



## Synthesis, Characterization and Properties of New Ferrocene Containing Compounds Bearing Naphthalene Unit

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### ABSTRACT

Naphthalene containing ferrocene derivatives (4a-4e) were prepared and have been evaluated for their material chemistry property. These compounds were found to be non-mesomorphic. Electron delocalization and rigidity of molecule plays an important role in alteration of mesomorphic behavior. POM and DSC study revealed that apart from orientation of central ester linkage, structural and geometrical features, electrostatic interaction and rotational motion can be effectively used to alter the material chemistry properties especially mesomorphic properties.

**Keywords:** Electron-delocalization, Ferrocene, Liquid Crystal, Naphthalene, Organometallic.

### INTRODUCTION

Organometallic compounds are attracting greater attention since last three decades because of their uses in biology<sup>1</sup>, chemical<sup>2-3</sup> and pharmaceutical industries<sup>4</sup>, catalytic processes<sup>5</sup> along with their large dominance in the field of materials chemistry.<sup>6-7</sup> The organometallic compounds have an ability to access the properties of both organic compounds as well as properties of the metals including optical, color, magnetic, electrical and polarizability.<sup>8</sup>

Ferrocene represents the well-established family of the organometallic compounds, which exhibits remarkable thermal stability and aromaticity along with their high solubility in common organic solvents makes their characterization easy. Ferrocene derivatives play vital role in many fields of chemistry including materials chemistry<sup>9-12</sup>, electro analytical chemistry<sup>13-14</sup>, hydrometallurgy<sup>15</sup>, biology<sup>12</sup>, medicine<sup>16-18</sup> and catalysis.<sup>12</sup> Because of the redox potential ability of the ferrocene they are used in several applications.<sup>19</sup> Ferrocene derivatives are well known to exhibit the wide range liquid crystalline properties<sup>20-21</sup> and these ferrocenomesogens have many more applications including in information storage devices and also in ferroelectric devices<sup>22-23</sup> along with formation of ferrocene based sensors.<sup>24-25</sup>

Naphthalene derivatives also play an important role in materials science<sup>26-27</sup> and pharmaceutical industries.<sup>28-31</sup> Many naphthalene derivatives are known to exhibit liquid crystalline behavior.<sup>32-33</sup> Ferrocene derivatives containing naphthalene unit are known to show many applications as in electro analytical techniques<sup>34-35</sup>, and can be used in electro chemical detection of aberrant methylated gene as well as in electro chemical detection of mRNA expression.<sup>34</sup> These ferrocene derivatives with naphthalene unit also have an application in materials chemistry as potential liquid crystalline materials.<sup>36</sup>

### MATERIALS AND METHODS

All reactions were carried out in oven-dried glassware under argon atmosphere unless otherwise stated. <sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75 MHz) spectra were recorded on Bruker AVANCE spectrometer (Bruker BioSpin AG, Fällanden, Switzerland; 300 MHz) using CDCl<sub>3</sub> ( $\delta$  7.26 for <sup>1</sup>H) and ( $\delta$  77.5/77.4 for <sup>13</sup>C) as solvent and TMS as an internal standard. Chemical shifts ( $\delta$ ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The peak multiplicities are given as follows s = singlet; d = doublet; dd = doublet of doublet; t = triplet; m = multiplet. Silica gel of commercial source (60–120 mesh) was used in column chromatography. UV spectra were scanned on Shimadzu 240 PC and Shimadzu 2450, Japan, Spectrophotometer. HRMS spectra were recorded on positive ion electrospray ionisation (ESI) mode. FT-Infrared spectra were recorded on a Perkin Elmer (Model-Frontier) spectrometer (Waltham, MA, USA). Mesomorphic nature was investigated by DSC analysis (Mettler-Toledo AG Analytical, Schwerzenbach, Switzerland) under a nitrogen atmosphere, with samples measured in closed-lid aluminium pans and POM using Mettler Toledo FP90 heating stage containing temperature control unit in conjunction with a Carl Zeiss polarizing optical microscope (Carl Zeiss MicroImaging GmbH, Koenigsallee, Goettingen, Germany). Unless otherwise stated, materials obtained from commercial suppliers were used without further purification. Dichloromethane (DCM) was dried using calcium hydride. All reactions involving N, N'-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were performed under dry atmosphere.

### Synthesis of compounds 2 and 3a–3e

Compounds **2** and **3a–3e** have been synthesized as per literature procedure<sup>37,32</sup> respectively.

**General procedure for the synthesis of compounds 4a–4e.**

4-Ferrocenylbenzoic acid (2) (3.26 mmol) and n-alkyl- 6-hydroxy-2-naphthoate (3a-3e) (3.26 mmol) and a catalytic amount of DMAP, was taken in 100 ml anhydrous CH<sub>2</sub>Cl<sub>2</sub>, and to this solution (3.92 mmol) DCC dissolved in 10 ml anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added. The reaction mixture was stirred at room temperature for 24 hrs. After the completion of reaction, dicyclohexylurea was filtered off and the solution was concentrated in vacuo at 30°C. The dark orange residue thus obtained was purified by column chromatography using silica gel adsorbent. Elution with mixture of petroleum ether and chloroform (60:40) followed by distillation for recovery of solvent gave an orange solid of n-alkyl- 6-((4-ferrocenylbenzoyl) oxy)-2-naphthoate (4a-4e).

**Spectral data for products****Octyl 6-((4-ferrocenylbenzoyl) oxy)-2-naphthoate (4a)**

Yield 1.81 g (85%) as orange solid; m.p.:119°C–121°C; UV (CHCl<sub>3</sub>): λ<sub>max</sub> (logε) 467.3 (3.38), 373.4 (3.75), 296.7 (4.59), 251.2 (4.59); <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 8.652 (s, 1H, Ar-H), 8.183 (d, *J* = 8.1 Hz, 1H, Ar-H), 8.137 (d, *J* = 8.7 Hz, 1H, Ar-H), 8.058 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.903 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.771 (s, 1H, Ar-H), 7.628 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.480-7.444 (m, 1H, Ar-H), 4.772 (s, 2H, C<sub>5</sub>H<sub>4</sub> of ferrocene), 4.443 (s, 7H, C<sub>5</sub>H<sub>5</sub> of ferrocene and -OCH<sub>2</sub>), 4.079 (s, 2H, C<sub>5</sub>H<sub>4</sub> of ferrocene), 1.866-1.322 (m, 12H, -CH<sub>2</sub> of aliphatic chain), 0.915 (t, *J* = 6.6 Hz, 3H, -CH<sub>3</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 166.6, 165.1, 150.5, 146.4, 136.1, 130.9, 130.7, 130.5, 130.4, 127.8, 127.7, 126.2, 126.0, 125.8, 122.2, 118.7, 82.9, 70.0, 69.9, 67.0, 65.3, 31.8, 29.2, 29.2, 28.7, 26.1, 22.6, 14.1; IR (neat, cm<sup>-1</sup>): 3084.55, 2919.95, 1732.19, 1709.04, 1630.93, 1474.24, 1262.10, 1189.90, 864.17, 476.38; HRMS: *m/z* cal. mass for C<sub>36</sub>H<sub>37</sub>O<sub>4</sub>Fe [M+H]<sup>+</sup> = 589.1963, obs. mass [M+H]<sup>+</sup> = 589.1920.

**Dodecyl 6-((4-ferrocenylbenzoyl) oxy)-2-naphthoate (4b)**

Yield 1.85 g (83%) as orange solid; m.p.: 95°C–97°C; UV (CHCl<sub>3</sub>): λ<sub>max</sub> (logε) 462.3(2.97), 371.8 (3.43), 297.9 (4.42), 247.6 (4.53); <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 8.652 (s, 1H, Ar-H), 8.182 (d, *J* = 8.4 Hz, 1H, Ar-H), 8.135 (d, *J* = 8.4 Hz, 1H, Ar-H), 8.056 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.901(d, *J* = 8.7 Hz, 1H, Ar-H), 7.772 (d, *J* = 1.8 Hz, 1H, Ar-H), 7.627 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.480-7.443 (m, 1H, Ar-H), 4.776 (s, 2H, C<sub>5</sub>H<sub>4</sub> of ferrocene), 4.447- 4.382 (m, 7H, C<sub>5</sub>H<sub>5</sub> of ferrocene and -OCH<sub>2</sub>), 4.083 (s, 2H, C<sub>5</sub>H<sub>4</sub> of ferrocene), 1.865-1.301 (m, 16H, -CH<sub>2</sub> of aliphatic chain), 0.924 (t, *J* = 6.6 Hz, 3H, -CH<sub>3</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 166.6, 165.1, 150.5, 146.4, 136.1, 130.9, 130.7, 130.5, 130.4, 127.8, 127.7, 126.2, 126.0, 125.8, 122.2, 118.7, 82.9, 70.0, 69.9, 67.0, 65.3, 31.9, 29.5, 29.3, 28.7, 26.0, 22.6, 14.1; IR (neat, cm<sup>-1</sup>): 3088.84, 2923.64, 1724.51, 1707.25, 1629.88, 1470.19, 1229.85, 1189.89, 886.33, 477.08; HRMS: *m/z* cal. mass for C<sub>38</sub>H<sub>41</sub>O<sub>4</sub>Fe [M+H]<sup>+</sup> = 617.2276, obs. mass [M+H]<sup>+</sup> = 617.2265.

**Dodecyl 6-((4-ferrocenylbenzoyl) oxy)-2-naphthoate (4c)**

Yield 1.86 g (80%) as orange solid; m.p.:119°C–121°C; UV (CHCl<sub>3</sub>): λ<sub>max</sub> (logε), 470.2(3.23), 374.4(3.62), 297.9 (4.53), 246.4 (4.55); <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 8.650 (s, 1H, Ar-H), 8.183 (d, *J* = 8.4 Hz, 1H, Ar-H), 8.138 (dd, *J* = 1.5 Hz & *J* = 1.5 Hz, 1H, Ar-H), 8.056 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.902 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.773 (d, *J* = 1.8 Hz, 1H, Ar-H), 7.627 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.481-7.444 (m, 1H, Ar-H), 4.776 (t, *J* = 1.8 Hz, 2H, C<sub>5</sub>H<sub>4</sub> of ferrocene), 4.447 (t, *J* = 1.8 Hz, 2H, C<sub>5</sub>H<sub>4</sub> of ferrocene), 4.428-4.078 (m, 7H, C<sub>5</sub>H<sub>5</sub> of ferrocene and -OCH<sub>2</sub>), 1.867-1.280 (m, 20H, -CH<sub>2</sub> of aliphatic chain), 0.939 (t, *J* = 6.6 Hz, 3H, -CH<sub>3</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 166.6, 165.0, 150.6, 146.4, 136.1, 130.9, 130.7, 130.5, 130.4, 127.9, 127.7, 126.2, 126.0, 125.8, 122.3, 118.7, 82.9, 70.0, 69.9, 67.0, 65.3, 31.8, 29.3, 29.2, 28.8, 26.1, 22.7, 14.1; IR (neat, cm<sup>-1</sup>): 3084.55, 2919.43, 1731.87, 1708.89, 1630.64, 1474.12, 1261.88, 1189.48, 852.91, 476.23; HRMS: *m/z* cal. mass for C<sub>40</sub>H<sub>45</sub>O<sub>4</sub>Fe [M+H]<sup>+</sup> = 645.2589, obs. mass [M+H]<sup>+</sup> = 645.2598.

**Tetradecyl 6-((4-ferrocenylbenzoyl) oxy)-2-naphthoate (4d)**

Yield 1.90 g (78%) as orange solid; m.p.:101°C–103°C; UV (CHCl<sub>3</sub>): λ<sub>max</sub> (logε) 467.8(3.28), 373.2(3.66), 297.9 (4.54), 248.8 (4.55); <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 8.649 (s, 1H, Ar-H), 8.182 (d, *J* = 8.4 Hz, 1H, Ar-H), 8.133 (dd, *J* = 1.5 Hz & *J* = 1.8 Hz, 1H, Ar-H), 8.058 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.902 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.770 (d, *J* = 2.1 Hz, 1H, Ar-H), 7.630 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.478-7.441 (m, 1H, Ar-H), 4.781 (t, *J* = 1.8 Hz, 2H, C<sub>5</sub>H<sub>4</sub> of ferrocene), 4.451 (t, *J* = 1.8 Hz, 2H, C<sub>5</sub>H<sub>4</sub> of ferrocene), 4.423-4.080 (m, 7H, C<sub>5</sub>H<sub>5</sub> of ferrocene and -OCH<sub>2</sub>), 1.864-1.277 (m, 24H, -CH<sub>2</sub> of aliphatic chain), 0.916 (t, *J* = 6.3 Hz, 3H, -CH<sub>3</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 166.6, 165.1, 150.5, 146.4, 136.1, 130.9, 130.7, 130.5, 130.4, 127.8, 127.7, 126.2, 126.0, 125.8, 122.2, 118.7, 82.9,70.0, 69.9, 67.0, 65.3, 31.9, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 28.7, 26.0, 22.7, 14.1; IR (neat, cm<sup>-1</sup>): 3088.48, 2922.24, 1724.69, 1707.32, 1629.45, 1470.40, 1259.87, 1189.65, 886.41, 476.89; HRMS: *m/z* cal. mass for C<sub>42</sub>H<sub>49</sub>O<sub>4</sub>Fe [M+H]<sup>+</sup> = 673.2903, obs. mass [M+H]<sup>+</sup> = 673.2897.

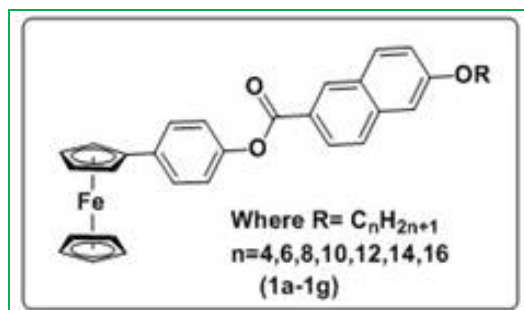
**Hexadecyl 6-((4-ferrocenylbenzoyl) oxy)-2-naphthoate (4e)**

Yield 1.94 g (77%) as orange solid; m.p.:100°C–102°C; UV: λ<sub>max</sub> (logε) (CHCl<sub>3</sub>), 496.0 (3.28), 372.0 (3.67), 295.5 (4.58), 251.4 (4.59); <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 8.649 (s, 1H, Ar-H), 8.182 (d, *J* = 8.4 Hz, 1H, Ar-H), 8.134 (dd, *J* = 1.5 Hz & *J* = 1.5 Hz, 1H, Ar-H), 8.058 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.901 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.772 (d, *J* = 1.8 Hz, 1H, Ar-H), 7.630 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.479-7.442 (m, 1H, Ar-H), 4.780 (t, *J* = 1.5 Hz, 2H, C<sub>5</sub>H<sub>4</sub> of ferrocene), 4.451 (t, *J* = 1.5 Hz, 2H, C<sub>5</sub>H<sub>4</sub> of ferrocene), 4.426-4.081 (m, 7H, C<sub>5</sub>H<sub>5</sub> of ferrocene and -OCH<sub>2</sub>), 1.865-1.277 (m, 28H, -CH<sub>2</sub> of aliphatic chain), 0.917 (t, *J* = 6.3 Hz, 3H, -CH<sub>3</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 166.6, 165.0, 150.5, 146.4, 136.1, 130.8, 130.7, 130.5, 130.4, 127.8, 126.2, 126.0, 125.8, 122.2, 118.7, 82.9, 70.0, 69.9, 67.0, 65.3, 31.9, 29.6, 29.6, 29.5, 29.3, 29.3, 28.7, 26.0, 22.6, 14.1; IR (neat, cm<sup>-1</sup>): 3088.48, 2923.69, 1731.58, 1708.39, 1629.69, 1470.97, 1260.60, 1190.94, 886.56,

477.97; HRMS:  $m/z$  cal. mass for  $C_{42}H_{53}O_4Fe$   $[M+H]^+ = 701.3203$ , obs. mass  $[M+H]^+ = 701.3208$ .

## RESULTS AND DISCUSSION

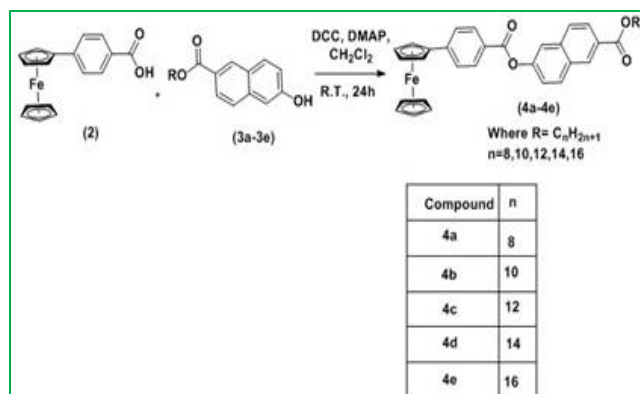
Recently, we have reported the synthesis of ferrocene derivatives containing naphthalene unit (**1a-1g**) (Figure 1) which show good mesomorphic behavior.<sup>36</sup>



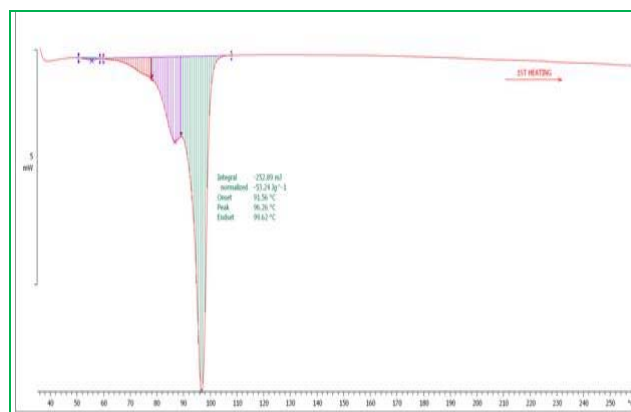
**Figure 1:** Ferrocene derivatives (**1a-1g**) which exhibit mesomorphism.

In view of the above observations from literature and our interest in the synthesis of new ferrocene compounds containing naphthalene unit, as potential candidates for materials chemistry especially for liquid crystals, we now report the synthesis of compounds (**4a-4e**) as delineated in Scheme.

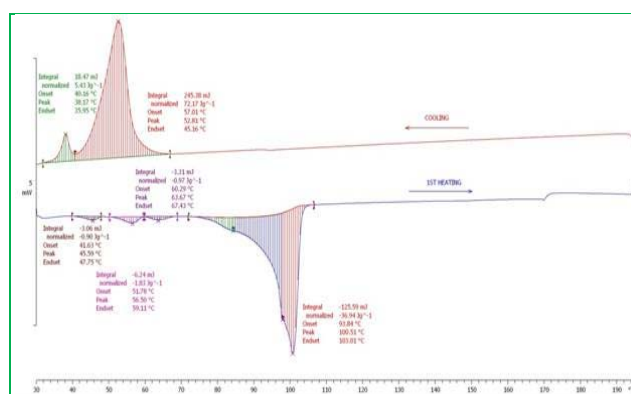
### Scheme. Synthesis of **4a-4e**.



All these newly synthesized ferrocene derivatives containing naphthalene unit (**4a-4e**) were scrutinized for their thermal and mesomorphic behavior by using Differential Scanning Calorimetry (DSC) and Polarizing Optical Microscopy (POM) study. Both DSC (Fig.2&3) and POM study revealed that none of the above synthesized compounds (**4a-4e**) exhibited mesomorphic behavior even after multiple heating and cooling cycles. All the newly synthesized derivatives (**4a-4e**) show only isotropic melting transitions or crystal to crystal transition as observed in (Fig.2 & 3) for compounds **4b** and **4e** respectively. The results obtained were very surprising as all the derivatives (**4a-4e**) synthesized have a structural similarity with our previously synthesized compounds (**1a-1g**). Only change was the orientation of central ester linkage is reversed and terminal alkoxy unit has been replaced by terminal ester unit.



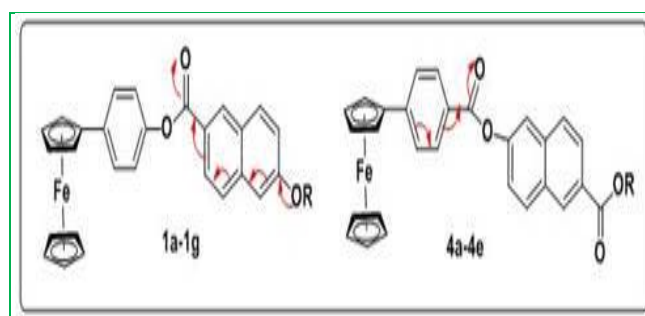
**Figure 2:** DSC thermogram of compound **4b**.



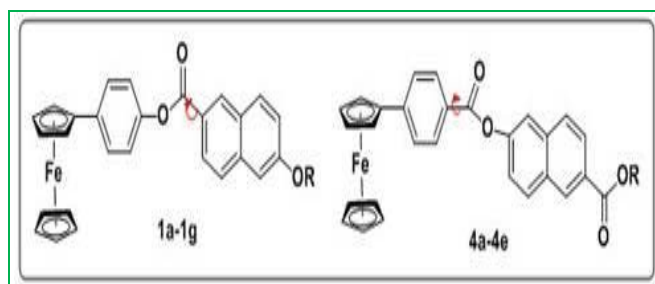
**Figure 3:** DSC thermogram of compound **4e**

The observed non-mesomorphic behavior of the synthesized compounds could be due to orientation of the central ester linkage<sup>38-41</sup>, electron delocalization (electrostatic interaction) and rotational motion (rigidity of the organic rod)<sup>42</sup>.

For compounds **1a-1g** electron delocalization can occur from O-atom of the alkoxy chain to the ester function that results in mesomorphism to take place in the external part of organic portion. However in **4a-4e** delocalization occurs in the inner part of the organic fragment and in reverse direction as compared with **1a-1g**. The details of the nature of electron delocalization for compounds (**1a-1g**) and (**4a-4e**) are shown in Fig.4. Further, rotation around C-C bond in **4a-4e** is more limited than in **1a-1e**, because for rotation of C-C bond in the former requires the motion of larger molecular portion (Figure 5).



**Figure 4:** Electron delocalization for compounds (**1a-1g**) and (**4a-4e**).



**Figure 5:** Rotation of C-C bond for compounds (1a-1g) and (4a-4e)

## CONCLUSION

In conclusion, novel ferrocene derivatives containing naphthalene unit have been synthesized, using inexpensive chemicals in a good yield. POM and DSC study revealed that apart from orientation of central ester linkage, structural and geometrical features, electrostatic interaction and rotational motion can be effectively used to alter the material chemistry properties especially mesomorphic properties.

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## REFERENCES

- Patra M, Gasser G, Organometallic Compounds: An Opportunity for Chemical Biology?, *Chembiochem.*, 13, 2012, 1232-1252.
- Parshall GW, Nugent WA, Chan DM-T, Tam W, A new role for organometallic reactions in organic synthesis in industry, *Pure & Appl. Chem.*, 57, 1985, 1809-1818.
- Kollonitsch J, Industrial use of organometallics in organic synthesis, *Annals of the New York Academy of Sciences*, 125, 2006, 161-171.
- Gasser G, Ott I, Metzler-Nolte N, Organometallic Anticancer Compounds, *J. Med. Chem.*, 54, 2011, 3-25.
- Parshall GW, Ittel SD, Homogeneous Catalysis, Wiley-Interscience, New York, 1992.
- Schwartz J, Bernasek, SL, Organometallic chemistry at the interface with materials science, *Catalysis Today*, 66, 2001, 3-13.
- Harrod JF, Laine RM, (Eds.), Applications of Organometallic Chemistry in the Preparation and Processing of Advanced Materials, Vol. 297, 1995, XII.
- Espinet P, Esteruelas MA, Oro LA, Serrano JL, Sola E, Transition metal liquid crystals: advanced materials within the reach of the coordination chemist, *Coord. Chem. Rev.*, 117, 1992, 215-274.
- Baldoli C, Oldani C, Licandro E, Ramani P, Valerio A, Ferruti P, Falciola L, Mussini P, Ferrocene derivatives supported on poly(*N*-vinylpyrrolidin-2-one) (PVP): Synthesis of new water-soluble electrochemically active probes for biomolecules, *J. Organomet. Chem.*, 692, 2007, 1363-1371.
- Jios JL, Kirin SI, Buceta NN, Weyhermuller T, Della Vedova CO, Metzler-Nolte N, Synthesis and structural characterization of metallated bioconjugates: C-terminal labeling of amino acids with aminoferrocene, *J. Organomet. Chem.*, 692, 2007, 4209-4214.
- Li C, Medina JC, Maguire GEM, Abel E, Atwood JL, Gokel GW, Neutral Molecule Receptor Systems Using Ferrocene's "Atomic Ball Bearing" Character as the Flexible Element, *J. Am. Chem. Soc.*, 119, 1997, 1609-1618.
- Togni A, Hayashi T (Eds.), Ferrocenes: Homogenous Catalysts, Organic Synthesis and Material Science, VCH, Weinheim, 1995.
- Atta NF, Galal A, Wassel AA, Ibrahim AH, Sensitive Electrochemical Determination of Morphine Using Gold Nanoparticles–Ferrocene Modified Carbon Paste Electrode, *Int. J. Electrochem. Sci.*, 7, 2012, 10501-10518.
- Skeika T, Zuconelli CR, Fujiwara ST, Pessoa CA, Preparation and Electrochemical Characterization of a Carbon Ceramic Electrode Modified with Ferrocenecarboxylic Acid, *Sensors*, 11, 2011, 1361-1374.
- Beer PD, Szemes F, Balzani V, Sala CM, Drew MGB, Dent SW, Maestri M, Anion Selective Recognition and Sensing by Novel Macrocyclic Transition Metal Receptor Systems. <sup>1</sup>H NMR, Electrochemical, and Photophysical Investigations, *J. Am. Chem. Soc.*, 119, 1997, 11864-11875.
- Biot C, Glorian G, Maciejewski LA, Brocard JS, Domarle O, Blampain G, Millet P, Georges AJ, Abessolo H, Dive D, Lebib J, Synthesis and Antimalarial Activity in Vitro and in Vivo of a New Ferrocene–Chloroquine Analogue, *J. Med. Chem.*, 40, 1997, 3715-3718.
- Fang J, Jin Z, Li Z, Liu W, Synthesis, structure and antibacterial activities of novel ferrocenyl-containing 1-phenyl-3-ferrocenyl-4-triazolyl-5-aryl-dihydropyrazole derivatives, *J. Organomet. Chem.*, 674, 2003, 1-9.
- Top S, Dauer B, Vaissermann J, Jaouen G, Facile route to ferrocifen, 1-[4-(2-dimethylaminoethoxy)]-1-(phenyl-2-ferrocenyl-but-1-ene), first organometallic analogue of tamoxifen, by the McMurry reaction, *J. Organomet. Chem.*, 541, 1997, 355-361.
- Taudien S, Riant O, Kagan HB, Synthesis of chiral carbocations linked to a ferrocene unit, *Tetrahedron Lett.*, 36, 1995, 3513-3516.
- Imrie C, Engelbrecht P, Loubser C, McClelland CW, Monosubstituted thermotropic ferrocenomesogens: an overview 1976–1999, *Appl. Organomet. Chem.*, 15, 2001, 1-15.
- Kadkin ON, Galyametdinov YG, Ferrocene containing liquid crystals, *Russ. Chem. Rev.*, 81, 2012, 675-699.
- Deschenaux R, Turpin F, Ferrocene-Containing Thermotropic Side-Chain Liquid-Crystalline Polymethacrylate from a Mesomorphic Trisubstituted Ferrocene Monomer, *Macromolecules*, 30, 1997, 3759-3765.
- Deschenaux R, Jauslin I, Scholten U, Turpin F, Ferrocene-Containing Thermotropic Side-Chain Liquid-Crystalline Polysiloxanes, *Macromolecules*, 31, 1998, 5647-5654.
- Deschenaux R, Monnet F, Serrano E, Turpin F, Levelut AM, Columnar Phases from Covalent and Hydrogen-Bonded

- Liquid-Crystalline Ferrocene Derivatives, *Helv. Chim. Acta*, 81, 1998, 2072-2077.
25. Massiot P, Imperor-Clerc M, Veber M, Deschenaux R, Supramolecular Metallomesogens: Hydrogen-Bonded Ferrocene-Containing Liquid Crystals Which Display Bicontinuous Cubic Phases, *Chem. Mater.*, 17, 2005, 1946-1951.
  26. Getmanenko YA, Polander LE, Hwang DK, Tiwari SP, Galán E, Seifried BM, Sandhu B, Barlow S, Timofeeva T, Kippelen B, Marder SR, Bis(naphthalene diimide) derivatives with mono- and dicarbonyl-fused tricyclic heterocyclic bridges as electron-transport materials, *Journal of Organic Semiconductors*, 1, 2013, 7-15.
  27. evgen P, Serap ALP, Banu K, Yusuf D, Siddik I, Photophysical Properties and Electrochemistry of the N,N'-bis-n-butyl Derivative of Naphthalene Diimide, *Turk. J. Chem.*, 28, 2004, 415-424.
  28. Matsushita Y, Jang IC, Imai T, Fukushima K, Lee JM, Park HR, Lee SC, Antioxidant and cytotoxic activities of naphthalene derivatives from *Diospyros kaki*, *J Wood Sci.*, 57, 2011, 161-165.
  29. Mkpene V, Ebong G, Obot IB, Abasiokong B, Evaluation of the Effect of Azo Group on the Biological Activity of 1-(4-Methylphenylazo)-2-naphthol, *E-Journal of chemistry*, 5, 2008, 431-434.
  30. Mital A, Negi VS, Ramachandran U, Synthesis and Biological Evaluation of Naphthalene-1,4-dione Derivatives as Potent Antimycobacterial Agents, *Medicinal Chemistry*, 4, 2008, 492-497.
  31. Upadhayaya RS, Vandavasi JK, Kardile RA, Lahore SV, Dixit SS, Deokar HS, Shinde PD, Sarmah MP, Chattopadhyaya J, Novel quinoline and naphthalene derivatives as potent antimycobacterial agents, *European Journal of Medicinal Chemistry*, 45, 2010, 1854-1867.
  32. Tsutomu I, Atsuo O, Yoshiyuki T, Motokazu H, Hiroe K, Masakatsu N, Naphthalene compound, and liquid crystal composition and liquid crystal element using the same (Mitsui Toatsu Chemicals), EP0757032A2 (1997).
  33. Kuo HM, Li SY, Sheu HS, Lai CK, Symmetrical mesogenic 2,5-bis(6-naphthalen-2-yl)-1,3,4-thiadiazoles, *Tetrahedron*, 68, 2012, 7331-7337.
  34. Sato S, Tsueda M, Takenaka S, Electrochemical detection of aberrant methylated gene using naphthalene diimide derivative carrying four ferrocene moieties, *J. Organomet. Chem.*, 695, 2010, 1858-1862.
  35. Sarhan AE, Kijima T, Izumi T, Synthesis and electrochemical properties of 1,1'-bis(benzo-1,3-dithiol-2-ylidene)ferrocene derivatives as novel electron donor compounds, *J. Organomet. Chem.*, 682, 2003, 49-58.
  36. Navale DN, Zotem SW, Ramana MMV, Synthesis of ferrocenomesogens exhibiting low temperature mesomorphism, *Liquid Crystals*, 2013, 40(10), 1333-1338.
  37. Carlescu I, Scutaru AM, Apreutesei D, Alupei V, Scutaru D, The liquid crystalline properties of some ferrocene-containing Schiff bases, *Appl. Organomet. Chem.*, 21, 2007, 661-669.
  38. Campillos E, Marcos M, Serrano JL, Alonso PJ, Paramagnetic rod-like liquid crystals, bis[5-(4-alkoxybenzoyloxy)salicylaldehyde]copper(II), *J. Mater. Chem.*, 1, 1991, 197-199.
  39. Sakurai Y, Takenaka S, Miyake H, Morita H, Ikemoto T, Molecular structure and smectic properties. Part 1. The effect of linkages on smectic a thermal stability in three aromatic ring compounds linked by ester groups, *J. Chem. Soc. Perkin Trans.-2*, 1989, 1199-1204.
  40. Takeda H, Sakurai Y, Takenaka S, Miyake H, Doi T, Kusabayashi S, Takagi T, Molecular structure and smectic properties: the substituent effect on the smectic A phase in biphenyl ester systems, *J. Chem. Soc. Faraday Trans.*, 86, 1990, 3429-3435.
  41. Centore R, Ciajolo MR, Roviello A, Sirigu A, Tuzi A, A comparative study of mesogenic structures. The crystal structures of bis[(4-butoxycarbonyl)-phenyl]terephthalate and bis[(4-valeroyloxy)-phenyl]terephthalate, *Liquid Crystals*, 9, 1991, 873-882.
  42. Deschenaux R, Marendaz JL, Santiago J, 1,1'-Disubstituted Ferrocene-Containing Thermotropic Liquid Crystals of structure  $[\text{Fe}\{\{\eta^5\text{-C}_5\text{H}_4\}\text{COOC}_6\text{H}_4\text{XC}_6\text{H}_4\text{OCnH}_{2n+1}\}_2]$  (X=OOC or COO). Influence of the orientation of the central ester function on the mesogenic properties, *Helv. Chim. Acta*, 76, 1993, 865-876.

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