

## A Novel Al-Bridged Trinuclear Iron(II) Bis(imino)pyridyl Complex with Catalytic Ethylene Polymerization Behavior

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A self-assembled Al-bridged diiminopyridine-based ligand (**3**) was synthesized and characterized by FT-IR, ESI-MS and NMR spectroscopy. Electron spectral titrations were performed to confirm the formation of a novel trinuclear bis(imino)pyridyl iron(II) complex (**4**) upon addition of FeCl<sub>2</sub> into Al-bridged ligand **3** in methanol solution. Simultaneously, a typical bis(imino)pyridine-iron(II) complex (**2**) was synthesized and fully characterized. The X-ray crystal study of the iron(II) complex **2** disclosed a five-coordinate, distorted square-pyramidal structure with the tridentate N<sup>^</sup>N<sup>^</sup>N ligand and chlorides. The optimal molecular structure of **4** was obtained by means of molecular mechanics, which showed that each iron atom in the complex **4** is surrounded by two chlorides, a tridentate N<sup>^</sup>N<sup>^</sup>N ligand and one oxygen atom, supporting considerations about the possibility of six-coordinate geometry from MMAO or the ethylene access. A comparison of **4** with the reference **2** revealed a remarkable decrease of the catalytic activity and MMAO consumption (activity up to  $0.41 \times 10^3 \text{ kg mol}_{\text{Fe}}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ , Al/Fe = 650 for **4** and  $7.02 \times 10^3 \text{ kg mol}_{\text{Fe}}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ , Al/Fe = 1600 for **2**).

**Key Words** : Self-assembly, Trinuclear iron(II) bis(imino)pyridyl complex, Ethylene polymerization, Structure modeling

### Introduction

Iron(II) and cobalt(II) coordinated compounds with bis(imino)pyridine ligands are well-known as catalyst precursors for olefin polymerization due to the ease of preparation and handling to the use of low-cost metals with negligible environment impact.<sup>1,2</sup> Among these compounds, iron complexes showed higher polymerization activities (activated with MAO up to 20 000 kg PE/mol<sub>Fe</sub> h bar) than corresponding to cobalt analogous, in some cases as high as those of the most efficient metallocenes.<sup>1-3</sup> Another intriguing feature is the fruitful structure of the bis(imino)pyridine ligands, allowing a rich steric and electronic modularity. It has been found that by changing the number, size, nature, and regiochemistry of substituents on the arylimino groups, the precatalysts can not only convert ethylene either to  $\alpha$ -olefins or to high molecular weight polyethylene, but also control over catalytic activity, as well as on the structure of the resulting products when activated with MAO.<sup>4</sup>

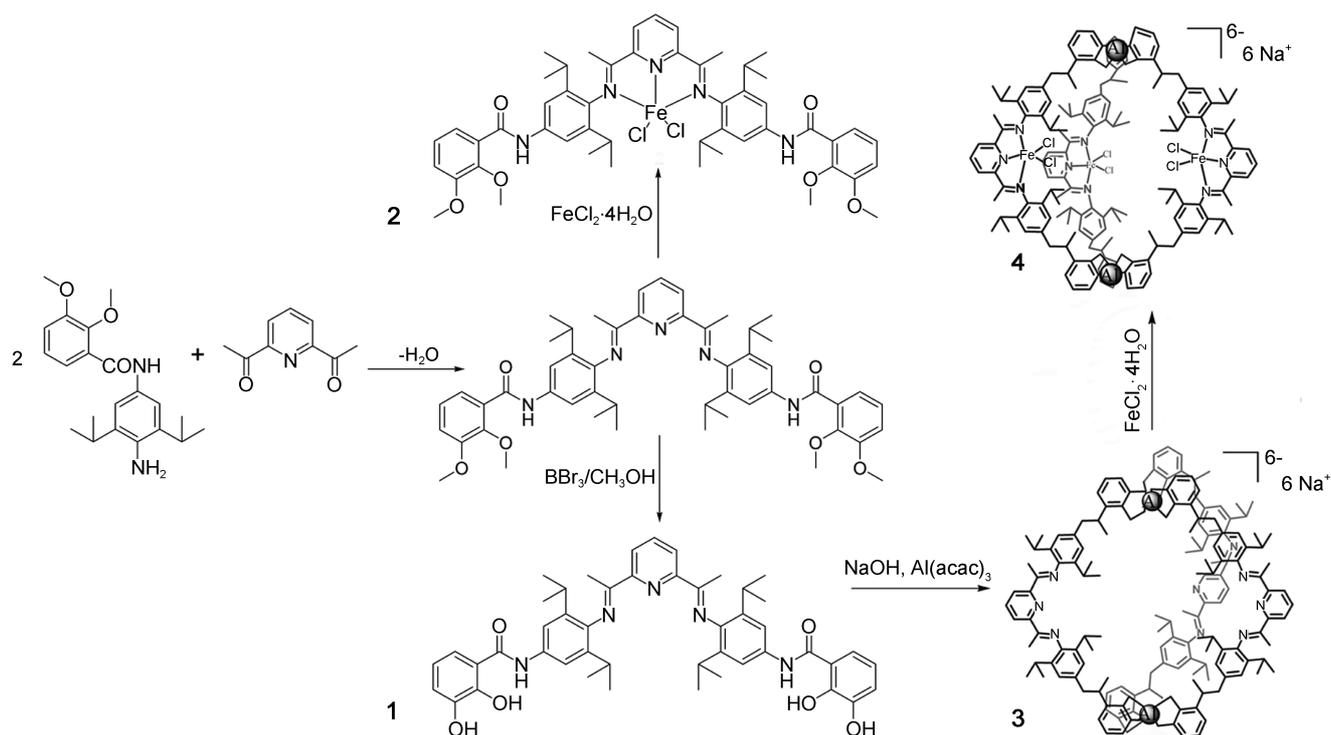
These structurally simple small molecules displayed most effective catalytic activities in homogeneous ethylene polymerization, which act by binding ethylene to the reaction site under activation with MAO or MMAO.<sup>5</sup> In contrast, enzymes are much larger and more complex; however, they can drive the substrates into orientations favoring specific reaction paths through multiple interactions in elaborate structure.<sup>6</sup> Therefore it attracts special attention to emulate these enzymes to build functionalized molecules capable of

catalyzing the polymerization reactions in a specific way to attain specified products.<sup>7,8</sup> Recently, considerable interest has been focused on combined catalytic systems in general chemical processes, and extensive investigations have also been drawn into their use in ethylene reactivity.<sup>9</sup> Respect to the preference toward iron and cobalt catalysts for use in ethylene reaction, the most common model in building the combined catalytic systems is by coupling multi-bis(imino)pyridyl or -(imino)pyridyl metal (iron or cobalt) moieties into a molecule,<sup>8,10,11</sup> based on expectations that their catalytic behavior may significantly differ from those simple derivatives.

In this paper, a self-assembly of Al<sup>3+</sup> with catecholate ligand in solution is obtained as similar as those reported.<sup>12-16</sup> Thus, the aluminum-bridged polymer is now readily accessible (Scheme 1) and whose spatial and electronic properties can be fine-tuned because of its unique structural features. In view of introducing bis(imino)pyridyl groups into the catecholate ligand, led us to consider the possibility of functionalizing late transition metal (such as iron) complex, resulting in multinuclear catalytic system in ethylene polymerization.

### Results and Discussion

**Synthesis.** Synthetic Procedure of the title complex was listed in Scheme 1. The starting material 2,6-diisopropyl-4-(2,3-dimethoxybenzoylamide)aniline was prepared from *N*-tosyl-2,6-diisopropyl-4-(2,3-dimethoxybenzoylamide)-

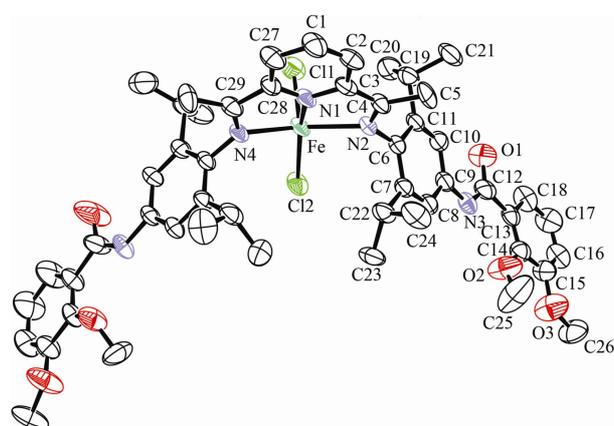


**Scheme 1.** Synthetic procedure of the title complex. Part of oxygen and nitrogen atoms is omitted for clarity in the complex **3** and **4**.

aniline by deprotection with sulfuric acid.<sup>17</sup> The ligand 2,6-bis[*N,N'*-bis(2,6-diisopropyl-4-(2,3-dimethoxybenzoylamide)phenylimino)]pyridine has been prepared by the condensation of 2.2 equiv of 2,6-diisopropyl-4-(2,3-dimethoxybenzoylamide)aniline with 1.0 equiv of 2,6-diacetylpyridine in refluxing methanol and in the presence a catalytic amount of trifluoroacetic acid. The free ligand is isolated as yellow solids in high yield (*ca.* 69%) after 48 h. The 2,6-bis[*N,N'*-bis(2,6-diisopropyl-4-(2,3-dihydroxybenzoylamide)phenylimino)]pyridine ligand (**1**) has been readily synthesized by demethylation and protonation of the ligand 2,6-bis[*N,N'*-bis(2,6-diisopropyl-4-(2,3-dimethoxybenzoylamide)phenylimino)]pyridine with an excess of  $\text{BBr}_3$  and methanol, respectively. The precatalyst **2** has been prepared by reaction of equimolar  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  with 2,6-bis[*N,N'*-bis(2,6-diisopropyl-4-(2,3-dimethoxybenzoylamide)phenylimino)]pyridine in freshly distilled methanol at room temperature, and is isolated as air-stably green solids in moderate yield. The aluminum-bridged polymer (**3**) is formed by a self-assembly of **1** and  $\text{Al}(\text{acac})_3$  dissolved in basic methanol solution. Degassed  $\text{Et}_2\text{O}$  was added to the above-mentioned solution and a dark-yellow solid was obtained with a moderate yield (*ca.* 40%). The trinuclear bis(imino)pyridyl iron(II) complex (**4**) has been synthesized by reaction of 3.0 equiv of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  with **3** in freshly distilled THF at room temperature, and is isolated as air-stably dark-blue solids in high yield (*ca.* 90%).

The crystals of **2** were grown by slow diffusion of  $\text{Et}_2\text{O}$  into its dichloromethane-methanol solution under nitrogen atmosphere at room temperature. The 2,6-bis[*N,N'*-bis(2,6-diisopropyl-4-(2,3-dimethoxybenzoylamide)phenylimino)]-

pyridyliron(II) chloride shows an approximate  $C_s$  symmetry about the plane defined by the iron atom, the two Cl atoms, and the pyridyl nitrogen atom (Fig. 1). The geometry around the iron center can be described as a distorted square pyramid ( $\tau$  value 0.16)<sup>20</sup> by apical Cl1 atom and with basal a tridentate  $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}$  ligand and the other chloride. The basal atoms are co-planar to within 0.004 Å, the central iron atom deviating from this plane *ca.* 0.58 Å. The Fe–N distances are between 2.06–2.23 Å, of which the Fe–N(pyridyl) bond is

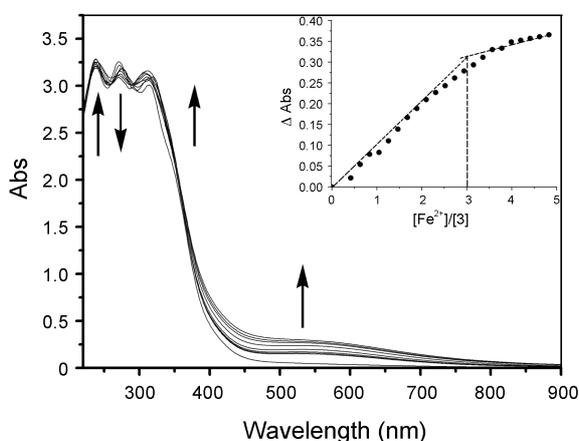


**Figure 1.** The molecular structure of **2**. Hydrogen atoms and the crystalline water molecules are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Fe–N1 2.062(5), Fe–N2 2.206(5), Fe–N4 2.226(5), Fe–Cl1 2.289(2), Fe–Cl2 2.246(2), C4–N2 1.278(8), C29–N4 1.287(8), N1–Fe–N2 73.0(2), N1–Fe–N4 73.3(2), N2–Fe–N4 139.6(2), N1–Fe–Cl1 95.04(17), N1–Fe–Cl2 149.05(17), N2–Fe–Cl2 98.07(14), N2–Fe–Cl1 102.79(15), N4–Fe–Cl1 101.79(15), N4–Fe–Cl2 99.40(16), Cl2–Fe–Cl1 115.91(10).

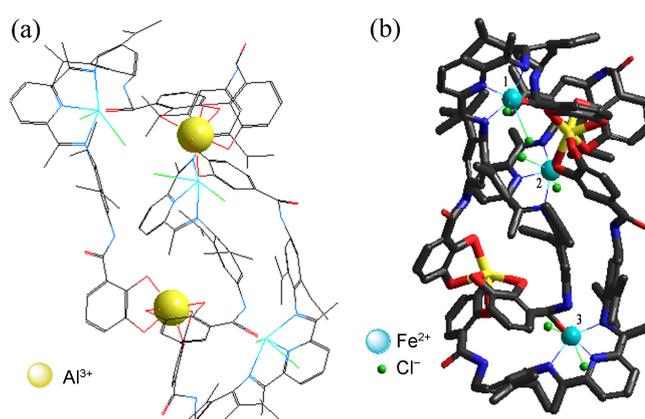


(a), a typical shift for hydroxyl protons at aryl rings. In DMSO- $d_6$ , the desired complex **3** is present: signal absence of the hydroxyl protons in catechol units and a low-field shift of NH signal over 0.5 ppm to  $\delta$  (ppm) = 12.80-13.18 ppm, respectively (Fig. 3(b)). It is also observed that the methyl and aromatic protons (3 and 6) shift to low-field more than 0.5 ppm by line broadening of their  $^1\text{H}$  NMR signals. Furthermore the aryl ring proton peaks 8-10 shifted to high-field over 1.0 ppm because of the increase of electron density by the coordinated cations in the catechol units. Specifically, the chemical shifts of the methyl protons (5) are changed in the region of  $\delta$  (ppm) = 0.27-1.34, each peak of which corresponds to a different environment. As a result,  $\text{Al}^{3+}$  binding is accompanied by large in specific imino, aromatic and methyl proton chemical shifts, indicating that a locally distorted structure forms.

The iron(II) binding properties were usually determined by UV-vis spectroscopy for its paramagnetism and the poor solubility in common solvents used for NMR spectroscopy.<sup>22</sup> The absorption spectra of **3** and its corresponding iron(II) complex are reported in Figure 4. These absorption bands at 239, 272 and 305 nm were assigned to the LC  $\pi$ - $\pi^*$  transitions of the free ligand **3** in methanol. With the addition of iron(II) chloride, a new absorption band was found at 545 nm in the visible region which was attributed to metal-to-ligand charge-transfer (MLCT). At the same time, the methanol solution of **3** was observed to change color from light yellow into dark blue. The result indicated that a rapid reaction was carried out between ferrous ions with the ligand **3**. Furthermore electron spectral titrations disclosed the course of the iron complex formation (Fig. 4). In contrast to the progressive shift of the absorbance bands upon adding small amounts of  $\text{Fe}^{2+}$ , it appears to have two fixed isosbestic wavelengths in the range of 250-350 nm at higher iron concentrations, which suggested the presence of two mainly absorbing species in solution relating the partial coordination case to the fully coordinated case. Moreover



**Figure 4.** UV-vis spectrum revealing the formation of the iron(II) complexed aluminum polymer of **3** ( $4.3 \times 10^{-5}$  mol  $\text{L}^{-1}$ ) upon increasing addition of  $\text{Fe}^{2+}$  in methanol. The inset shows the change in the absorption band at  $\lambda = 545$  nm as a function of  $\text{Fe}(\text{II})$ : **3** and a break at 3 represents **4** formation.



**Figure 5.** Optimized molecule of **4** as obtained by molecular mechanics MM+ force field, H atoms have been omitted for clarity. (a) A distorted helical structure constructed by the six-coordinate  $\text{Al}^{3+}$  self-assembly; (b) The oxygen atoms are assumed as the  $\text{Fe}^{2+}$  cofactor from five-coordinate to six-coordinate upon formation of the trinuclear complex.

the plot given in Figure 4 (inset) represented the variation of the ratio of  $[\text{Fe}^{2+}]/[\mathbf{3}]$  versus absorption intensity at 545 nm, which revealed a break at 3 as expected for the formation of the 3:1 metal-ligand complex of type  $[\text{Fe}_3\text{Cl}_6\mathbf{3}]^{6-}$ .

**Structure Modeling for 4.** The MM+ force field was specifically developed for variety of organic compounds, which is an extension of the MM2 method and is critical for the accurate simulation of molecules including heavy atoms.<sup>23</sup> Therefore a 3D complex **4** model was built in a MM+ force field using atomic charges and geometrical optimization, implemented in the HYPERCHEM software package. The molecular structure corresponding to the minimum potential energy was determined by the conjugate gradient algorithm following the Polak-Ribiere method.<sup>24</sup> From IR and  $^1\text{H}$  NMR spectrum, it was known that two Al atom forms individually a five-membered chelate ring with each **1** (Fig. 5(a)). The optimized model was shown in Figure 5 which corresponded to the lowest energy ( $-1896$  kcal/mol) with a distorted helical structure. Furthermore the imine and carbonyl group showed rather remarkable bathochromic shift (*ca.*  $17$   $\text{cm}^{-1}$ ) in the complex **4** which may be attributed to coordination interaction between  $\text{Fe}(\text{II})$  atoms and the imine and carbonyl oxygen atoms. In Figure 5(b), the oxygen atoms of the carbonyl group is rather close to Fe (1) and Fe (3), as well as the one of the catechol oxygen atoms to Fe (2), which seems to accept one lone pair electron coordinating from oxygen atoms. As a result, the coordination number for  $\text{Fe}^{2+}$  may increase up to six where one oxygen and two chlorides bind the  $\text{Fe}^{2+}$  ion on the other side of a tridentate  $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}$  ligand to complete the octahedral complex. So, vacant coordination site may also be the actual catalytic site.<sup>22</sup>

**Ethylene Polymerization.** Treatment of iron(II) complex **2** and **4** with modified methylaluminoxane (MMAO) reagent led to the formation of catalytically active species for the ethylene polymerization. Table 2 is listed individually the highest activities of the complex **2** and **4** under the tested conditions. The higher yields were obtained with 1  $\mu\text{mol}$  of

**Table 2.** Results of ethylene polymerization by iron catalysts activated with MMAO<sup>a</sup>

Catalyst	Usage ( $\mu\text{mol}$ )	Al/Fe (mol/mol)	Time (min)	Temp ( $^{\circ}\text{C}$ )	Yield (g)	Activity <sup>b</sup>
<b>2</b>	1	1600	15	15	1.81	7.02
<b>4</b>	1	650	15	15	0.31	0.41

<sup>a</sup>Conditions: ethylene of 1 bar; co-catalyst: MMAO, 1.84 mol/L; solvent: 30 mL toluene. <sup>b</sup>Polymers ( $10^3 \text{ kg mol}_{\text{Fe}}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ ).

**2** ( $1.81 \text{ g}$ ,  $7.02 \times 10^3 \text{ kg mol}_{\text{Fe}}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ ) than that of **4** ( $0.31 \text{ g}$ ,  $0.41 \times 10^3 \text{ kg mol}_{\text{Fe}}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ ) at  $15 \text{ }^{\circ}\text{C}$  after 15 min upon treatment with an adequate of MMAO at 1 bar ethylene pressure. In fact, the complex **4** is composed of three identical parts, and each part is similar to its mother analogue **2**. However, the multi-polymeric iron(II) complex **4** showed a rather low activity and MMAO usage for each active iron in the polymerization process. The result showed that the iron atom located in complex **4** may adopt 6-coordinated model reducing labile or vacant sites for MMAO or ethylene access.<sup>22</sup>

### Conclusion

The Al-bridged trinuclear bis(imino)pyridyl iron(II) complex **4** was synthesized in a conventional reaction pathway. The key precursor **3** was obtained in moderate yield and the coordination of iron(II) chloride proceeded almost quantitatively. Microanalysis and mass spectrometry provided evidence of the formation of the Al-bridged ligand in the three step synthesis starting from 2,6-diisopropyl-4-(2,3-dimethoxybenzoylamide)aniline. The structure modeling analysis of **4** has been carried out in a MM+ force field to get the optimal conformation with the lowest energy since its single crystal is not available. Simultaneously, the complex **4** has been characterized by IR and UV-vis spectroscopy, which confirmed the coordination interaction of  $\text{Fe}^{2+}$  with the tridentate N<sup>^</sup>N<sup>^</sup>N ligand. Moreover the result indicates that part of oxygen atoms from the carbonyl groups and catechol took part in the coordination to iron as well. The polymerization experiments show that the oxygen introduced into the coordinate structure can prevent the activation of iron center, resulting in low catalytic activity.

### Experimental

All manipulations of water and/or moisture sensitive compounds were performed by means of standard high-vacuum Schlenk techniques under a  $\text{N}_2$  atmosphere. The NMR spectra of the intermediates and ligand were recorded on a Mercury plus-400 spectrometer at ambient temperature. Elementary analyses were performed on a VarioEL instrument from Elementar Analysensysteme GmbH. FT-IR spectra were measured with an HP5890II GC/NEXUS870. ESI-MS measurements were carried out with a Waters ZQ-4000 instrument (Waters, Manchester, UK). Electronic absorption spectra were performed on an HP-8453 diode array spectrophotometer. Solvents were refluxed over an appropriate drying agent and distilled under nitrogen prior to use. Modified methylaluminumoxane (MMAO) (7% aluminum in heptanes

solution) was purchased from Akzo Nobel Chemical Inc. All other chemicals were purchased from commercial resources and used without further purification.

**General.** Polymerization was carried out in a 100 mL Schlenk flask equipped with a magnetic stirrer. The flask was repeatedly evacuated and refilled with nitrogen and finally filled with ethylene gas (1 bar). MMAO and toluene were added *via* a gastight syringe. The catalyst, dissolved in toluene under a dry nitrogen atmosphere, was transferred into the Schlenk flask to initiate the polymerization. The polymerization was carried out with 1  $\mu\text{mol}$  of iron complex **2** or **4** and quenched with methanol containing 10% (v/v) hydrochloric acid. The resulted polyethylene was isolated by filtration washed with methanol, and dried in a vacuum oven at  $50 \text{ }^{\circ}\text{C}$ .

**Synthesis of 2,6-Diisopropyl-4-(2,3-dimethoxybenzoylamide)aniline.** *N*-Tosyl-2,6-diisopropyl-4-(2,3-dimethoxybenzoylamide)aniline ( $1.48 \text{ g}$ ,  $2.91 \text{ mmol}$ ) was added to a solution of  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  (95:5) and the mixture was cooled at  $0 \text{ }^{\circ}\text{C}$  for 2 h. Then the mixture was stirred at rt for 12 h. After this time the brown solution was poured onto ice and the mixture made basic by the addition of NaOH pellets. The solution was extracted into dichloromethane and dried over anhydrous  $\text{MgSO}_4$  before removal of the solvent under reduced pressure yielding a light yellow oil which was dried under high vacuum for 2 h. And a yellow solid was obtained ( $0.79 \text{ g}$ , 76%). mp  $42\text{--}43 \text{ }^{\circ}\text{C}$ ; IR (KBr,  $\text{cm}^{-1}$ ): 3319 ( $\text{--NH}_2$ , N-HCO), 1673 (C=O), 1580 and 1545 (N-H<sub>brend</sub>). <sup>1</sup>H NMR ( $\text{CDCl}_3/400 \text{ MHz}$ ): 1.29 (d,  $J = 7.2 \text{ Hz}$ , 12H, CH-CH<sub>3</sub>); 2.96 (m,  $J = 6.8 \text{ Hz}$ , 2H, CH-Me); 3.69 (s, 2H, Ar-NH<sub>2</sub>); 3.93 and 3.98 (s, 6H, O-CH<sub>3</sub>); 7.08 (d, 1H,  $J = 7.6 \text{ Hz}$ , Ar-H); 7.20 (t,  $J = 7.6 \text{ Hz}$ , 1H, Ar-H); 7.37 (s, 2H, Ar-H); 7.79 (d,  $J = 8.8 \text{ Hz}$ , 1H, Ar-H); 9.80 (s, 1H, CO-NH). <sup>13</sup>C NMR ( $\text{CDCl}_3/400 \text{ MHz}$ ): 22.30 (CH-CH<sub>3</sub>); 27.98 (CH-Me); 56.01–61.61 (O-CH<sub>3</sub>); 115.18 (Ar-C); 115.61 (Ar-C); 122.75 (COAr-C); 124.63 (Ar-Cc); 127.32 (Ar-C); 129.90 (NHAr-C); 133.05 (CHAr-C); 137.11 (NH<sub>2</sub>Ar-C); 146.99 and 152.51 (OAr-C); 162.41 (NHCO). ESI-MS:  $m/z$  357.4 [M+H]<sup>+</sup>. Anal. Calc. for  $\text{C}_{21}\text{H}_{28}\text{N}_2\text{O}_3$ : (cal) C, 70.76; H, 7.92; N, 7.86; (Found) C, 70.62; H, 7.89; N, 7.86.

**Synthesis of 2,6-Bis[*N,N'*-bis(2,6-diisopropyl-4-(2,3-dimethoxybenzoylamide)phenylimino)]pyridine.** 2,6-Diisopropyl-4-(2,3-dimethoxybenzoylamide)aniline ( $1.57 \text{ g}$ ,  $4.4 \text{ mmol}$ ) was added to a solution of 2,6-diacetylpyridine ( $0.34 \text{ g}$ ,  $2.1 \text{ mmol}$ ) with a catalytic amount of trifluoroacetic acid ( $0.2 \text{ mL}$ ) in tetraethyl silicate ( $1 \text{ mL}$ )/methanol ( $5 \text{ mL}$ ) under nitrogen atmosphere. The mixture was refluxed for 24 h under nitrogen until no reactant 2,6-diacetylpyridine remained. The solvents were evaporated under reduced pressure and the yellow solid was subsequently purified by

column chromatography on silica gel with light petroleum ether/EtOAc (4:1) as the eluent. The yellow solid thus obtained was recrystallized by dichloromethane/light petroleum ether (1:5) to give a yellow solid (1.21 g, 69%). mp 182–183 °C. IR (KBr,  $\text{cm}^{-1}$ ): 3364 (N-HCO, m), 1676 (C=O, C=N, s), 1593 and 1582 (N-H<sub>brend</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>/400 MHz, ppm): 1.21 (d,  $J = 6.8$  Hz, 24H, CH-CH<sub>3</sub>), 2.30 (s, 6H, N=CCH<sub>3</sub>), 2.80 (m,  $J = 6.8$  Hz, 4H, CH-Me), 3.95 and 4.03 (s, 12H, O-CH<sub>3</sub>), 7.10 (d,  $J = 7.6$  Hz, 2H, Ar-H), 7.23 (t,  $J = 7.6$  Hz, 2H, Ar-H), 7.52 (s, 4H, Ar-H), 7.82 (d,  $J = 8.6$  Hz, 2H, Ar-H), 7.94 (t,  $J = 7.6$  Hz, 1H, Py-H), 8.50 (d,  $J = 8.8$  Hz, 2H, Py-H), 9.97 (s, 2H, CO-NH). <sup>13</sup>C NMR (CDCl<sub>3</sub>/400 MHz): 17.16 (N=CCH<sub>3</sub>), 22.75 and 22.11 (CH-CH<sub>3</sub>), 28.43 (CH-Me), 56.09 and 61.73 (O-CH<sub>3</sub>), 115.42 (Ar-C), 122.19 (Ar-C), 122.88 (Ar-C), 124.71 (Ar-C), 127.24 (Ar-C), 134.43 (Py-C), 136.61 (Py-C, Ar-C), 136.82 (Ar-C), 143.14 (Ar-C), 147.15 (Ar-C), 152.59 (Ar-C), 155.09 (Py-C), 162.72 (N=C), 167.61 (C=O). ESI-MS:  $m/z$  840.7 [M+H]<sup>+</sup>. Anal. Calc. for C<sub>51</sub>H<sub>61</sub>N<sub>5</sub>O<sub>6</sub>: N, 8.34; C, 72.92; H, 7.32. Found: N, 8.29; C, 73.20; H, 7.39%.

**Synthesis of 2,6-Bis[*N,N'*-bis(2,6-diisopropyl-4-(2,3-dihydroxybenzoylamide)phenylimino)]pyridine (1).** BBr<sub>3</sub> (3.5 mL, 29 mmol) was added dropwise through a syringe to a stirring solution of 2,6-bis[*N,N'*-bis(2,6-diisopropyl-4-(2,3-dimethoxybenzoylamide)phenylimino)]pyridine (0.2 g, 0.24 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (4 mL), at 0 °C and under N<sub>2</sub>. The resulting white-yellow suspension was allowed to stir during 2 d at rt. Then to the reaction mixture, CH<sub>3</sub>OH (5 mL) was added at 0 °C and the clear solution was stirred at rt for 1 h. Upon repeated addition and evaporation of CH<sub>3</sub>OH (4 × 10 mL) to remove the borate ester, the product was dissolved in CH<sub>3</sub>OH, precipitated with Et<sub>2</sub>O and collected by filtration. The final product was dried under vacuum, which is yellow powder (0.094 g, 50%). mp 186–188 °C. IR (KBr,  $\text{cm}^{-1}$ ): 3390 (OH-Ar and N-HCO, broad), 1650 (C=O, C=N, s), 1591 (N-H<sub>brend</sub>). <sup>1</sup>H NMR (DMSO/400 MHz, ppm): 1.08 and 1.18 (m, 24H, CH-CH<sub>3</sub>), 2.47 and 2.71 (s, 6H, C=N-CH<sub>3</sub>), 3.13 (t, 4H, CH-Me), 3.71 (s, 4H, Ar-OH), 6.73 (t,  $J = 8.0$  Hz, 2H, Ar-H), 6.94 (d,  $J = 7.6$  Hz, 2H, Ar-H), 7.38 and 7.46 (d, 2H,  $J = 8.0$  Hz, Py-H), 7.53 and 7.62 (s, 4H, Ar-H), 8.12 (t,  $J = 7.6$  Hz, 1H, Py-H), 8.45 (s,  $J = 8.0$  Hz, 2H, Ar-H), 10.22 and 10.30 (s, 2H, CONH<sub>2</sub>). <sup>13</sup>C NMR (DMSO/400 MHz): 22.55, 22.96 and 23.53 (CH-CH<sub>3</sub>), 23.53 (CH-CH<sub>3</sub>), 25.49 and 27.93 (N-CH<sub>3</sub>), 27.27 (CH-Me), 116.65 (Ar-C), 116.99 (Ar-C), 117.06 (Ar-C), 118.29 (Ar-C), 118.42 (Ar-C), 118.99 (Py-C), 139.03 (Py-C), 152.18 (Py-C), 167.84 (C=N), 142.03 (Ar-C), 148.19 (Ar-C). ESI-MS:  $m/z$  784.8 [M+H]<sup>+</sup>. Anal. Calc. for C<sub>47</sub>H<sub>53</sub>N<sub>5</sub>O<sub>6</sub>: N, 8.93; C, 72.01; H, 6.81 Found: N, 8.59; C, 72.20; H, 7.29%.

**Synthesis of 2,6-Bis[*N,N'*-bis(2,6-diisopropyl-4-(2,3-dimethoxybenzoylamide)phenylimino)]pyridyl iron(II) chloride (2).** A mixture of FeCl<sub>2</sub>·4H<sub>2</sub>O (0.059 g, 0.30 mmol) with 2,6-bis[*N,N'*-bis(2,6-diisopropyl-4-(2,3-dimethoxybenzoylamide)phenylimino)]pyridine (0.16 g, 0.2 mmol) in freshly distilled methanol (5 mL) was stirred at rt for 24 h. The dark green precipitate formed was filtered and washed

with methanol (2 × 2 mL) and freshly distilled diethyl ether (2 × 5 mL). After dried in vacuum, the iron(II) complex **2** was obtained as a green powder (yield: 0.13 g, 70%). mp > 300 °C. IR (KBr,  $\text{cm}^{-1}$ ): 3312 (N-HCO, w), 1668 (C=O, C=N, s), 1597 and 1579 (N-H<sub>brend</sub>). ESI-MS:  $m/z$  448.3 [M-2Cl]<sup>2+</sup>. Anal. Calc. for C<sub>51</sub>H<sub>61</sub>Cl<sub>2</sub>FeN<sub>5</sub>O<sub>6</sub>·1.2CH<sub>2</sub>Cl<sub>2</sub>: N, 6.55; C, 58.66; H, 5.98. Found: N, 6.25; C, 58.42; H, 6.37%.

**Synthesis of 3.** A Schlenk flask was filled with methanol (5 mL) and degassed under N<sub>2</sub>, compound **1** (50 mg, 0.06 mmol) and Al(acac)<sub>3</sub> (8.3 mg, 0.04 mmol) were added. The suspended solids were sonicated for a few minutes to break up the aggregates. NaOH (3.2 mg, 0.08 mmol) was added as a small solid pellet, and the suspension slowly dissolved to form a light brownish-yellow solution. After the reaction was stirred for 24 h, the solvent was partially removed under vacuum until a dark yellow precipitate began to appear. Degassed Et<sub>2</sub>O (10 mL) was added to precipitate more product. The amorphous solid was collected *via* filtration through a glass frit under a stream of nitrogen through the solid residue on the frit for a few minutes and placing the product (20.7 mg, 41%) in a desiccator under vacuum. <sup>1</sup>H NMR (DMSO/400 MHz, ppm): 0.27–1.34 (m, 72H, CH-CH<sub>3</sub>), 1.92–2.20 (m, 18H, N-CH<sub>3</sub>), 2.66 (s, 12H, CH-Me), 6.08–6.58 (m, 18H, Ar-H), 6.87–7.45 (m, 6H, Py-H), 8.00 (s, 3H, Py-H), 8.27–8.57 (d, 12H, Ar-H), 12.80–13.18 (s, 6H, CONH). IR (KBr,  $\text{cm}^{-1}$ ): 3418 (N-HCO), 1638 (C=O, C=N, s), 1594 (N-H<sub>brend</sub>). ESI-MS spectrum of Na<sub>6</sub>[Al<sub>2</sub>I<sub>3</sub>] in CH<sub>3</sub>CN. Three different charge states of the cluster are visible: 2- for  $m/z = 1209.54$  {NaH<sub>3</sub>[Al<sub>2</sub>I<sub>3</sub>]}<sup>2-</sup> and  $m/z = 1198.55$  {H<sub>4</sub>[Al<sub>2</sub>I<sub>3</sub>]}<sup>2-</sup>, and 3- for  $m/z = 806.49$  {NaH<sub>2</sub>[Al<sub>2</sub>I<sub>3</sub>]}<sup>3-</sup>. Anal. Calc. for C<sub>141</sub>H<sub>147</sub>Al<sub>2</sub>N<sub>15</sub>Na<sub>6</sub>O<sub>18</sub>: N, 8.30; C, 66.89; H, 5.85. Found: N, 8.25; C, 67.30; H, 6.26%.

**Synthesis of 4.** A mixture of FeCl<sub>2</sub>·4H<sub>2</sub>O (38.8 mg, 0.20 mmol) with **3** (169.6 mg, 0.067 mmol) in freshly distilled THF (6 mL) was stirred at room temperature for 24 hr and degassed under N<sub>2</sub>. The dark precipitate formed was filtered and washed with THF (2 × 2 mL) and freshly distilled Et<sub>2</sub>O (2 × 5 mL), respectively. Then the product was dried in vacuum. The iron(II) complex was obtained as a dark-blue powder (yield: 175.6 mg, 90%). mp > 300 °C. IR (KBr,  $\text{cm}^{-1}$ ): 3443 (N-HCO), 1621 (C=O, C=N, s), 1591 (N-H<sub>brend</sub>). Anal. Calc. for C<sub>141</sub>H<sub>147</sub>Al<sub>2</sub>Cl<sub>6</sub>Fe<sub>3</sub>N<sub>15</sub>Na<sub>6</sub>O<sub>18</sub>: N, 7.22; C, 58.16; H, 5.09. Found: N, 6.85; C, 58.38; H, 5.14%.

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**Appendix A. Supplementary Material.** CCDC 820691 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data\_request/cif.

## References

1. Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem. Int. Ed.* **1999**, *38*, 428.

2. Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.
  3. Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745.
  4. Britovsek, G. J. P.; Mastroianni, S.; Solan, G. A.; Baugh, S. P. D.; Redshaw, C.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; Elsegood, M. R. *J. Chem. Eur. J.* **2006**, *6*, 2221.
  5. Yoshizawa, M.; Tamura, M.; Fujita, M. *Science* **2006**, *312*, 251.
  6. Abraham, S.; Ha, C.-S.; Kim, I. *Macromol. Rapid Commun.* **2006**, *27*, 1386.
  7. Liu, J.; Li, Y.; Liu, J.; Li, Z. *Macromolecules* **2005**, *38*, 2559.
  8. Wasilke, J.-C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001.
  9. Zhang, S.; Vystorop, I.; Tang, Z.; Sun, W.-H. *Organometallics* **2007**, *26*, 2456.
  10. Barbaro, P.; Bianchini, C.; Giambastiani, G.; Rios, I. G.; Meli, A.; Oberhauser, W.; Segarra, A. M.; Sorace, L.; Toti, A. *Organometallics* **2007**, *26*, 4639.
  11. Meyer, M.; Kersting, B.; Powers, R. E.; Raymond, K. N. *Inorg. Chem.* **1997**, *36*, 5179.
  12. (a) Kersting, B.; Meyer, M.; Powers, R. E.; Raymond, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 7221. (b) Hou, Z.; Sunderland, C. J.; Nishio, T.; Raymond, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 5148.
  13. (a) Enemark, E. J.; Stack, T. D. P. *Inorg. Chem.* **1996**, *35*, 2719. (b) Enemark, E. J.; Stack, T. D. P. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 996.
  14. Albrecht, M.; Mirtschin, S.; de Groot, M.; Janser, I.; Runsink, J.; Raabe, G.; Kogej, M.; Schalley, C. A.; Froehlich, R. *J. Am. Chem. Soc.* **2005**, *127*, 10371.
  15. Haino, T.; Shio, H.; Takano, R.; Fukazawa, Y. *Chem. Commun.* **2009**, 2481.
  16. Long, Z.; Yang, P.; Xia, Y.; Yang, Z.; Wu, B. *Tetra. Lett.* **2009**, *50*, 1820.
  17. Carver, F. J.; Hunter, C. A.; Livingstone, D. J.; McCabe, J. F.; Seward, E. M. *Chem. Eur. J.* **2002**, *8*, 2848.
  18. Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc. Dalton Trans.* **1984**, 1349.
  19. Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Strömberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728.
  20. Seitz, M.; Milius, W.; Alt, H. G. *J. Mol. Cat A: Chem.* **2007**, *261*, 246.
  21. García-Cuesta, M. C.; Lozano, A. M.; Meléndez-Martínez, J. J.; Luna-Giles, F.; Ortiz, A. L.; González-Méndez, L. M.; Cumbreira, F. L. *J. Appl. Cryst.* **2004**, *37*, 993.
  22. Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8576.
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