

# Synthesis and liquid crystal properties of copper(II) and palladium(II) chelates with new ferrocene-containing enamino ketones

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## ARTICLE INFO

### Article history:

Received 9 December 2008

Accepted 30 January 2009

Available online 3 March 2009

### Keywords:

Ferrocene

Liquid crystal

Metallomesogen

$\beta$ -Aminovinylketone

Heteronuclear complex

## ABSTRACT

Heterometallic liquid crystals are of special interest because of the possibility to combine optical, magnetic and electric properties of different metal ions in one mesogenic molecule. In order to investigate new heteropolynuclear mesogenic systems, a series of  $\beta$ -aminovinylketone ligands derived from acetyl ferrocene have been synthesized. Subsequently Cu(II) and Pd(II) ions were incorporated into the enamino ketone chelate core. The obtained ligands and complexes were characterized by element analysis,  $^1\text{H}$  NMR, IR and UV–Vis spectroscopies. According to thermal polarizing microscopy and DSC studies, the ligands and Cu(II) complexes exhibit disordered soft crystal phases upon cooling from the isotropic liquid state. The Pd(II) complexes showed monotropic smectic C mesomorphism. The metal centres in the synthesized heteropolynuclear mesogens are in close vicinity to each other, which is of considerable interest from the viewpoint of the potential electron-transfer interactions between a ferrocene core and the central ions.

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## 1. Introduction

Metallomesogens attract considerable interest of many researchers due to their special properties brought by metal atoms in addition to liquid crystallinity [1–8]. Moreover, various new molecular shapes can be realized in metal-containing liquid crystals, such as square, folded square, lantern, pyramidal and octahedral geometrical shapes, which are difficult to achieve in conventional organic mesogens. Metallomesogen systems with multiple metal centres are of special interest from the standpoint of bringing various functional properties into liquid crystalline materials, e.g. colour, luminescence, metamagnetism or electric conductivity. This inspired many research groups to focus on molecular design and the synthesis of new examples of heteropolynuclear metallomesogens [9–21]. Earlier we developed an approach which utilizes the advantages of a ferrocene unit, such as chemical and thermal stability, three-dimensional structure, and aromatic chemistry, for obtaining heteropolynuclear mesogenic structures [15–21]. Ferrocene is an exceptional building block for introducing metal atoms into liquid crystal molecules because of its unique properties [22–35]. In this paper, we report promesogenic ferrocene derivatives containing a  $\beta$ -aminovinylketone chelate core, which were used as versatile ligands for the syntheses of heteronuclear metallomesogens. It is noteworthy that an enamino ketone framework has been widely applied earlier for the syn-

theses of various liquid crystalline metallocomplexes [36–48]. In comparison with the earlier reported ferrocene- and [3] ferrocenophane-containing enamino ketone complexes, the metal centres in the present compounds are positioned in a close proximity to each other [17,21]. Indeed, it was interesting to compare the liquid crystal properties of these structurally isomorphous heteronuclear systems. Potentially, the electronic exchange interactions between the metal centres in the obtained complexes may lead to interesting magnetic, optical and redox properties.

## 2. Experimental

### 2.1. General details

Reagent grade chemicals and solvents were purchased from Aldrich, TCI and Fluka. Solvents were dried and freshly distilled just before use.  $^1\text{H}$  NMR spectra were measured on a Bruker Avance/DPX 250 using the internal TMS standard and  $\text{CDCl}_3$  as a solvent. FT-IR spectra were recorded on a Nicolet Avatar-360 FT-IR spectrometer in KBr pellets. DSC thermographs were obtained on a Perkin Elmer Diamond DSC with a scan rate of  $10^\circ\text{C}/\text{min}$ . Thermo-optical observations were carried out on a Nikon Eclipse E600 Pol optical polarizing microscope equipped with a Mettler Toledo FP82 HT hot stage system and a Mettler FP90 central processor. Microphotographs were obtained with a Moticam 2300 digital camera. UV and visible spectra in the region of 200–800 nm were recorded on a Shimadzu UV-1650PC spectrophotometer using  $\text{CH}_2\text{Cl}_2$  as a solvent. Elemental analyses were performed on a Fisons instrument 2A1108 at the Korea Institute of Science and

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Technology. Column chromatographic separations were carried out on neutral Al<sub>2</sub>O<sub>3</sub> from Aldrich. Alumina TLC plates D-5160 Duran from Macherey–Nagel were used for selecting eluants and controlling the separation process. The literature procedure was used for the syntheses of the 4-aminophenyl alkyloxybenzoates [49–54].

### 2.1.1. Ferrocenylketoacetaldehyde sodium (**2**)

Ethyl formate (1.2 mL, 14.9 mmol) and **1** (2.00 g, 8.77 mmol) in absolute benzene (Caution: carcinogen! Consult MSDS) (15 mL) were refluxed for 6 h in the presence of metallic sodium (Caution: highly reactive material! Consult MSDS) (0.60 g, 26.1 mmol) [55]. A precipitate of sodium enolate was filtered off and recrystallized from ethanol. Yield 2.44 g (86%), orange powder. Used without further characterization.

### 2.1.2. 1-Ferrocenyl-1-[[4-(4-dodecyloxybenzoyloxy)phenyl]amino]propen-2-one (**3a**)

The *p*-aminophenyl ester of *p*-dodecyloxy benzoic acid (1.165 g, 2.93 mmol) and **2** (0.815 g, 2.93 mmol) were dissolved separately in hot ethanol, and then mixed together. Concentrated aqueous HCl (26 μL, 0.30 mmol) was added dropwise to the mixture by a syringe, and then the mixture was refluxed for 30 min. An orange precipitate was filtered out after the mixture cooled down. The precipitate was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered through Celite 545. The solvent was evaporated using a rotary evaporator. Recrystallization from *n*-butanol gave 0.472 g (25%) of an orange powder. <sup>1</sup>H NMR (250 MHz): δ 0.89 (t, 3H, CH<sub>3</sub>), 1.27 (br. s, 16H, CH<sub>2</sub>), 1.48 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.82 (quintet, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 4.04 (t, 2H, OCH<sub>2</sub>), 4.19 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.47 (t, 2H, C<sub>5</sub>H<sub>4</sub>), 4.80 (t, 2H, C<sub>5</sub>H<sub>4</sub>), 5.61 (d, *J*<sub>H,H</sub> = 7.5 Hz, 1H, H1), 6.98 (d, *J*<sub>H,H</sub> = 10 Hz, 2H, H6), 7.09 (d, *J*<sub>H,H</sub> = 8 Hz, 2H, H3), 7.17 (d, *J*<sub>H,H</sub> = 8 Hz, 2H, H4), 7.30 (dd, *J*<sub>H,H</sub>(1) = 7.5 Hz, *J*<sub>H,H</sub>(2) = 12.5 Hz, 1H, H2), 8.13 (d, *J*<sub>H,H</sub> = 10 Hz, 2H, H5), 11.84 (d, *J*<sub>H,H</sub> = 12.5 Hz, 1H, NH). FT-IR (cm<sup>-1</sup>): 2915 (C–H), 2846 (C–H), 1727 (C=O), 1627 (C=O), 1602 (COC=C), 1515 (C=C aryl), 1508 (C=C aryl), 1489 (C=C aryl), 1256, 1199, 1165, 1083, 1072, 1029, 1010, 823, 788, 759, 525, 504, 486. Anal. Calc. for C<sub>38</sub>H<sub>45</sub>FeNO<sub>4</sub>: C, 71.81; H, 7.13; N, 2.20. Found: C, 71.81; H, 7.22; N, 2.45%.

### 2.1.3. 1-Ferrocenyl-1-[[4-(4-hexadecyloxybenzoyloxy)phenyl]amino]propen-2-one (**3b**)

This compound was prepared in an analogous manner to the previous reaction from 3.295 mmol of the appropriate reagents. Yield 0.64 g (28%). <sup>1</sup>H NMR (250 MHz): δ 0.88 (t, 3H, CH<sub>3</sub>), 1.26 (br. s, 24H, CH<sub>2</sub>), 1.48 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.82 (quintet, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 4.04 (t, 2H, OCH<sub>2</sub>), 4.20 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.47 (t, 2H, C<sub>5</sub>H<sub>4</sub>), 4.80 (t, 2H, C<sub>5</sub>H<sub>4</sub>), 5.61 (d, *J*<sub>H,H</sub> = 7.5 Hz, 1H, H1), 6.97 (d, *J*<sub>H,H</sub> = 10 Hz, 2H, H6), 7.09 (d, *J*<sub>H,H</sub> = 9 Hz, 2H, H3), 7.18 (d, *J*<sub>H,H</sub> = 9 Hz, 2H, H4), 7.31 (dd, *J*<sub>H,H</sub>(1) = 7.5 Hz, *J*<sub>H,H</sub>(2) = 12.5 Hz, 1H, H2), 8.13 (d, *J*<sub>H,H</sub> = 10 Hz, 2H, H5), 11.84 (d, *J*<sub>H,H</sub> = 12.5 Hz, 1H, NH). FT-IR (cm<sup>-1</sup>): 2917 (v, C–H), 2849 (v, C–H), 1727 (v, C=O), 1626 (v, C=O), 1603 (v, COC=C), 1514 (v, C=C aryl), 1509 (v, C=C aryl), 1490 (v, C=C aryl), 1257, 1201, 1164, 1082, 1072, 1030, 1008, 824, 790, 757, 524, 509, 489. Anal. Calc. for C<sub>42</sub>H<sub>53</sub>FeNO<sub>4</sub>: C, 72.93; H, 7.72; N, 2.02. Found: C, 72.85; H, 7.69; N, 1.98%.

### 2.1.4. Bis-[1-ferrocenyl-1-[[4-(4-dodecyloxybenzoyloxy)phenyl]amino]propen-2-onato} copper(II) (**4a**)

The ligand **3a** (104.3 mg, 0.1641 mmol) and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (17.1 mg, 0.0856 mmol) were dissolved separately in hot ethanol. The solutions were mixed and refluxed for 15 min. A brown precipitate was formed after cooling, which was centrifuged and washed 3 times with ethanol using the centrifugation method. Yield 90.0 mg (82%). FT-IR (cm<sup>-1</sup>): 2924 (C–H), 2850 (C–H), 1735 (C=O), 1597 (C=N), 1567 (C=C), 1515 (C=C aryl), 1508 (C=C aryl), 1489 (C=C aryl), 1424, 1338, 1333, 1247, 1201, 1199, 1161, 1070,

1014, 1009, 849, 815, 771, 578, 564, 549, 523, 490. Anal. Calc. for C<sub>76</sub>H<sub>88</sub>CuFe<sub>2</sub>N<sub>2</sub>O<sub>8</sub>: C, 68.49; H, 6.65; N, 2.10. Found: C, 68.59; H, 6.58; N 2.26%.

### 2.1.5. Bis-[1-ferrocenyl-1-[[4-(4-hexadecyloxybenzoyloxy)phenyl]amino]propen-2-onato} copper(II) (**4b**)

This complex was synthesized in an analogous manner to the previous reaction. Yield 97.0 mg (87%). FT-IR (cm<sup>-1</sup>): 2923 (C–H), 2848 (C–H), 1734 (C=O), 1599 (C=N), 1568 (C=C), 1513 (C=C aryl), 1509 (C=C aryl), 1490 (C=C aryl), 1425, 1337, 1331, 1250, 1201, 1198, 1160, 1072, 1014, 1009, 847, 811, 770, 579, 564, 550, 524, 489. Anal. Calc. for C<sub>84</sub>H<sub>104</sub>CuFe<sub>2</sub>N<sub>2</sub>O<sub>8</sub>: C, 69.82; H, 7.25; N, 1.94. Found: C, 69.58; H, 7.19; N, 2.04%.

### 2.1.6. Bis-[1-ferrocenyl-1-[[4-(4-dodecyloxybenzoyloxy)phenyl]amino]propen-2-onato} palladium(II) (**5a**)

The ligand **3a** (98.8 mg, 0.154 mmol) was dissolved completely in freshly distilled 1,4-dioxane (2 mL) in a one-neck 25 mL round flask. Pd(OAc)<sub>2</sub> (20.4 mg, 0.091 mmol) was dissolved in 1,4-dioxane (1 mL) in a separate flask. The prepared solutions were mixed and refluxed for 15 min. The product was precipitated by adding ethanol (~4 mL). The precipitate was filtered off and recrystallized from hot ethanol. Yield 48.2 mg (45.5%), brown powder. <sup>1</sup>H NMR (250 MHz): δ 0.89 (t, 3H, CH<sub>3</sub>), 1.28 (br. s, 16H, CH<sub>2</sub>), 1.50 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.83 (quintet, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 3.96 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 4.07 (s overlapped with t, 7H, OCH<sub>2</sub> and C<sub>5</sub>H<sub>5</sub>), 4.23 (t, 2H, C<sub>5</sub>H<sub>4</sub>), 5.31 (d, *J*<sub>H,H</sub> = 7.5 Hz, 1H, H1), 6.91 (d, *J*<sub>H,H</sub> = 7.5 Hz, 1H, H2), 7.01 (d, *J*<sub>H,H</sub> = 9 Hz, 2H, H6), 7.25 (d overlapped with CDCl<sub>3</sub>, 2H, H3), 7.44 (d, *J*<sub>H,H</sub> = 8 Hz, 2H, H4), 8.20 (d, *J*<sub>H,H</sub> = 9 Hz, 2H, H5). FT-IR (cm<sup>-1</sup>): 2920 (C–H), 2850 (C–H), 1731 (C=O), 1605 (C=N), 1575 (C=C), 1506 (C=C aryl), 1500 (C=C aryl), 1411, 1350, 1251, 1191, 1165, 1074, 1014, 1010, 845, 811, 759, 564, 560, 500, 490. Anal. Calc. for C<sub>76</sub>H<sub>88</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>8</sub>Pd: C, 66.36; H, 6.45; N, 2.04. Found: C, 65.70; H, 6.43; N, 2.26%.

### 2.1.7. Bis-[1-ferrocenyl-1-[[4-(4-hexadecyloxybenzoyloxy)phenyl]amino]propen-2-onato} palladium(II) (**5b**)

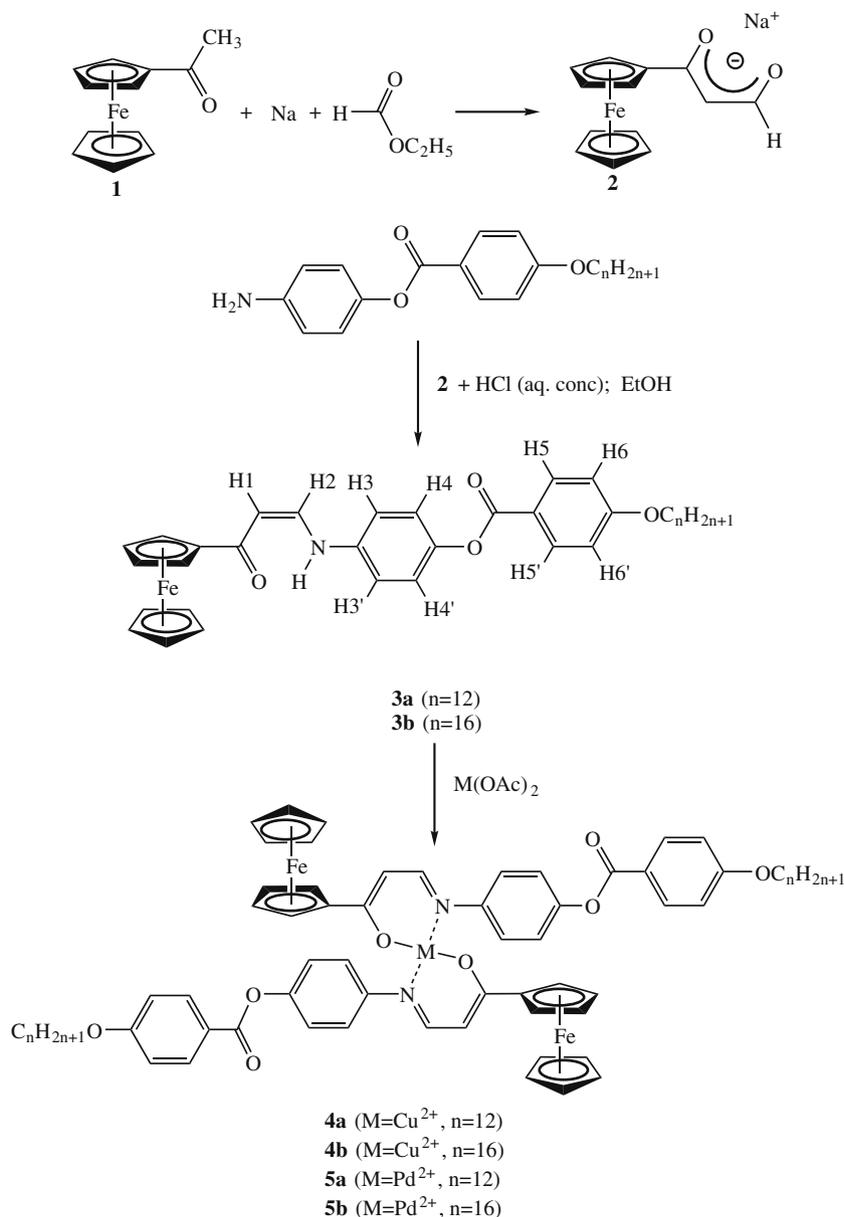
This complex was synthesized in an analogous manner to the previous reaction. Yield 44.0 mg (37%). <sup>1</sup>H NMR (250 MHz): δ 0.88 (t, 3H, CH<sub>3</sub>), 1.27 (br. s, 24H, CH<sub>2</sub>), 1.50 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.84 (quintet, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 3.96 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 4.07 (s overlapped with t, 7H, OCH<sub>2</sub> and C<sub>5</sub>H<sub>5</sub>), 4.23 (t, 2H, C<sub>5</sub>H<sub>4</sub>), 5.31 (d, *J*<sub>H,H</sub> = 7.5 Hz, 1H, H1), 6.91 (d, *J*<sub>H,H</sub> = 7.5 Hz, 1H, H2), 7.01 (d, *J*<sub>H,H</sub> = 9 Hz, 2H, H6), 7.25 (d overlapped with CDCl<sub>3</sub>, 2H, H3), 7.44 (d, *J*<sub>H,H</sub> = 8 Hz, 2H, H4), 8.19 (d, *J*<sub>H,H</sub> = 9 Hz, 2H, H5). FT-IR (cm<sup>-1</sup>): 2924 (C–H), 2849 (C–H), 1732 (C=O), 1604 (C=N), 1576 (C=C), 1504 (C=C aryl), 1502 (C=C aryl), 1410, 1350, 1250, 1192, 1164, 1074, 1013, 1011, 847, 810, 760, 563, 561, 503, 489. Anal. Calc. for C<sub>84</sub>H<sub>104</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>8</sub>Pd: C, 67.81; H, 7.05; N, 1.88. Found: C, 67.99; H, 7.01; N, 1.96%.

## 3. Results and discussion

### 3.1. Synthesis and characterization

The syntheses of the compounds reported in this paper were performed according to Scheme 1. Acetyl ferrocene **1** can be prepared using a Friedel–Crafts acylation procedure, as was established in the early classical works on ferrocene [55–58]. The addition of AlCl<sub>3</sub> catalyst in small portions to equimolar amounts of ferrocene and acetyl chloride allowed the yield of the mono-acetylated product to increase to over 70%. Compound **1** was separated by column chromatography on Al<sub>2</sub>O<sub>3</sub> from the mixture of products.

The crossed Claisen condensation of the acetyl ferrocene **1** with ethyl formate gave the sodium salt of the appropriate ketoaldehyde.



**Scheme 1.** Syntheses of ligands **3a–b** and heteronuclear complexes **4a–b** and **5a–b**.

hyde **2**. The reaction of compound **2** with *p*-alkoxybenzoyloxy aniline in ethanol in the presence of an equimolar amount of concentrated HCl (aq) led to the  $\beta$ -aminovinyl ketones **3a–b**. The copper(II) complexes **4a–b** and palladium(II) complexes **5a–b** were obtained by treatment of **3a–b** with the corresponding acetate salts in ethanol and 1,4-dioxane, respectively.

The chemical compositions of the synthesized compounds are in good agreement with the data of elemental analyses. The FT-IR spectra of **3a–b** are distinguished by characteristic stretching bands of the ester carbonyl near 1726 cm<sup>-1</sup>, and ketone carbonyl at 1627 cm<sup>-1</sup>. In addition, the C=C bond stretching of the ethenyl group is exposed near 1603 cm<sup>-1</sup>. There is a group of absorption peaks in the area 1480–1515 cm<sup>-1</sup> which are connected with the deformations of the aromatic rings. Metal-ring vibrations of the ferrocene moiety are displayed in the long-wave area, at 485–525 cm<sup>-1</sup>. The C=O stretches of the ester group are shifted in the complexes **4a–b** and **5a–b** to a higher frequency region by 8 and 4 cm<sup>-1</sup>, respectively. The valence vibration of the ketone carbonyl near 1627 cm<sup>-1</sup> disappears upon complex formation and addi-

tional peaks connected with the C=N and C=C bonds in the region 1570–1600 cm<sup>-1</sup> are generated. In addition vibration modes of the M–O and M–N bonds in the area 560–600 cm<sup>-1</sup> are displayed in the IR spectra of the metallochelates. Thus, considerable changes occur in the infrared spectra of **4a–b** and **5a–b** in comparison with the free ligands **3a–b**, undoubtedly indicating the successful complex formation.

The UV–Vis spectra of the ligands **3a–b** are represented by three absorption bands (see Table 1). The first band with a maxima near 260 nm is associated with  $\pi$ – $\pi^*$  electronic transitions of the aromatic rings. The next band is related to the carbonyl chromophore, which is shifted bathochromically to 366 nm due to the conjugational effect of the adjacent ethenyl and cyclopentadienyl groups [59]. The less intensive band at  $\sim$ 465 nm belongs to d–d type transitions of the iron atoms [60–62].

An additional shoulder appears near 292–298 nm upon complex formation, which is connected to a ligand-to-metal charge transfer transition in the case of the copper(II) complexes **4a–b** [63], and a metal-to-ligand charge transfer transition in the case

**Table 1**  
UV–Vis spectral data for **3a–b**, **4a–b** and **5a–b**.

Compound	Absorption max, nm ( $\log \epsilon$ , $L \times \text{cm}^{-1} \times \text{mol}^{-1}$ )			
	I band	II band (shoulder)	III band	IV band
<b>3a</b>	260 (4.40)		366 (4.36)	465 (3.43)
<b>4a</b>	263 (4.94)	278 (4.39)	383 (4.47)	454 (3.82)
<b>5a</b>	259 (4.75)	295 (4.45)	374 (4.60)	462 (4.08)
<b>3b</b>	260 (4.50)		367 (4.51)	466 (3.50)
<b>4b</b>	262 (4.64)	290 (4.36)	382 (4.47)	450 (3.77)
<b>5b</b>	263 (4.74)	298 (4.25)	388 (4.28)	457 (3.68)

of the palladium(II) complexes **5a–b** [64]. It is noteworthy, that in the metal complexes an absorption band associated with the carbonyl group is bathochromically shifted in comparison with the free ligand. The shift can be explained by the added electronic conjugational effect due to involving this group into the metallochelate cycle. The ferrocenyl group in the complexes **4a–b** and **5a–b** reveals d–d electronic transitions in the same area, 465 nm, as the free ligands **3a–b**.

The ligands **3a–b** and complexes **5a–b** are also characterized by  $^1\text{H}$  NMR. It is interesting to note that the proton signals of the

**Table 2**  
Data of thermo-optical and DSC studies of **3a–b**, **4a–b** and **5a–b**.

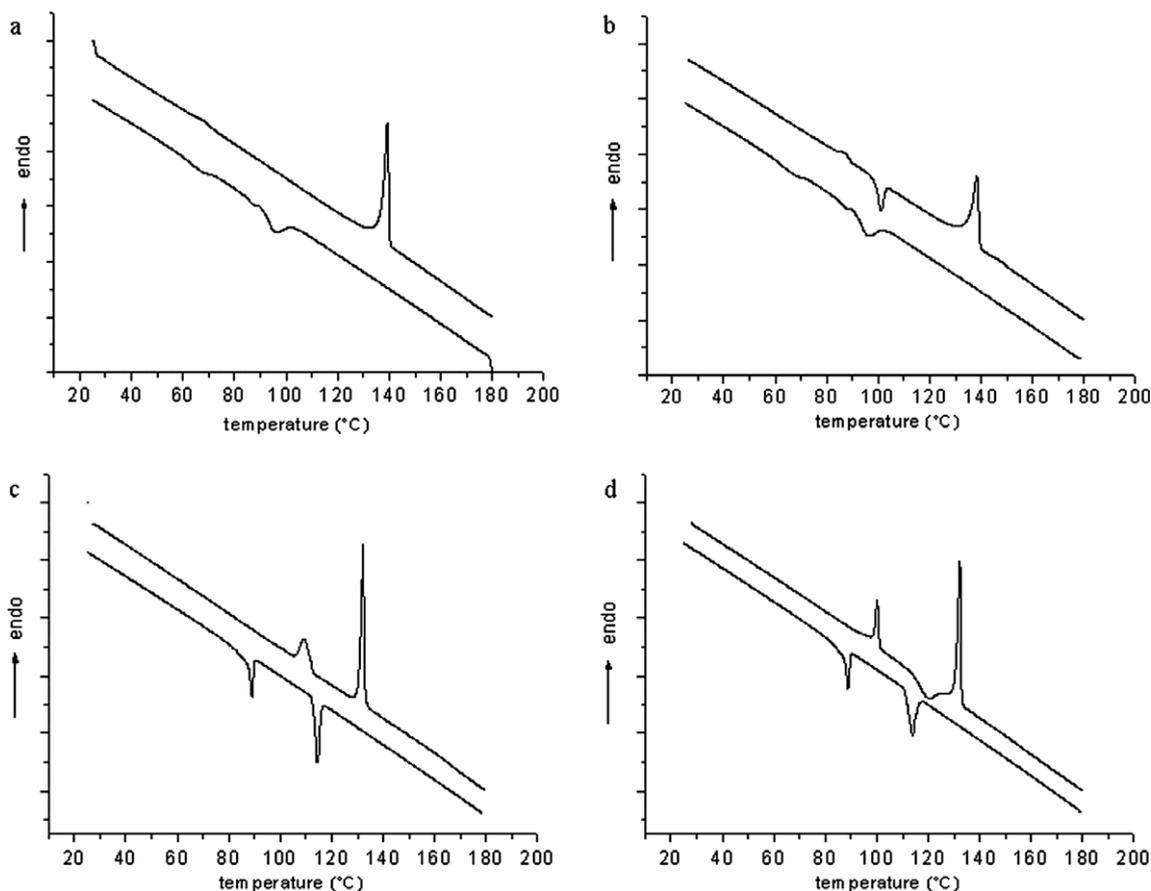
Compound	Phase transitions, <sup>a</sup> °C ( $\Delta H$ , kJ/mol)	
	Heating process	Cooling process
<b>3a</b>	1st cycle: Cr <sub>1</sub> 68(1.5) Cr <sub>2</sub> 139(34.3) I 2nd cycle: Cr 88(1.9) Cr <sub>1</sub> 01(–9.1) Cr <sub>2</sub> 138(28.7) I	I [99.5(–20.0)] <sup>b</sup> X 87(–0.9) Cr <sub>2</sub> 67(–1.9) Cr I [96(–12.0)] X 87(–1.0) Cr <sub>2</sub> 67(–2.3) Cr
<b>4a</b>	Cr <sub>1</sub> 150.5(–7.0) Cr <sub>2</sub> 164.5(50.7) I	I [107] <sup>c</sup> X
<b>5a</b>	Cr <sub>1</sub> 183.5(24.5) Cr <sub>2</sub> 221(58.0) I	I [140] SmC <sup>d</sup>
<b>3b</b>	1st cycle: Cr <sub>1</sub> 109(18.4) Cr <sub>2</sub> 132(39.5) I 2nd cycle: Cr 100(13.8) Cr <sub>1</sub> 119(–16.1) Cr <sub>2</sub> 132(38.7) I	I [114(–21.5)] X 89(–11.0) Cr I [114(–21.4)] X 88(–13.8) Cr
<b>4b</b>	Cr 145(65.8) I	I [120] <sup>c</sup> X
<b>5b</b>	Cr <sub>1</sub> 201(64.1) I	I [136] SmC <sup>d</sup>

<sup>a</sup> Cr: crystal; X: soft crystal; SmC: smectic C; I: isotropic liquid phases.

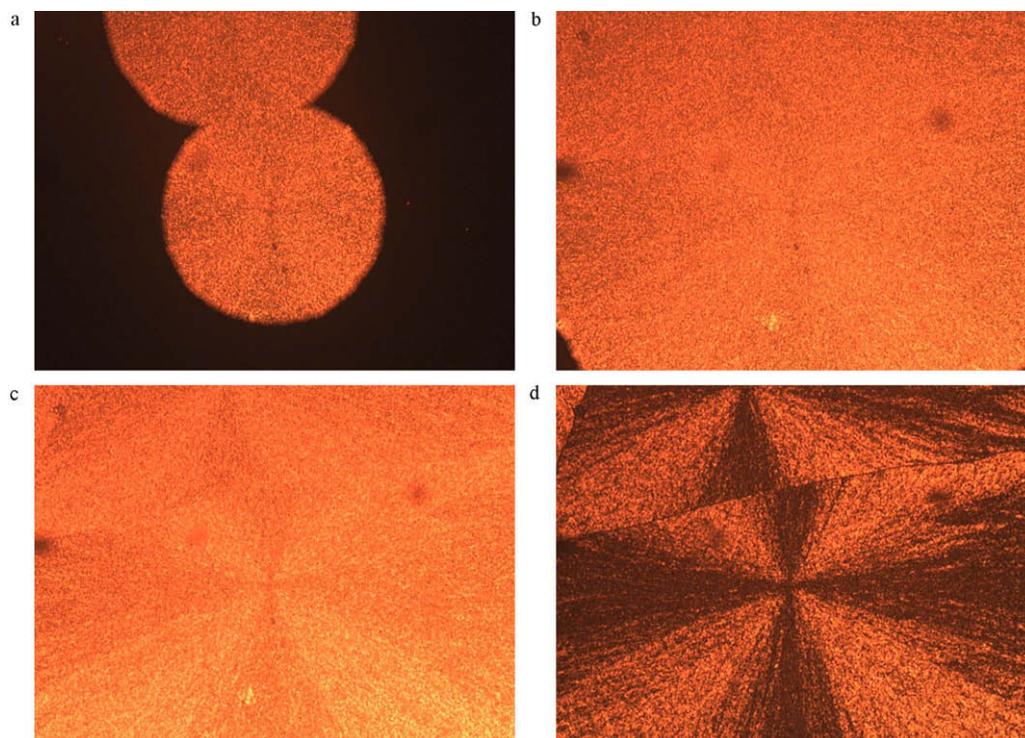
<sup>b</sup> Monotropic mesophase transitions are shown in square brackets.

<sup>c</sup> No peaks were observed on the DSC cooling course in the point where star-like domains were observed under POM.

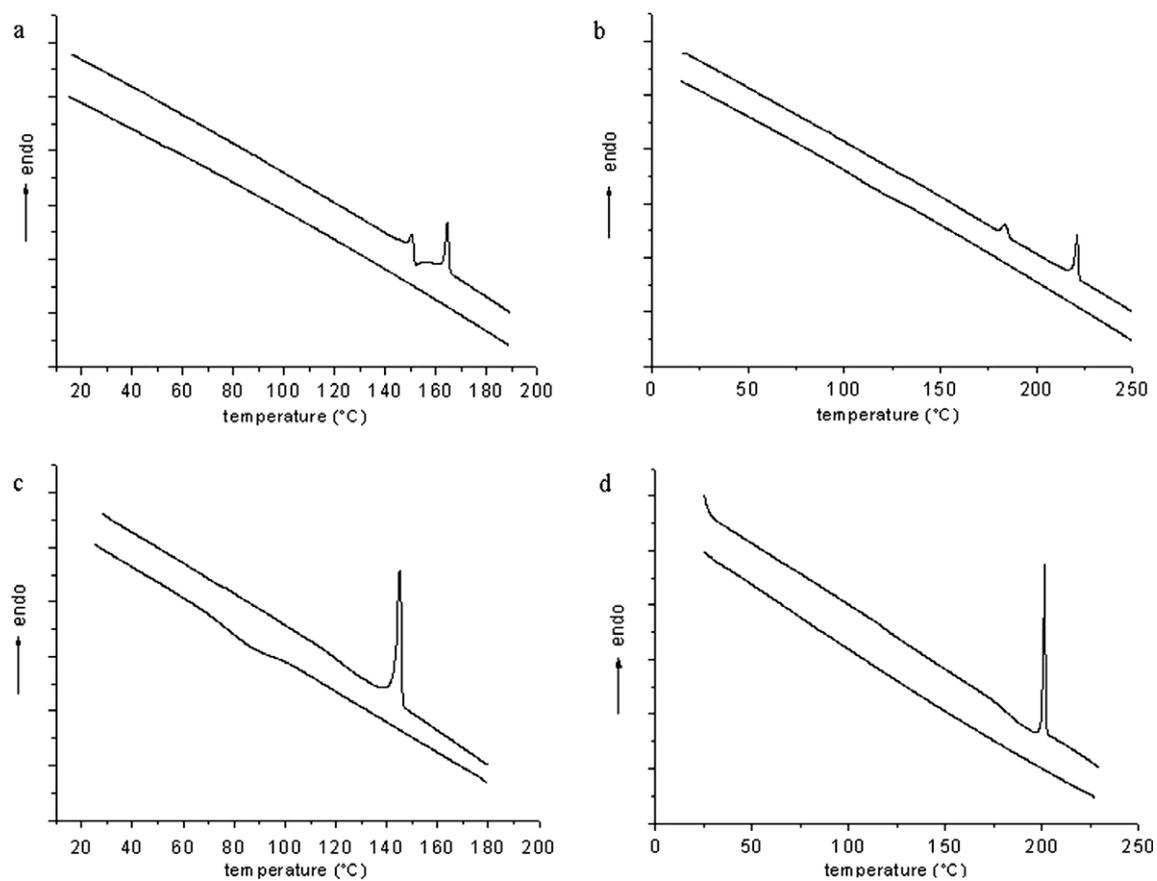
<sup>d</sup> The mesophase was observed upon rapid cooling in a polarizing microscope, while the corresponding DSC peaks were not resolved.



**Fig. 1.** DSC thermograms of **3a–b**: (a) the first heating and cooling cycle, **3a**; (b) the second heating and cooling cycle, **3a**; (c) the first heating and cooling cycle, **3b**; (d) the second heating and cooling cycle, **3b**.



**Fig. 2.** Optical textures of **3a** under a polarizing microscope: (a) two spherical soft crystal domains growing from the isotropic liquid; (b) the spherical domains mixed with each other; (c and d) development of the spherulitic crystalline structure.



**Fig. 3.** DSC thermograms of heteronuclear complexes: (a) **4a**; (b) **5a**; (c) **4b** and (d) **5b**.

substituted cyclopentadiene ring of the ferrocene moiety in **5a–b** are high-field shifted by 0.6 ppm in relation to comparable signals in the free ligands **3a–b**. Such a significant shift is due to the fact that the ferrocene unit in these complexes is situated very close to the central chelate core, and there is a considerable electron-donor effect from the Pd(II) ion on it. As for the protons of the ethenyl link, a similar high-field shift is also observed, though the effect is weaker in this case.

### 3.2. Mesomorphism

Liquid crystal properties of the new synthesized metallomesogens have been investigated by thermal polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The obtained data on the thermal behaviour of the ligands **3a–b** and two series of heteronuclear complexes **4a–b** and **5a–b** are presented in Table 2.

In the first heating cycle of the DSC measurements, crystal-to-crystal phase transition peaks were observed for the ligands **3a–b** (Fig. 1), although it was small in the case of  $n = 12$ . In the cooling course, there are several broad responses in the DSC thermogram of **3a** and two sharp peaks in a case of **3b**. During the second heating cycle exothermic peaks appeared in both cases between the first crystal-to-crystal and crystal-to-isotropic liquid phase transitions. This can be explained by partial vitrification of the samples in the first cooling cycle, accomplishing a low energy crystal packing at higher temperatures when increased mobility of molecules allows it to be completed. Enthalpy values of the first DSC peaks after cooling from the isotropic liquid state are relatively high in both **3a** and **3b**. Presumably, these peaks are the result of the tran-

sition from the isotropic liquid to a highly disordered soft crystal phase. Two other smaller peaks in the cooling cycle can be assigned to crystal polymorphic phase transitions. A series of microphotographs in Fig. 2 illustrates the development of spherical domains on cooling from the isotropic liquid state in a sample of **3a** under a polarizing microscope. The spherical shape of the domains reveals a possible organization into supramolecular assemblies. The last assumption is founded on the presence of C=O and polar NH groups in **3a–b**, which are capable of forming intermolecular hydrogen bonds. Upon further cooling these spherical formations are transformed into big spherulitic crystals, similar to those observed frequently during crystallization from smectic mesophases. Exactly the same textures were observed under a polarizing microscope in the case of **3b**.

Two DSC peaks corresponding to the crystal-to-crystal and crystal-to-isotropic liquid transitions were observed in the first heating cycle of **4a**, and only one peak from the isotropic liquid phase transition was observed in the case of **4b** (Fig. 3). In the cooling cycle any phase transition peaks were not resolved. The main information about the phase transition behaviour of **4a–b** in the cooling path was obtained from POM observations. Typical optical textures developed from the isotropic liquid state of **4a–b** under a polarizing microscope are presented in Fig. 4. Most likely the observed star-like and flower-like formations are associated with a disordered soft crystal phase. Samples in this state had limited flowability when subjected to stress.

Similar DSC thermograms were obtained for **5a–b** in the heating cycle: two peaks corresponding to the crystal-to-crystal and crystal-to-isotropic liquid transitions in the case of **5a**, and only one peak due to an isotropic liquid transition in the case of **5b**

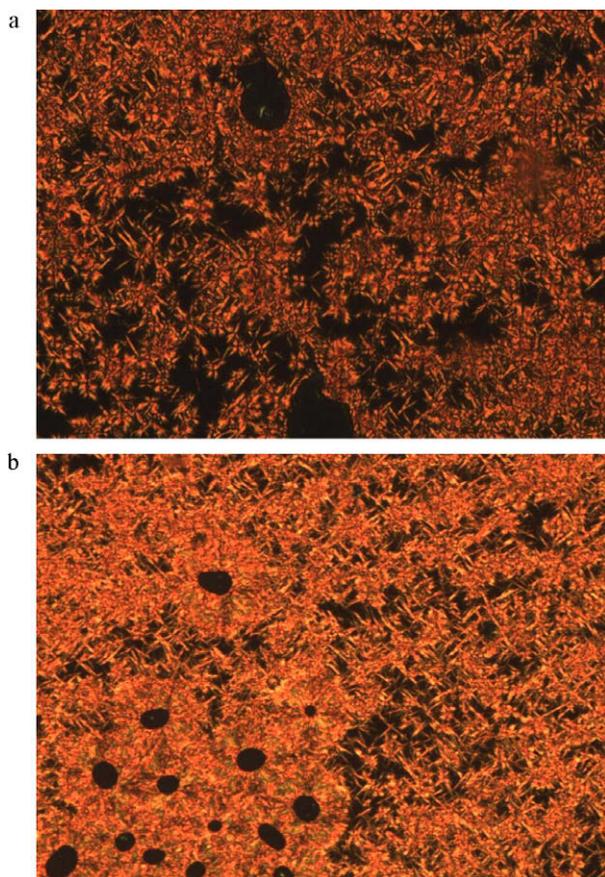


Fig. 4. Emergence of star-like and flower-like domains from the isotropic liquid state in: (a) **4a** and (b) **4b**.

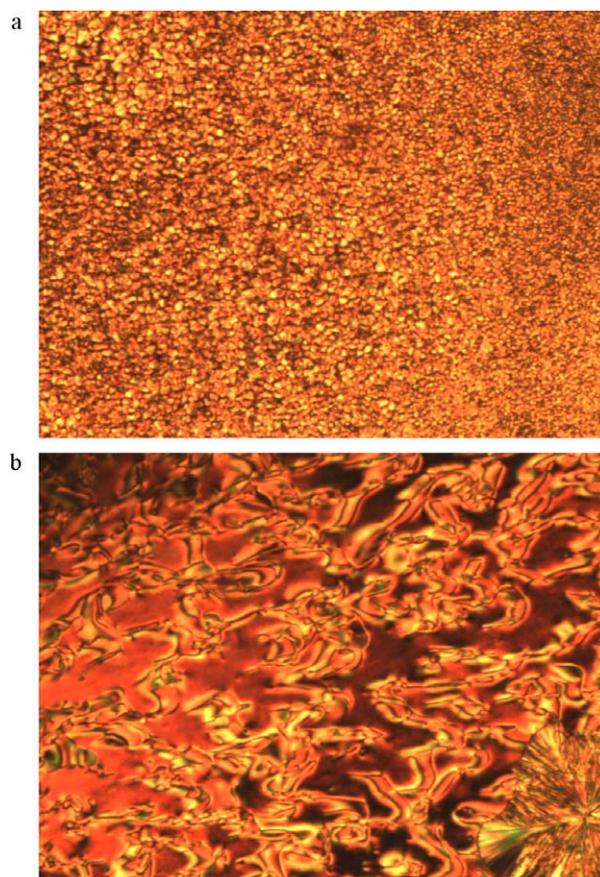


Fig. 5. Optical textures of **5a** under a polarizing microscope: (a) sand-like optical texture and (b) schlieren texture of smectic C.

(Fig. 3). DSC peaks were not revealed on cooling. Monotropic smectic C mesophases were identified for both Pd(II) complexes **5a** and **5b** by polarizing optical microscopy. The typical sand-like and schlieren textures of smectic C were observed upon cooling from the isotropic liquid state (Fig. 5).

Thus, in comparison with the earlier synthesized heteronuclear mesogens with ferrocene- [17] and ferrocenophane-containing [21]  $\beta$ -aminovinylketones, the present compounds exhibited rather poor mesomorphism. In fact the bulky ferrocene moieties in the latter case pile up the central rigid core of a mesogenic molecule rather than being considered as terminal substituents. As a consequence, the geometrical anisotropy of the present complexes is smaller and less favourable for exhibiting liquid crystal properties.

#### 4. Conclusions

Novel ferrocene-containing  $\beta$ -aminovinylketone derivatives containing terminal alkyl chains with 12 and 16 carbon atoms have been synthesized and fully characterized by elemental analyses,  $^1\text{H}$  NMR, FT-IR and UV-Vis spectroscopies. The synthesized ligands exhibited disordered soft crystal phases. New heteropolynuclear metallomesogen systems were generated from these ligands by incorporating Cu(II) and Pd(II) ions into the enaminketone chelating site. The synthesized heteronuclear complexes of copper(II), like the free ligands, showed a soft crystal phase. The Pd(II) complexes exhibited a monotropic smectic C mesophase.

#### Acknowledgements

This work has been supported by a grant from the Korea Science and Engineering Foundation (KOSEF) through the Center for Bioactive Molecular Hybrids (CBMH), and the program Brain Korea 21 (BK-21).

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