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Magnetic and liquid crystalline property of long-alkyl chain appended Iron (II) Imidazole complexes

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1 Abstract

2 $Fe[((py)im-C16)_3](BF_4)_2$ (1) and $Fe[((py)imH)_3](BF_4)_2$ (2), the Iron(II) compounds 3 with C16 long alkyl chain appended (py)imH and unmodified (py)imH [(py)imH=2-(2-4 pyridyl)imidazole] have been synthesized and characterized by NMR, IR spectra and 5 elemental analysis. For containing C16 long alkyl chain, complex 1 exhibits the liquid 6 crystalline property around room temperature. The magnetic study suggests that 1 exists 7 only in low spin state but 2 exhibits gradual spin crossover behavior. These observation suggests the possibility for synchronizing liquid crystallinity and spin crossover behavior of 8 9 (py)imH complex in near future.

10 Keywords: Iron(II); 2-(2-pyridyl)imidazole; Liquid crystal (LC); Spin crossover (SCO);
11 C16-alkylchain

12

13 1. Introduction

Appending long alkyl chains into ligand groups of metal complexes can result in 14 15 some unique physical and chemical phenomena including the synchronicity between spinstate transitions and crystal-liquid crystal phase transitions. The nature of magnetic metal 16 17 center and the effect of thermal motion on long alkyl chains play the major role for such 18 external stimuli aided synergetic effect [1]. In a more specific way, the modulation of 19 temperature or intensity of irradiated photon can result in some change in spin state or phase 20 transition process. In molecular material chemistry the spin crossover (SCO) behavior 21 corresponds to spin state switching [2]. The mesogenic materials having liquid crystalline 22 (LC) properties and SCO behavior have attracted considerable interest in recent years. As 23 these materials can exhibit spin transition signals with phase transition phenomena at

1 different temperature regions, they can be used as photo and thermo-chromic switching 2 materials [3]. Iron complex possesses wide interests in SCO chemistry since Cambi et al. 3 observed the SCO behavior in an iron (III) tris-dithiocarbamate complex at 1930 by 4 studding the temperature-dependent magnetic moments [4]. The first iron (II) SCO complex was reported and recognized in 1964 and 1967, respectively [5]. SCO phenomenon 5 6 represents the external stimuli (e.g. temperature, pressure, magnetic field, light etc.) aided 7 reversible transformation of electronic arrangement between high spin (HS) and low spin (LS) state in the complexes of first raw transition metal ions having $3d^n$ (n = 4-7) electronic 8 configuration [6]. On the otherhand, the liquid crystalline property of metal complexes 9 10 having C16 long alkyl chain has been reported by several groups [7]. Liquid crystals of transition-metal complexes, called metallomesogens are well known for their 11 12 multifunctional aspects [8]. The development of metallomesogens with functionalities including spin-crossover, mixed-valence, magnetism, conductivity etc. are important for 13 14 achieving the co-occurrence of various physical properties in functional molecular-based 15 materials. Mononuclear iron (II) complexes with heterocyclic N-donor ligands are well known for their spin-crossover behavior and low-temperature spin-trapping phenomenon. A 16 significant number of such compounds undergo thermal spin-transitions upon cooling or 17 18 heating [9]. Todate, a number or reports on the Iron complexes of (py)imH and its 19 derivatives has been reported so far [10]. Herein, we observed the mesogenic nature and 20 SCO behavior in (py)imH based Iron (II) complexes.

(py)imH, a derivative of imidazole is one of the most important nitrogen containing
bioactive ligand. The ligand in its pure form is capable to form hydrogen bond [11]. It is a
bidentate ligand having both the pyridinic and pyrrolic N atoms functioning as the electron

1 donors for the formation of coordination complexes [12]. Compared with the closely related 2,2'-bipyridine, (py)imH can coordinate as a weaker σ donor and π acceptor ligand [13]. 2 3 Previously, N-functionalized imidazole, its derivatives and complexes with some transition 4 metals were studied extensively for therapeutic applications including antibacterial, 5 antifungal and antitubercular agents [14]. The anomalous magnetic behavior of Iron (II) complexes with (py)imH having ${}^{5}T_{2g}$ - ${}^{1}A_{1g}$ equilibrium was reported long before [15]. Also 6 7 Goodgame et al. reported the cooperative thermal spin-transition behavior of Fe[((py)imH)₃](ClO₄)₂ [16]. Later, Wilson *et al.* reported the solution state equilibrium 8 between high and low spin state in $Fe[((py)imH)_3](BF_4)_2$ [17]. In recent years the 9 10 temperature dependent variable magnetic properties of Iron complex of (py)imH having 11 phenyl derivatives have been studied by Michelle et al. [18]. (py)imH can be N-12 functionalized through deprotonation by base [7]. Based on this previous observation in this study, we attempt to insert long alkyl chain by replacing H from the pyrrolic N-H. Previous 13 abiotic study suggested that the activity and functionality of alkylated imidazole precursor 14 15 depends on the chain lengths. For example the biological functionality was found to be pronounced when the alkyl chain have at least 12 carbons [19]. Apart from biological 16 17 application, almost no efforts have been noticed to justify the liquid crystalline nature and 18 magnetic behavior of (py)imH based materials. In this respect, we considered the N-19 functionalization of (py)imH to devise functional metal complexes. By replacing the proton 20 in basic medium, we inserted C16 alkyl chain at (py)imH and synthesized corresponding 21 Iron (II) complexes 1 and 2. Complex 1 and 2 exhibited the liquid crystallinity and gradual 22 spin crossover property, respectively.

23

1 2. Experimental Section

2 2.1. Materials

3 Pyridine-2-carboxaldehyde, glyoxal (40%), ammonia (25%), one bromohexadecane, 4 sodium hydride, tetra-n-butylammonium bromide (TBAB), ethyl alcohol and tetrahydrofuran (THF) was purchaged from Wako Chemical Co. Ltd. Pyridine-2-5 6 carboxaldehyde was distilled at reduced pressure and was preserved on brown bottle by 7 wrapping aluminum foil until using. All other chemicals were used without further 8 purification except mentioned differently.

9

10 2.2. Instrumentation

Elemental analysis (C, H and N) were carried out at the Instrumental Analysis Center of 11 Kumamoto University. ¹H-NMR spectra were recorded on a JEOL (500-ECX) 12 Instrument (500 MHz) using deuterated solvents with TMS as internal reference. Magnetic 13 14 Susceptibilities were measured on a Quantum Design MPMS-5S. Samples were put into a 15 gelatin capsules and mounted inside plastic straws. They were then fixed at the end of the sample transport rod and were conveyed inside the magnet core fitted with field strength 16 17 and temperature scanning facilities. Thermal analysis through differential scanning 18 calorimetry (DSC) was carried out on a SHIMADZU DSC 50 differential scanning 19 calorimeter. Powder X-ray diffraction (XRD) studies were performed on a Rigaku X-ray 20 diffractometer RAD-2A with a 2.0 kW Cu Ka X-ray. Polarized Optical Microscopy (POM) 21 was carried out on a polarization microscope (OPTICAL POL with a Yanagimoto factory 22 model MP-J3) micromelting point meter, devised by Nippon Chemical Industrial 23 Corporation.

2 2.3. Synthesis of (py)imH

3 The overall route for synthesis is depicted by scheme 1. The ligand was synthesized by 4 some modification of Radziszewski method [20]. In a typical procedure, 5.0 g freshly distilled pyridine-2-carboxaldehyde in 5.0 ml EtOH at 0 °C was added dropwise into 6.75 5 ml glyoxal (dissolved in 5.0 ml EtOH) of 0 °C and was stirred for 30.0 minutes. 19.2 ml 6 7 ammonia at 0 °C was added very slowly with constant stirring at 0 °C for 4.0 hours. The mixture was stirred further for 18.0 hours at room temperature to achieve a deep brown 8 solution. The volume of the content was then reduced to 30% by rotary evaporator. The 9 10 remaining content was extracted by diethyl ether (10 times \times 30 ml). The ether from the extracted was removed by rotary evaporator and a red oily product was found. It was 11 12 distilled at 132.0 °C under low pressure. Pale yellow needle like crystals were found. Yield 32%, melting point 136.0 °C. ¹H-NMR (500 MHz, CDCl₃): 8.46 (d, J = 4.8, 1H), 8.09 (d, J 13 14 = 7.6, 1H); 7.71 (td, J= 7.6, 3.8 1H); 7.68 (s, 1H), 7.18 (q, 1H), 7.13 (s, 1H). UV/Vis 15 (MeOH): 273 (11900), 294 (15600). IR (KBr): ca. 3352 w, 1614 s, 1595 s, 1508 m, 1481 s, 1458 s, 1414 s, 1379 m, 1307 s, 1280 m, 1252 m, 1171 m, 1150 s, 1136 s, 1107 m, 991 s, 16 955 s, 901 m, 789 s, 758 s, 737 s, 708 m, 621 s, 657 m, 499 m, 462 m, 430 w. 17

18

19 2.4. Synthesis of (py)im-C16

NaH (0.024 g, 1.0 mmol) in 5.0 ml THF was cooled to 0 °C. (py)imH (0.145 g, 1.0 mmol) in 5.0 ml THF was added dropwise and was stirred for 30.0 hour in an ice bath. Then
the temperature of the solution was increased to room temperature and stirred for another
30.0 minutes. 0.01 g TBAB was then added as phase transfer catalyst followed by a slow

1	addition of C16-Br (0.305 g, 1.0 mmol). Finally 10.0 ml THF was added and the mixture
2	was refluxed overnight at 65.0 $^{\circ}$ C. The solvent was then removed by stirring it in open air at
3	65.0 °C. The product was dissolved in chloroform and filtered. The solvent was removed
4	and the final product was washed by water and dried under vacuum. Brown oily product
5	was found. ¹ H-NMR (500 MHz, CDCl ₃): 8.46 (d, J = 4.8, 1H), 8.09 (d, J = 7.6, 1H); 7.71 (td,
6	J = 7.6, 3.8, 1H); 7.68 (s, 1H), 7.18 (q, 1H), 7.13 (s, 1H); 1.22 (m, 31H, -CH ₂ CH ₂ CH ₂ -). IR
7	(KBr): ca. 3448 w, 1605 s, 1578 s, 1556 m, 1535 m, 1472 m, 1425 s, 1371 m, 1310 m,
8	1263 s, 1150 m, 1123 s, 1088 m, 1063 s, 1032 s, 1031 m, 980 s, 953 m, 920 m, 780 s, 731 m,
9	704 s, 612 s.

11 2.5. Synthesis of 1 and 2

Previously, almost similar compound of 2 with different counter anion (BPh₄) was 12 reported by Wilson et al [17]. Herein, we have introduced different counter anion. In a 13 typical synthetic method, NaBF₄ (0.095 mg, 0.25 mmol), ascorbic acid (0.176 mg, 0.1 14 15 mmol) and FeCl₂.4H₂O (0.02 mg, 0.1 mmol) was dissolved in 10 ml MeOH by 10 minutes stirring at room temperature. The solution was filtered and added dropwise into a solution of 16 17 (py)im-C16 (0.107 mg, 0.29 mmol) in 10.0 ml methanol under argon at room temperature. 18 The mixture was stirred for 4.0 hours and crystallized at room temperature. The product was 19 filtered from methanol, washed with water and finally was recrystallized from methanol. 20 After drying, red powder of 1 was found. Yield (0.11 g, 0.76%). Element. Anal. Calcd. For 21 C₇₈H₁₃₅B₂F₈FeN₉: C, 63.12; H, 9.17; N, 8.49 Found: C, 63.40; H, 9.12; N, 8.56%. In a 22 similar way, 2 was synthesized using the ligand (py)imH. Element. Anal. Calcd. For 23 C₂₄H₂₁B₂F₈FeN₉: C, 43.35; H, 3.18; N, 18.96 Found: C, 43.40; H, 3.22; N, 19.01%. The powdered and crystalline products of 1 and 2, respectively were obtained from slow evaporation of solvent through the pinholes of parafilm cover at room temperature. The crystals were larger in size, when they were precipitated from methanol at room temperature. Crystals obtained from hot methanol or by rapid cooling using refrigeration were comparatively smaller in size. Above room temperature, the solubility of the complexes increases. Therefore, room temperature was preferred for obtaining the products.

7 **3.** Results and discussion

8 3.1. Synthesis and structure:

9 For synthesizing (py)imH we followed the Debus-Radziszewski reaction [21], where a 10 dicarbonyl, an aldehyde and ammonia react to form imidazole or its derivatives. We used 11 glyoxal and pyridine-2-carboxaldehyde as the dicarbonyl and aldehyde. The reaction takes 12 place in two steps. In the first step, dicarbonyl and ammonia condense to give a diimine. In second stage, the diimine condenses with the aldehyde. Therefore, glyoxal is necessary to 13 obtain diimine, which reacts with pyridine-2-carboxaldehyde to form (py)imH. The 14 formation of (py)imH and its modification into (py)im-16 was confirmed by ¹H-NMR and 15 IR spectra. The hydrogen atom attached to the pyrroline ring is labile and was possible to 16 substitute by -C₁₆H₃₁ alkyl group by base catalyzed reaction in presence of TBAB. TBAB is 17 18 an ionic compound which can be deionized to form $(C_4H_9)_4N^+(TBA^+)$ and Br⁻. The function 19 of TBAB is similar to the mechanism of phase transfer catalyst reported previously by 20 Starks. [22] (py)im-16 is formed through a two step reaction. In the first step, (py)imH and 21 NaH reacts to form (py)im⁻Na⁺. Ionic (py)im⁻Na⁺ is sparingly soluble in organic phase, 22 which prohibits its interaction with Br-C₁₆H₃₁ dissolved in THF. Therefore, the phase transfer catalyst TBAB is necessary to convert (py)im Na⁺ into (py)im TBA⁺ complex, 23

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which is soluble in THF. The polar part (N⁺) electrostatically bounds the (py)im⁻ precursor, whereas the non polar part (-C₄H₉) dissolves in THF. In the final stage (py)im⁻TBA⁺ reacts with Br-C₁₆H₃₁ to form (py)im-16 and TBAB again. The Br⁻ and Na⁺ form insoluble NaBr salt and precipitated out from the system. TBAB therefore is necessary for successful completion of the reaction.

The NMR spectra for (py)imH matches with theoretical calculation and some previous 6 7 report [8]. Characteristic NMR peak at low field (1.22 (m, 31H, -CH₂CH₂CH₂-)) confirms the successful insertion of C16-long alkyl chain during the reaction. This NMR 8 9 spectroscopy based characterization for successful ligand alkylation process is well reported [23]. The insertion of Fe^{2+} ion for formation of the complexes was followed by previous 10 11 report [12]. Unfortunately, we failed to get the single crystals, as it is expected that the 12 thermal motion of long alkyl chain could prohibits the crystal packing [24]. Even we synthesized complex having the ligand with shorter alkyl chains (C1 and C4), stable crystal 13 packing was not possible to avail. As some alternative, elemental analysis and IR spectra 14 15 could confirm the formation of the complexes. Figure 1 represents the IR spectra of (py)imH, (py)im-C16, 1 and 2. In Figure 1(a), the diffused peak at 3100-3500 cm⁻¹ and the 16 sharp peak at 1595 cm⁻¹ rises from the stretching and bending mood of vibration, 17 18 respectively for pyrrilic hydrogen atom bonded to N. This N-H bond is polar due to the 19 variation in electronegativity between N and H. Therefore, the positively charged hydrogen 20 atom takes part in intermolecular hydrogen bond and the resultant IR adsorption peak is 21 broad. The pyridinic, and pyrrilic C-N bond stretching frequencies lie within the range of 1250-1350 cm⁻¹. When the pyrrilic H atom is substituted by C16 alkyl chain, the IR 22 23 spectrum of resulted (py)im-16 is characterized by the appearance of peaks at 2850 and

2920 cm⁻¹ (Figure 1b). These peaks are resulted from the stretching mood of aliphatic C-H 1 bond of long alkyl chain. In addition, the IR spectrum of (py)im-C16 shows the 2 disappearance of broad peak at 3100-3500 cm⁻¹ due to the removal of pyrrilic H atom and 3 the breaking of the hydrogen bonded networks. The IR spectra in Figure 1c and Figure 1d 4 indicate the formation of complex 1 and 2 through clear indication for the existence of Fe-N 5 bond. When Fe²⁺ was inserted near the pyridinic and pyrrilic N, the characteristic IR 6 stretching frequencies of Fe-N bond formed at ~1000 cm⁻¹ indicated the formation of iron 7 (py)imH/(py)im-C16 compounds [25]. Besides, the peaks position and intensity for 8 pyridinic and pyrrilic C-N bond in the ligands near 1300 cm⁻¹ undergo some change in **1** and 9 2. When the ligands co-ordinate to Fe^{2+} ion, the electron density from C-N bond is partly 10 shifted to C-Fe bond, which is responsible for the respective change in the band intensity. 11

12

3.2. 13

Liquid crystalline behavior of 1

The liquid-crystalline property of 1 was justified firstly by phase transition enthalpy 14 15 changes, which were measured by carrying out thermal analysis with DSC in a wide range of temperature. As shown in **Figure 2**, an endothermic peak at 306 K ($\Delta H = 53.81 \text{ kJmol}^{-1}$) 16 on cooling process and an exothermic peak at 330 K ($\Delta H = -41.58 \text{ kJmol}^{-1}$) on heating 17 18 process were observed. These results indicate the possibility for crystal to mesophase phase 19 transition near room temperature. The meso-phase structure of 1 was further studied by powder XRD and hot-stage polarized optical microscopy (POM). Figure 3 shows the 20 21 powder XRD patterns of the solid and mesophase states for 1 observed at 330 and 455 K, respectively. At room temperature, the XRD pattern displays two reflections at $2\theta = 3.06^{\circ}$ 22 (d-spacing = 28.38 Å) and 6.15 ° (d-spacing = 14.14 Å) in the small-angle region and a 23

broad scattering halo centered at 21.2 (d-spacing = 4.43 Å) in the wide-angle region. 1 However at 455 K, the XRD pattern reveals three reflections at $2\theta = 2.52$, 5.14 and 7.74 ° 2 with respective d-spacing values as 34.46, 16.91 and 11.24 Å in the small-angle region. The 3 4 ratio of the d-spacing values becomes 1:1/2:1/3 and could be indexed as the (001), (002) and 5 (003) reflections of a lamellar phase. Besides, a diffuse and broad scattering halo centered at 4.08 Å ($2\theta = 21.7^{\circ}$) in the wide-angle region is indicative of the liquid-like order of the 6 7 aliphatic chains. POM images for 1 (Figure 4) show the conversion of the compounds directly into isotropic liquid. At 330 K, typical fan shaped texture of lamellar phase during 8 9 heating and cooling process indicates the crystal to mesophase phase transformation.

10

11

3.3. Spin Crossover behavior of 1 and 2

12 Spin transitions between the high-spin (HS) and low-spin (LS) states for 1 and 2 were investigated by the measurement of the molar magnetic susceptibility χ_m as function of the 13 temperature. Complex 1 exists only in low spin state within the temperature range 5-400 K 14 (Figure 5a). The $\chi_m T$ value is around 0.5 cm³Kmol⁻¹ at 5 K and decrease slightly at higher 15 temperature. The rate of this lowering is comparatively higher at 5-25 K. Beyond 25 K, the 16 $\chi_m T$ values lie below 0.26 cm³Kmol⁻¹ and represents the low spin state of Iron (II). The 17 18 cooling process resulted in the reversible thermal curve. The magnetic study indicates the 19 diamagnetic behavior of the complex. Slightly higher $\chi_m T$ values at low temperature are 20 insignificant but indicate the presence of impurity in 1. The product seems to adsorb traces 21 of impurity (FeCl₂ or related ions) during precipitation. Though the result of elemental 22 analysis indicates the close match between calculated and experimental values for C, H and 23 N content in 1 and 2, there exist some possibility for the existence of adsorbed impurity. Especially, as 1 was found in powdered form, it is more likely to adsorb impurity. The
magnetic data for 1 was reproducible, while we repeated the experiment several times.
Apart from the impurity effect, any other reason behind this slightly higher susceptibility
values at low temperature is presently unknown. However, our future plan includes tuning
the length of alkyls chain to study the magnetic behavior of the series in details.

6 The temperature dependent magnetic susceptibility for 2 reveals a gradual SCO 7 behavior without hysteresis loop in the temperature region from 5 to 400 K (Figure 5b). This behavior is a typical phenomenon occurring in some Iron (II) complexes [7b]. The $\gamma_m T$ 8 value is equal to 0.26 cm³Kmol⁻¹ at 5 K and lies within the range of expected χ_m T value for 9 10 LS Iron (II) ions [26]. As the temperature is increased from 5 K, the $\chi_m T$ value remains constant upto 150 K. Beyond 150 K, the $\chi_m T$ value gradually increases to 2.7 cm³Kmol⁻¹ at 11 12 400 K and is consistent with HS state. Upon cooling process, the behavior of magnetic 13 susceptibility exhibits the reversible thermal curve.

Soft metal complexes become interesting not only as some functional materials, but 14 15 also for the phase transitions with synchronicity between the central metal complex and the long alkyl chains [27]. The liquid crystalline behavior of some metal complexes having long 16 17 alkyl chain (especially C16) is well reported [28]. We propose that the observed mesophase 18 structure of 1 around room temperature originates from the equilibrium between thermal 19 motion of the flexible C16 alkyl chain and its rigidity in crystal packing. The packing of 20 polar headed moiety ((py)im) with C16 alkyl tail in an atmosphere of bulk polar liquid 21 resulted in the diffraction pattern of lamellar phase. Previously, some complexes of (py)imH with Fe^{2+} and Cr^{3+} was reported to exhibit octahedral crystal structure [29]. Therefore, we 22 23 also expect similar structure for 1. In octahedral packing the long alkyl chains are extended

1 and supposed to limit the tilting motion of the packing through interchain interaction with 2 neighboring alkyl groups. Therefore, the liquid crystalline property could sustain around 3 room temperature. In future, we are intending to study further the liquid crystallinity, by 4 changing the counter anion and modulating the chain lengths. Present magnetic study suggests the possibility for SCO behavior in (py)imH based Fe^{2+} complexes. Though the 5 6 increase in chain length renders the spin transition phenomenon, the liquid crystallinity was 7 availed with longer alkyl chain. Achieving simultaneous electron transitions across all 8 molecules to obtain abrupt SCO behavior is highly desirable. Establishing cooperativity 9 among the molecules is the primary condition for such achievement and the best way to 10 increase cooperativity between molecules is to functionalize the side chain by polar groups. 11 Our future endeavor includes such trials. The present form of this manuscript is important 12 for further advancement in this filed. This manuscript indicates the possibility of both the SCO behavior and liquid liquid crystallinity in Iron based (Py)imH complex. We are 13 expecting the coalescence of these two functionalities in a single molecule in near future. 14

15

16 4. Conclusion

We have synthesized novel (py)imH based Iron(II) complexes as [Fe((py)im-C16)₃](BF₄)₂ and [Fe((py)imH)₃](BF₄)₂. The DSC track, powder XRD pattern and POM images were indicative for the liquid crystalline lamellar phase of [Fe((py)im-C16)₃](BF₄)₂.
[Fe((py)im-C16)₃](BF₄)₂ exists only in low spin state, whereas, [Fe((py)imH)₃](BF₄)₂ exhibits gradual SCO property with respect to the modulation of temperature. All these complexes indicate the possibility of designing (py)imH based novel multifunctional mesogenic materials in future.

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Figure 1. IR spectra for charecterization of the ligands and complexes. (a) (py)imH, (b)
(py)im-C16 (c) 1 and (d) 2.

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