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<td>Author(s)</td>
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Iron(II) Spin Crossover Complexes with Branched Long Alkyl Chain

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Abstract

The bzimpy iron(II) complexes, 1-3, containing branched long alkyl chains were synthesized and characterized in detail. The temperature-dependant magnetic susceptibility of 1 showed gradual spin crossover behavior from low spin to high spin state, while 2 retained only low spin state in the same condition. Interestingly, 3 displayed an abrupt spin transition in temperature range from $T_{1/2}^\uparrow = 236K$ to $T_{1/2}^\downarrow = 230K$ with the thermal hysteresis loop about 6 K. The differential scanning calorimetric analysis of 3 revealed two species of liquid crystal phase transitions at 236K and 351K, respectively.

Key words: spin crossover; iron(II) complex; long alkyl chain, liquid crystal

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1. Introduction

Labile electronic configurations of metal complexes switchable between diamagnetic low spin (LS) and paramagnetic high spin (HS) states have aroused a great deal of interests for the development of a switching devices because it leads to a distinctive changes in structure, color, and magnetism by external stimuli such as temperature, pressure, magnetic field or light [1]. Among them, one of the most well-known spin crossover compounds is iron(II) complex with octahedral geometry in coordination sphere [2]. In iron(II) spin crossover compounds, cooperative effects play an important role in the generation of much steeper transition curve and hysteresis behavior leading to the sufficient magnitude of the intermolecular interactions to overcome the threshold value [3]. For this reason, the utilization of long alkyl chain may be one of efficient approaches not only for the formation of cooperativity, but also for the combination of spin crossover and liquid crystalline behavior capable of resulting in novel physical properties [4].

Organic liquid crystals (LCs) have also caused a huge amount of concern in liquid crystal displays, which rely on the optical properties of certain liquid crystalline substances in the presence of electric fields [5]. In this case, strong magnetic fields, however, are necessary to align diamagnetic organic liquid crystals. On the contrary, metallomesogens are paramagnetic liquid crystals due to unpaired electrons, and need much smaller magnetic field strength than that of diamagnetic organic liquid crystals [6]. Recently, there are some literatures reported on flexible metal complexes with long alkyl chains exhibiting unique metallomesogen property [7].

R. Boča and his coworkers have reported an iron(II) complex, [Fe(bzimpy)₂]^{2+} exhibiting an abrupt spin transition at 400K, which was perfectly reversible with a hysteresis width of 12 K [8]. In our previous works, it has been reported that two bzimpy iron(II) complexes with linear long alkyl chains, [Fe(C16-O-bzimpy)₂(BF₄)₂ and [Fe(C16-O-bzimpy)₂(BF₄)₂ showed a spin crossover behavior in a wide range of temperature and crystal-liquid crystal phase transitions, while it did not show cooperative effect between metal complex and linear long alkyl chain [9].

Keeping the aforementioned research in mind, we herein report the synthesis of new bzimpy iron (II) complexes involving branched long alkyl chains with the higher flexibility and their physical properties in a wide range of temperature.

2. Experimental
2.1. Synthesis of the ligands

Bzimpy (bzimpy = 2,6-di(1H-benzo[d]imidazol-2-yl)pyridine) [10], and OH-bzimpy (OH-bzimpy = 2,6-di(1H-benzo[d]imidazol-2-yl)pyridin-4-ol) [11] were prepared according to literature procedures.

2.1.2. Preparation of 11-(bromomethyl)tricosane

A solution of 2-decyltetradecan-1-ol (42.1g, 0.12 mol) and triphenylphosphine (50g, 0.19 mol) in CH₂Cl₂ (300 mL) was cooled to 0°C, and then N-bromosuccinimide (33.5g, 0.19 mol) was added slowly to the reaction mixture. The ice bath was removed and the solution stirred overnight at room temperature under an argon atmosphere. The solvent was evaporated to dryness and extracted with hexane. Chromatography on silica gel with hexane gave 35 g as a colorless oil (yield: 70%). 1H NMR (500 MHz, CDCl₃) δ 3.45 (t, J = 4.5, 2H, CH₂), 1.65 (m, 2H, CH₂), 1.27 (m, 39H, CH and CH₂), 0.91 (t, J = 7.0, 6H, CH₃).

2.1.3. Preparation of 5-decylheptadecan-1-ol

To a mixture of 11-(but-3-enyl)tricosane (20 g, 52.8 mmol) and NaBH₄ (2.0 g, 52.8 mmol) in dry
diglyme (50 mL) was added BF₃·OEt₂ (4.3 mL, 37 mmol) dropwise for 1h and stirred at room temperature for 2h under an argon atmosphere. Water (5 mL) and 3M NaOH (20 mL) were added slowly in order and stirred more 2h at 40 °C. The solution was treated with H₂O₂ (20 mL) slowly and stirred 1h at room temperature. After extraction with diethyl ether, chromatography on silica gel with ethylacetate/hexane (1:8) gave 17.3 g as a colorless oil (yield: 83%). 1H NMR (500 MHz, CDCl₃) δ 3.61 (t, 2H, J = 7.0, CH₂), 1.79 (s, 1H, OH), 1.54 (quintet, J = 7.0, 2H, CH₂), 1.32 (m, 45H, CH and CH₂), 0.87 (t, J = 7.0, 6H, CH₃).

2.1.4. Preparation of 11-(4-bromobutyl)tricosane

A solution of 5-decylheptadecan-1-ol (5.0g, 12.6 mmol) and triphenylphosphine (5.0g, 19.0 mmol) in CH₂Cl₂ (50 mL) was cooled to 0 °C and N-bromosuccinimide (4.0g, 22.5 mol) was added slowly to the reaction mixture. The ice bath was removed and the solution stirred overnight at room temperature under an argon atmosphere. The solvent was evaporated to dryness and extracted with hexane. Chromatography on silica gel with hexane gave 4.1 g as a colorless oil (yield: 71%). 1H NMR (500 MHz, CDCl₃) δ 3.33 (t, 2H, J = 6.5, CH₂), 1.78 (quintet, J = 6.5, 2H, CH₂), 1.34 (m, 2H, CH₂), 1.25 (m, 43H, CH and CH₂), 0.81 (t, J = 6.5, 6H, CH₃).

2.1.5. Preparation of 2,2’-(4-(5-decylheptadecyloxy)pyridine-2,6-diyl)bis(1H-benzo[d]imidazole) (L1)

A mixture of OH-bzimpy (1.1g, 3.4 mmol), K₂CO₃ (0.70g, 5.0 mmol), and 11-(4-bromobutyl)tricosane (1.7g, 3.7 mmol) in dry DMF (100 mL) was refluxed for 24h under an argon atmosphere and evaporated under reduced pressure. Chromatography on silica gel with ethylacetate/ hexane (1:4) gave 0.9 g as white solid (yield: 38%). 1H NMR(500 MHz,CDCl₃) δ 7.85 (s, 2H, ArH), 7.05(s, 8H, ArH), 3.56 (t, J = 6.5, 2H, CH₂), 1.35 (t, J = 5.5, 2H, CH₂), 1.16-1.02 (m, 47H, CH and CH₂), 0.79 (t, J = 6.5, 6H, CH₃).

2.1.6. Preparation of 2,6-bis(1-(5-decylheptadecyl)-1H-benzo[d]imidazol-2-yl)pyridine (L2)

A mixture of bzimpy (0.6g, 2.0 mmol), K₂CO₃ (1.1, 8.0 mmol), and 11-(4-bromobutyl)tricosane (2.5g, 5.4 mmol) in dry DMF (100 mL) was refluxed for 24h under an argon atmosphere and evaporated under reduced pressure. Chromatography on silica gel with ethylacetate/ hexane (1:4) gave 1.5 g as colorless oil (yield: 70%). 1H NMR(500 MHz,CDCl₃) δ 8.28 (d, J = 8.0, 2H, ArH), 7.99 (t, J = 8.0, 1H, ArH), 7.82 (m, 2H, ArH), 7.40 (m, 2H, ArH), 7.30 (m, 4H, ArH), 4.66 (t, J = 7.5, 4H, CH₂), 1.67 (t, J = 7.0, 4H, CH₂), 1.24-0.89 (m, 90H, CH and CH₂), 0.82 (t, J = 6.0, 12H, CH₃).

2.1.7. 2,2’-(4-(5-decylheptadecyloxy)pyridine-2,6-diyl)bis(1-(5-decylheptadecyl)-1Hbenzo[d]imidazole) (L3)

A mixture of OH-bzimpy (1.0g, 3.1 mmol), K₂CO₃ (2.5g, 18.3 mmol), and 11-(4-bromobutyl)-
tricosane (6.5g, 14.0 mmol) in dry DMF (100 mL) was refluxed for 24h under an argon atmosphere and evaporated under reduced pressure. Chromatography on silica gel with ethylacetate/ hexane (1:8) gave 3.2 g as colorless oil (yield: 71%). 1H NMR(500 MHz,CDCl3) δ 7.97 (s, 1H, ArH), 7.79 (d, J= 8.0, 1H, ArH), 7.75 (d, J= 7.5, 1H, ArH), 7.61 (s, 1H, ArH), 7.31-7.29 (m, 3H, ArH), 7.25 (d, J= 7.0, 1H, ArH), 7.08 (m, 1H, ArH), 4.09 (t, J= 6.0, 2H, CH2), 3.59 (m, 4H, CH2), 1.56 (quintet, J= 7.5, 2H, CH2), 1.48 (quintet, J= 6.5, 4H, CH2), 1.17-0.86 (m, 135H, CH and CH2), 0.80 (t, J= 7.0, 18H, CH3).

2.2. Preparation of the iron(II) compounds

2.2.1. Preparation of [Fe(L1)2](BF4)2 (1)

A mixture of FeCl2·4H2O (0.03g, 0.14 mmol), NaBF4 (0.03g, 0.28 mmol), and ascorbic acid (~0.1g) in methanol (30 mL) was added to a solution of L1 (0.2g, 0.28 mmol) in MeOH/CHCl3 (50 mL, 1:1) and refluxed for 1h. After cooling to room temperature, the solvent was evaporated under reduced pressure until it was remained around 5 mL and then filtered and washed with cold methanol. The red-purple solid was dried in vacuo to give 0.2g (yield: 87%). Anal. Calc. for C92H134B2F8FeN10O2: C, 67.31; H, 8.23; N, 8.53. Found: C, 67.85; H, 8.02; N, 8.68.

2.2.2. Preparation of [Fe(L2)2](BF4)2 (2)

A mixture of FeCl2·4H2O (0.02g, 0.10 mmol), NaBF4 (0.02g, 0.2 mmol), and ascorbic acid (~0.1g) in methanol (30 mL) was added to a solution of L2 (0.2g, 0.19 mmol) in MeOH/CHCl3 (50 mL, 1:1) and refluxed for 1h. After cooling to room temperature, the solvent was evaporated under reduced pressure until it was remained around 5 mL and then filtered and washed with cold methanol. A sticky dark-purple solid was obtained after dryness in vacuo (yield: 0.13g, 55%). Anal. Calc. for C146H244B2F8FeN10: C, 74.02; H, 10.38; N, 5.91. Found: C, 74.56; H, 10.78; N, 6.02.

2.2.3. Preparation of [Fe(L3)2](BF4)2 (3)

A mixture of FeCl2·4H2O (0.02g, 0.1 mmol), NaBF4 (0.02g, 0.2 mmol), and ascorbic acid (~0.1g) in methanol (30 mL) was added to a solution of L3 (0.2g, 0.14 mmol) in MeOH/CHCl3 (50 mL, 1:1) and refluxed for 1h. After cooling to room temperature, the solvent was evaporated under reduced pressure until it was remained around 5 mL and then filtered and washed with cold methanol. A sticky dark-purple solid was obtained after dryness in vacuo. (yield: 0.15g, 70%). Anal. Calc. for C200H352B2F8FeN10O2: C, 76.05; H, 11.23; N, 4.43. Found: C, 76.41; H, 11.05; N, 4.55.

2.3. Physical experiments
Elemental analyses of carbon, hydrogen, and nitrogen were carried out at The Instrumental Analyses Center of Kumamoto University. 1H NMR was measured on a JEOL USA instrument operating at 500 MHz (using the deuterated solvent). Magnetic susceptibilities of ground samples were measured on a Quantum Design MPMS-5S. Samples were put into a gelatin capsule, mounted inside the straw, and then fixed to the end of the sample transport rod. Differential scanning calorimetry (DSC) thermal analysis was carried out on a SHIMADZU DSC50 differential scanning calorimeter. X-Ray powder diffraction (XRD) studies were performed on a Rigaku X-ray diffractometer RAD-2A with a 2.0 kW Cu Kα X-ray.

3. Results and Discussion

Three bzimpy derivatives (L1-L3) possessing flexible long alkyl chains were readily synthesized by the simple alkylation reaction between bzimpy or OH-bzimpy and branched long alkyl bromide in basic condition. Each of ligands was reacted with iron(II) chloride in the presence of NaBF₄ and ascorbic acid in methanol/chloroform mixed solvent media (see Fig. 1).

The temperature-dependant magnetic susceptibility on 1-3 was measured in the form of the $\chi_m T$ versus $T$ curve, where $\chi_m$ is the molar magnetic susceptibility and $T$ is the temperature. As depicted in Fig. 2, the $\chi_m T$ value of 1 is equal to 1.84 cm$^3$ K mol$^{-1}$ at 35 K, showing that about 54% of iron(II) ions remain the high-spin states. The decrease of the $\chi_m T$ value below 35K is due to zero-field splitting. Upon heating process from 35K to 103K, the $\chi_m T$ values were almost constant, then gradually increased to the spin transition temperature centered around $T_{1/2}$ = 280K. With further heating, the $\chi_m T$ value was reached ~ 3.42 cm$^3$ K mol$^{-1}$ at 400K, which is consistent with the spin transition from LS to HS states. However, the temperature dependence of magnetic susceptibility of 2 has a constant value of almost 0 cm$^3$ K mol$^{-1}$ in the temperature range from 5K to 400K, indicating that it remains low spin state steadily without the interconversion of spin state under temperature changes. In case of 3, the $\chi_m T$ value is equal to 1.44 cm$^3$ K mol$^{-1}$ at 33 K, showing that about 43% of iron(II) ions retain the high-spin states. Upon heating, the $\chi_m T$ values were almost unchanged up to 123K and gradually elevated from 1.35 cm$^3$ K mol$^{-1}$ at 124K to 1.86 cm$^3$ K mol$^{-1}$ at 233K in turn, whereas upon further heating it was abruptly decrease at around $T_{1/2}$ = 236K due to solid-liquid crystal phase transition of complex as shown Table 1. With further heating, $\chi_m T$ value at 400K is about 3.34 cm$^3$ K mol$^{-1}$ corresponding to spin transition from LS to HS state. Additionally, upon cooling processes, the behavior of temperature-dependant molar magnetic susceptibility displays the reversible thermal curve similar with heating process including an abrupt increase of $\chi_m T$ value at around $T_{1/2}$ = 230K. It means that LS moieties were restored to the HS with a hysteresis loop ($\Delta T$ = 6K).
Fig. 2. $\chi m T$ vs. $T$ plots for 1 (□), 2 (○), and 3 (△ on heating, ▲ on cooling).

To investigate the phase transition behavior of 1-3, a differential scanning calorimetry (DSC) measurement was conducted in a wide range of temperature as illustrated in Table 1. In case of 2, two endothermic peaks at 249 K ($\Delta H = 42$ kJ mol$^{-1}$), 424 K ($\Delta H = 6$ kJ mol$^{-1}$) on heating process and two exothermic peaks at 410K ($\Delta H = -33$ kJ mol$^{-1}$), 242K ($\Delta H = -13$ kJ mol$^{-1}$) on cooling process were observed, respectively corresponding not only to a crystal-mesophase transition at 249K and a mesophase-liquid transition at 424 K on heating but also to a reversible mode of that at 410K and 242K on cooling mode. This DSC cycle indicates that 2 shows phase transition in temperature range from crystal to liquid crystal reversibly.

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<th>Compound</th>
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<tr>
<td></td>
<td>Cr-LQ</td>
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<tr>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>249</td>
</tr>
<tr>
<td>3</td>
<td>236</td>
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Cr is solid state, LQ is liquid state, and L is liquid state.

Interestingly, upon heating processes of 3, three endothermic peaks were observed at 236K, 351K and 454K. The first peak at 236K ($\Delta H = 32$ kJ mol$^{-1}$) refers to a crystal-mesophase transition and the second peak at 351K ($\Delta H = 172$ kJ mol$^{-1}$) is assigned to a mesophase-mesophase transition, finally the
third peak at 454K is indicative of the mesophase-liquid transition, respectively. On cooling mode, the reversible exothermic transition phases from mesophase to crystal for 3 are also observed at 421K, 334K, and 229K, respectively. However, 1 did not give any intriguing phase transition according to temperature change.

Fig.3 demonstrates the phase transition of 3 measured by hot-stage polarized optical microscopy (POM) at different temperatures. These textures are suggestive of the indirect information on phase transition of 3 as function of temperature. Although the identification of the liquid crystal phase based on the texture by POM is not possible, nevertheless, it is useful for comparison with DSC results. Fig. 3(a) shows a solid crystalline state like chestnut burr forms at 203K. Upon the increase of temperature under polarized light, the texture reveals two species of mesomorphism images not only with the relatively high-order anisotropic structure of molecules at 293K but also with somewhat disordered molecular arrangement at 423K due to thermotropic crystal phase change. With further heating, the compound displays an isotropic fluid-like flow behavior with conventional liquid phase at 469K. In addition, the compound 2 also showed a crystal phase at 213K, a mesophase at 298K, and liquid phase at 424 K, respectively.

Fig. 3. Optical textures of 3 under crossed polarizers at (a) 203K, (b) 293K, (c) 423K, and (d) 469K.
Further detail investigations to confirm the mesophase of 2-3 were carried out with temperature-dependant powder X-ray diffraction measurements as illustrated in Fig. 4. As expected, the powder X-ray diffraction diffractograms at room temperature reveals a mesophase state of 2 and 3 in the range of low angle. According to the results, 2 displays three sharp reflections in the low angle region with $d$-spacing ratio 1:1/2:1/3. The first diffraction peak assumed to be (001) corresponding to a $d$-spacing of about 30.7Å. Reflections up to 3rd order of the (001) diffraction suggest clearly that the powder XRD pattern of 2 shows the characteristics of an ordered layered structure. At 298K, 3 also shows a sharp peak at $2\theta=5.5^\circ$ with $d$-spacing 16.1Å. On the other hand, at 450K the peak intensity at $2\theta = 2.8^\circ$ decreased dramatically and the peak at $2\theta = 5.5^\circ$ was almost disappeared which is in accordance with isotropic fluid phase.

**Conclusion**

In summary, three bzimpy iron(II) complexes, 1-3, involving the different number of branched long alkyl chains were synthesized and characterized with physical and optical analyses in detail. The iron(II) complex 1 showed gradual spin crossover behaviors from low spin to high spin state, while 2 retained only low spin state in the same condition. Interestingly, 3 displayed abrupt spin transition in temperature range from $T_{1/2}^\uparrow= 236K$ to $T_{1/2}^\downarrow= 230K$ with the thermal hysteresis loop about 6 K due to crystal-liquid crystal phase transition. The differential scanning calorimetric analysis of 3 revealed two species of liquid crystal phase transitions at 236K and 351K. Consequently, we found that the introduction of a branched alkyl chain to bzimpy iron(II) complex is capable of not only forming spin crossover phenomenon but also generating the cooperative effect on the spin crossover iron(II) complex, whereas these were influenced by the position of branched alkyl chain on the bzimpy
skeleton.

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