([$OC6H4CO]^+$, 65.18). IR (KBr, cm^{-1}): 2919.6 (C-H), 2849.7 (C-H), 1731.2, 1602.7, 1510.2, 1254.3, 1198.0, 1160.0, 1063.6, 1007.6, 843.2. ^1H NMR (CDCl$_3$, δ, ppm): 0.88 (3H, t, CH_3), 1.25 – 1.35 (18H, m, CH_2), 1.82 (2H, m, C$\underline{H}_2$CH$_2$O), 1.88 – 1.97 (4H, m, Fc-CH_2), 2.10 (1H, m, Fc-CH_2), 2.45 (1H, m, Fc-CH_2), 3.26 (1H, m, Cp), 3.96 (1H, m, Cp), 4.03 (1H, m, Cp), 4.05 (2H, t, CH_2O), 4.14 (2H, m, Cp), 4.31 (1H, m, Cp), 4.37 (1H, m, Cp), 6.98 (2H, m, C_6H_4), 7.18 (2H, m, C_6H_4), 7.33 (2H, m, C_6H_4), 7.46 (2H, m, C_6H_4), 7.98 (2H, m, C_6H_4), 8.15 (2H, m, C_6H_4), 8.53 (1H, s, CH=N). $C_{45}H_{51}FeNO_3$: Calc. 709.7498, Found 709.6663.

*3,4-Di-[4-(4-dodecyloxybenzaldimino)phenyl][3]ferrocenophane **(7a)***: Yield 82.5 %. Yellowish orange amorphous solid. Mass spectrum (m/e): 952 (M^+, 100). ^1H NMR (CDCl$_3$, δ, ppm): 0.88 (3H, t, CH_3), 1.24 – 1.37 (18H, m, CH_2), 1.80 (2H, m, C$\underline{H}_2$CH$_2$O), 1.95 (2.10 (3H, m, Fc-CH_2), 3.81 (1H, m, Cp), 4.01 (2H, t, CH_2O), 4.22 (1H, m, Cp), 4.44 (1H, s, Cp), 6.97 (2H, m, C_6H_4), 7.05 (2H, m, C_6H_4), 7.37 (2H, m, C_6H_4), 7.83 (2H, m, C_6H_4), 8.42 (1H, s, CH=N). $C_{63}H_{80}FeN_2O_2$: Calc. 953.1854, Found 953.1212.

*3,4-Di-{4-[4-(4-dodecyloxybenzoyloxy)benzaldimino]phenyl}[3]ferrocenophane **(7b)***: Yield 88.0%. Yellowish orange powder. Mass spectrum (m/e): 1192 (M^+, 88.61), 903 ([M-C12H25OC6H4CO]$^+$, 15.76), 289 ([C12H25OC6H4CO]$^+$, 19.11), 120 ([OC6H4CO]$^+$, 100). IR (KBr, cm^{-1}): 2921.8 (C-H), 2850.9 (C-H), 1734.0, 1604.0, 1510.9, 1466.5, 1257.3, 1200.9, 1165.6, 1064.5, 843.7. ^1H NMR (CDCl$_3$, δ, ppm): 0.88 (3H, t, CH_3), 1.25 – 1.35 (18H, m, CH_2), 1.82 (2H, m, C$\underline{H}_2$CH$_2$O), 1.95 – 2.10 (3H, m, Fc-CH_2), 3.83 (1H, m, Cp), 4.05 (2H, t, CH_2O), 4.23 (1H, m, Cp), 4.46 (1H, s, Cp), 6.98 (2H, m, C_6H_4), 7.08 (2H, m, C_6H_4), 7.33 (2H, m, C_6H_4), 7.40 (2H, m, C_6H_4), 7.97 (2H, m, C_6H_4), 8.15 (2H, m, C_6H_4), 8.52 (1H, s, CH=N). $C_{77}H_{88}FeN_2O_6$: Calc. 1193.4005, Found 1192.8614.

*3,4'-Bis-[4-(4-dodecyloxybenzaldimino)phenyl][3]ferrocenophane **(8a)***: Yield 73.4%. Yellowish orange powder. Mass spectrum (m/e): 952 (M^+, 100). IR (KBr, cm^{-1}): 2922.4 (C-H), 2850.8 (C-H), 1607.5, 1570.0, 1520.8, 1464.5, 1422.1, 1306.0, 1249.3, 1162.8, 844.3. ^1H NMR (CDCl$_3$, δ, ppm): 0.88 (3H, t, CH_3), 1.24 – 1.50 (18H, m, CH_2), 1.80 (2H, m, C$\underline{H}_2$CH$_2$O), 2.00 (3H, m, Fc-CH_2), 3.91 (1H, m, Cp), 4.02 (2H, t, CH_2O), 4.35 (1H, m, Cp), 4.45 (1H, m, Cp), 6.98 (2H, m, C_6H_4), 7.13 (2H, m, C_6H_4), 7.35 (2H, m, C_6H_4), 7.85 (2H, m, C_6H_4), 8.46 (1H, s, CH=N). $C_{63}H_{80}FeN_2O_2$: Calc. 953.1854, Found 953.1243.

*3,4'-Bis-{4-[4-(4-dodecyloxybenzoyloxy)benzaldimino]phenyl}[3]ferrocenophane **(8b)***: Yield 78.1%. Yellowish orange powder. Mass spectrum (m/e): 1192 (M^+, 69.12), 903 ([M-C12H25OC6H4CO]$^+$, 15.76), 289 ([C12H25OC6H4CO]$^+$, 26.39), 120 ([OC6H4CO]$^+$, 100). IR

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(KBr, cm^{-1}): 2920.8 (C-H), 2850.3 (C-H), 1729.8, 1603.0, 1510.1, 1255.0, 1197.9, 1158.1, 1064.4, 843.4. ^{1}H NMR (CDCl$_3$, δ, ppm): 0.88 (3H, t, CH$_3$), 1.25 − 1.35 (18H, m, CH$_2$), 1.83 (2H, m, CH$_2$CH$_2$O), 1.99 − 2.05 (3H, m, Fc-CH$_2$), 3.94 (1H, m, Cp), 4.05 (2H, t, CH$_2$O), 4.23 (1H, m, Cp), 4.47 (1H, m, Cp), 6.98 (2H, m, C$_6$H$_4$), 7.17 (2H, m, C$_6$H$_4$), 7.34 (2H, m, C$_6$H$_4$), 7.38 (2H, m, C$_6$H$_4$), 7.99 (2H, m, C$_6$H$_4$), 8.15 (2H, m, C$_6$H$_4$), 8.56 (1H, s, CH=N). C$_{77}$H$_{88}$FeN$_2$O$_6$: Calc. 1193.4005, Found 1193.3039.

*3-{4-[1-(4-Dodecyloxybenzoyl)ethenyl-2-amino]phenyl}[3]ferrocenophane **(14)***: 0.4261 g (0.575 mol) of ethyl formiate, which was obtained by refluxing equimolar amounts of absolute ethanol and formic acid over an anhydrous CaCl$_2$ during 30 min and distilling off ethyl ester of formic acid (b.p. 53 − 54ºC), 1.7501 g (0.575 mol) of 4-dodecyloxyacetophenone **12** and 0.1322 g (0.575 mol) of Na were refluxed in 10 ml of absolute benzene during 6 hrs. A precipitate was filtered off and recrystallized from benzene. 1.3562 g (66.6 %) of white powder was obtained. 0.3348 g (0.944 mmol) of the obtained sodium enolate **13** was refluxed 15 min with 0.2996 g (0.944 mmol) of the amine **1** in 10 mL of ethanol and 0.2 mL of 5N HCl. A precipitate was filtered off, dissolved in CH$_2$Cl$_2$ and filtered through Celite 545. Dichloromethane was evaporated from a filtrate, and the residue was recrystallized from n-butanol. Yield 0.4670 g (78.3 %). Yellowish orange powder. Mass spectrum (m/e): 631 (M$^+$, 100), 462 ([M-C12H25]$^+$, 6.32). IR (KBr, cm^{-1}): 2920.5 (C-H), 2850.1 (C-H), 1626.4, 1599.7, 1573.1, 1531.7, 1465.9, 1279.5, 1244.9, 1168.4, 1038.8, 831.2. ^{1}H NMR (CDCl$_3$, δ, ppm): 0.88 (3H, t, CH$_3$), 1.15 − 1.65 (18H, m, CH$_2$), 1.80 (2H, m, CH$_2$CH$_2$O), 1.90 − 2.15 (3H, m, Fc-CH$_2$), 3.42 (1H, m, Cp), 3.90 (1H, m, Cp), 4.01 (2H, t, CH$_2$O), 4.11 (1H, m, Cp), 4.21 (2H, m, Cp), 4.46 (2H, m, Cp), 5.97 (1H, d, J$_1$ = 7.88 Hz, CH-CO), 6.93 (2H, m, C$_6$H$_4$), 6.97 (2H, m, C$_6$H$_4$), 7.37 (2H, m, C$_6$H$_4$), 7.45 (1H, dd, J$_1$ = 7.88 Hz, J$_2$ = 12.25 Hz, CH=CH) 7.90 (2H, m, C$_6$H$_4$), 12.14 (1H, d, J$_2$ = 12.25 Hz, N-H). C$_{40}$H$_{49}$FeNO$_2$: Calc. 631.6796, Found 631.9114.

V.   Acknowledgements

VI.   References

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