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Synthesis, characterization and ethylene polymerization behavior of binuclear iron complexes bearing *N*,*N*'-bis(1-(6-(1-(arylimino)ethyl) pyridin-2-yl)ethylidene)benzidines[†]

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A series of *N*,*N*'-bis(1-(6-(1-(arylimino)ethyl)pyridin-2-yl)ethylidene)benzidines and the bi-metallic iron complexes thereof have been synthesized and fully characterized. All iron complexes, when activated by MAO or MMAO, exhibited high activities of up to 1.3×10^7 g mol⁻¹ (Fe) h⁻¹ for the polymerization of ethylene. On comparison with their mononuclear counterparts, such bi-metallic complexes not only retain a relatively high activity at elevated temperatures (up to 70 °C), but also exhibit increased lifetimes. The polyethylenes obtained were characterized by GPC, DSC and high temperature NMR spectroscopy, which indicated multimodal and highly linear features.

Introduction

Highly active ethylene polymerization complex pre-catalysts based on 2,6-bis(imino)pyridyl metal complexes (metal = iron or cobalt),¹ which were found to possess activities higher than those observed for a-diimino-nickel (or palladium) complex pre-catalysts,² were a breakthrough in late transition metalbased pre-catalysts for polyolefin production. On comparison with commercial Ziegler-Natta3 or metallocene4 catalytic systems, late transition metal complex pre-catalysts display significant advantages⁵ such as ease of preparation, enhanced stability as well as the ability to finely tune the properties of the obtained polyethylene via simple modification of the ancillary ligands or by controlling the parameters of the catalytic reaction. The key in designing complex pre-catalysts is to develop heterocyclic compounds as suitable ligands,⁵⁻⁸ in which the bulky substituted bis(imino)pyridines enhance the catalytic behavior of their metal (Fe or Co) complexes.⁸ Moreover, synergistic effects have commonly been considered in multinuclear complexes, and in our laboratory and elsewhere,

binuclear complexes⁹⁻¹¹ as well as multi-nuclear complexes¹² have been studied.

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In the case of the most investigated complex pre-catalysts bearing 2,6-bis(imino)pyridine derivatives, positive synergic effects were observed for the bi-nuclear complex models A^{13a} and B^{13b} and the multinuclear complex C,^{12a} all of which displayed higher activity than did the corresponding mononuclear complexes.1 In addition, binuclear complexes bearing hybrid ligands of both bidentate and tridentate coordination, e.g. D^{13c} and E^{9a-c} were capable of both ethylene oligomerization and polymerization. In the course of pursuing binuclear complex pre-catalysts,¹⁴ we found that the tetramethylbenzidine-based metal complex pre-catalysts (F) produced polyethylene of high molecular weight and narrow polydispersity,14a whilst the methyl-bridged dianiline derived dinuclear nickel pre-catalysts (G) generally provided both polyethylenes and oligomers.^{14b} The significant catalytic behavior exhibited by nickel complex precatalysts bearing ligands based on benzidines and methylbridged anilines inspired us to revisit the binuclear complexes bearing 2,6-bis(imino)pyridyl motifs connected via tetraalkylbenzidines H, which differ from the analog models A13a and B.13b Various bulky benzidines were designed and were used to synthesize complex pre-catalysts with better thermostability. Fortunately, the newly designed bi-metallic iron (π) complexes, when activated with MAO or MMAO, revealed high activities toward ethylene polymerization when operating at high temperatures of around 70 °C. Herein, the synthesis and characterization of the organic compounds and their metal complexes are reported, and the ethylene polymerization behavior is discussed.

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Results and discussion

Synthesis and characterization of the organic compounds and their iron complexes

Benzidine derivatives¹⁵ and 2-acetyl-6-aryliminopyridine¹⁶ were prepared according to the literature. The condensation reactions of the two aforementioned substances were conducted in toluene in the presence of a catalytic amount of 4-methylbenzenesulfinic acid to form the target compounds, N,N'-bis(1-(3-(1-aryliminoethyl)pyridin-2-yl)ethylidene)tetraalkylbenzidine derivatives (L1-L11, Scheme 2). The newly synthesized compounds were reacted with $iron(\pi)$ dichloride in methanol to form the corresponding binuclear iron complexes in good yields (Fe-1-Fe-11, Scheme 2). All compounds were consistent with their elemental analyses. The structures of the organic compounds were further confirmed by ¹H and ¹³C NMR spectroscopic measurements. The effective coordination to iron was reflected in the FT-IR spectra, where the C=N stretching vibration bands appeared in the range of 1620-1632 cm⁻¹ for iron complexes versus 1639–1650 cm⁻¹ for the ligands as free compounds. In addition, the structures of the iron complexes were also verified by MALDI-TOF measurements. Our attempts to obtain single-crystals of the iron complexes have thus far been unsuccessful; however the representative compound L5 was re-crystallized from a saturated dichloromethane solution.



Scheme 2 Synthetic procedure.



Scheme 1 Representative models of multinuclear and target complexes.

Fig. 1 ORTEP drawing of L5 with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

 Table 1
 The selected bond lengths (Å) and angles (°) for complexes L5

Bond length (Å)		Bond angle (°)			
N(2)-C(6) N(2)-C(20) N(1)-C(1) N(1)-C(5) N(3)-C(8) N(3)-C(10)	$\begin{array}{c} 1.267(5) \\ 1.432(5) \\ 1.327(5) \\ 1.336(5) \\ 1.268(6) \\ 1.427(6) \end{array}$	$\begin{array}{c} C(6)-N(2)C(20)\\ C(1)-N(1)-C(5)\\ C(8)-N(3)-C(10)\\ N(1)-C(1)-C(2)\\ N(1)-C(1)-C(8)\\ N(2)-C(20)-C(21)\\ N(2)-C(25)-C(20)\\ N(1)-C(5)-C(4)\\ N(1)-C(5)-C(6) \end{array}$	$121.3(4) \\119.1(4) \\122.2(4) \\121.6(4) \\117.7(4) \\120.0(4) \\119.2(4) \\122.0(4) \\116.1(4)$		

X-ray crystallographic studies

The molecular structure of L5 was confirmed by single crystal X-ray diffraction and is shown in Fig. 1; selected bond lengths and angles are collected in Table 1. It is clear that the bonds N(2)-C(6) and N(3)-C(8) are shorter than the bonds N(2)-C(20) and N(3)-C(10), each being consistent with double and single bond features, respectively. In addition, the bonds N(1)-C(1)

Table 2 Ethylene polymerization by Fe-4^a

and N(1)-C(5) are hybrids between double and single bonds due to the conjugated cyclic pyridine ring.

The molecular structure of **L5** reveals the co-planar nature of the two benzene rings within the tetraalkylbenzidine motif. However, the pyridyl plane is almost perpendicular to the phenyl plane of the benzidine with a dihedral angle of *ca.* 88.77°, whilst a similar dihedral angle between the pyridyl and phenyl of the aniline is observed at *ca.* 86.71°.

Catalytic behavior towards ethylene

According to previous publications,⁵ co-catalysts such as methylaluminoxane (MAO) or modified methylaluminoxane (MMAO) are commonly employed in combination with iron complex pre-catalysts. Therefore, complex **Fe-4** was used to optimize the suitable catalytic parameters in the presence of either methylaluminoxane (MAO) or modified methylaluminoxane (MMAO).

Optimizing polymerization parameters by complex Fe-4. The catalytic behavior of complex **Fe-4** was evaluated using different molar ratios of Fe/Al, differing ethylene pressures and over different reaction temperatures, in the presence of either MAO (entries 1–14, Table 2) or MMAO (entries 15–22, Table 2).

With the Al/Fe molar ratio fixed at 1000, the reaction temperature was varied over the range 30 °C–80 °C (entries 1–6, Table 2) and significantly affected the catalytic activities; the optimum temperature was found to be *ca.* 60 °C. Considering the highly exothermic nature of the polymerization process, the critical factor for late-transition metal complex pre-catalysts is to maintain good activity at the operational temperature employed in industry.¹⁷ The optimum observed temperature of

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Entry	Co-cat.	Al/Fe	$T/^{\circ}\mathrm{C}$	<i>t</i> /min	Activity ^b	$T_{\rm m}{}^c/{}^{\circ}{ m C}$	$M_{\rm w}^{~d}/10^3~{ m g~mol}^{-1}$	$M_{ m w}/M_{ m n}{}^d$
1	MAO	1000	30	30	5.30	133.4	153	7.90
2	MAO	1000	40	30	5.50	132.5	165	12.0
3	MAO	1000	50	30	7.50	132.3	179	16.0
4	MAO	1000	60	30	9.40	133.0	195	17.0
5	MAO	1000	70	30	9.30	132.6	164	13.0
6	MAO	1000	80	30	7.30	132.2	77.0	11.0
7	MAO	1500	60	30	12.5	133.0	240	27.1
8	MAO	2000	60	30	8.40	131.7	88.9	15.9
9	MAO	2500	60	30	7.30	129.5	35.0	10.6
10	MAO	1500	60	15	23.0	131.7	194	20.9
11	MAO	1500	60	45	8.60	131.8	248	29.1
12	MAO	1500	60	60	6.70	133.6	262	37.2
13^e	MAO	1500	60	30	1.70	129.7	87.0	67.0
14^{f}	MAO	1500	60	30	10.9	132.2	159	19.0
15	MMAO	1500	40	30	9.00	131.2	127	35.6
16	MMAO	1500	50	30	9.10	128.3	112	32.8
17	MMAO	1500	60	30	11.7	130.6	11.5	4.20
18	MMAO	1500	70	30	11.1	128.9	10.9	10.5
19	MMAO	1500	80	30	3.70	123.4	9.80	9.40
20	MMAO	1000	60	30	7.70	130.2	25.0	6.90
21	MMAO	2000	60	30	10.5	129.0	2.20	1.20
22	MMAO	2500	60	30	9.20	128.3	1.80	1.40

^{*a*} Conditions: 1.0 µmol of **Fe-4**; 10 atm of ethylene; total volume 100 mL. ^{*b*} Activity: 10^6 g PE mol⁻¹ (Fe) h⁻¹. ^{*c*} Determined by DSC. ^{*d*} Determined by GPC. ^{*e*} 1 atm of ethylene.

around 60 °C should be highlighted as an advantage of these newly designed binuclear iron complex, particularly when compared against pre-catalyst model A^{13a} at around 20 °C and B^{13b} at around 30 °C. Further increasing the temperature using **Fe-4** resulted partly in decomposition of the active species along with a lower solubility of ethylene.¹⁸

The GPC measurements revealed wide polydispersities for the obtained polyethylenes (Fig. 2), consistent with multi-site catalysis. According to the main peaks of the GPC curves, the catalytic system at lower temperature generally preferred to form polyethylenes with higher molecular weights; this is consistent with previous observations for iron complex precatalysts.⁸ Moreover, various Al/Fe molar ratios were screened, and the best activity was obtained at Al/Fe 1500 : 1 (entries 4, 7– 9, Table 2); higher molar ratios of Al/Fe resulted in polyethylene of lower molecular weight (Fig. 3), indicating that chain-transfer from the iron species to the aluminium was enhanced, resulting in increased polymer chain termination on either increasing the reaction temperature or the Al/Fe molar ratio.¹⁸



Fig. 2 The GPC curves of polyethylenes obtained by Fe-4 at different temperatures (entries 1–6, Table 2).



Fig. 3 The GPC curves of polyethylenes obtained by Fe-4 with various Al/Fe ratios (entries 4, 7–9, Table 2).

Regarding the influence of ethylene pressure (entries 7, 13,14, Table 2), the catalytic activity increased remarkably on increasing the ethylene pressure, whilst the GPC curves of the obtained polyethylene (Fig. 4) possessed higher molecular weights and narrow polydispersity. Moreover, the catalytic system under higher pressure produced polyethylene possessing close to unimodel features.

On checking the lifetime of the active species for **Fe-4/MAO** (entry 7, entries 10–12, Table 2), the activity over 15 min reached as high as 2.3×10^7 g mol⁻¹ (Fe) h⁻¹, and over 60 min, the activity remained at 6.7×10^6 g mol⁻¹ (Fe) h⁻¹. There was no induction time for the catalytic system, and active species only slowly deactivated. The obtained polyethylenes possessed higher molecular weights with wider polydispersity on prolonging the reaction time, during which the termination of polymeric chains at different times was considered to produce polyethylene with wide molecular polydispersity.¹⁹

To elucidate the structural features of the resultant polyethylene, ¹³C NMR spectroscopy was conducted in dichlorobenzene and revealed (entry 9) only a single peak besides the solvent *d*-1,2-dichlorobenzene (Fig. 5), indicating a highly linear polyethylene.



Fig. 4 The GPC curves of the polyethylenes by Fe-4 under different pressure (entries 7, 13, and 14, Table 2).



Fig. 5 The ¹³C-NMR spectrum of the polyethylene produced by Fe-4 (entry 9, Table 2).

In a similar manner, the co-catalyst modified methylaluminoxane (MMAO) was used to explore the catalytic behavior of complex Fe-4 under various parameters (entries 1–22, Table 2). In all cases, high activity toward ethylene polymerization was observed. Typically, the catalytic system using MAO exhibited better activity than did the system with MMAO; it is noteworthy that better thermo-stability with MMAO was observed (entries 17–19, Table 2). Moreover, the quenched solutions after removing polyethylenes were analyzed and no oligomers were observed. Compared to the binuclear iron-complex pre-catalysts derived from bis(imino)pyridines, the current model system showed better activity and higher thermo-stability than did those of the analogs A^{13a} and $B.^{13b}$

Ethylene polymerization by various iron complexes Fe-*n*. All the iron complexes were explored following activation by MAO under the optimum conditions determined for Fe-4, and the data are collected in Table 3.

These iron complexes can be divided into groups according to the different benzidine-bridges present, and catalytic trends can be observed due to the influence of the substituents present at the aniline moiety. According to the performances by Fe-1 through Fe-3 obtained using the tetramethylbenzidine-bridged ligands (entries 1-3, Table 3), the iron complex Fe-2 derived from 2,6-diethylaniline exhibited higher activities than the analogs Fe-1 and Fe-3, which is consistent with previous observations for bis(imino)pyridyl iron complex pre-catalysts due to the optimum bulkiness of the ethyl substituent versus both methyl and *i*-propyl.¹ Regarding the groups, Fe-4 to Fe-6 from tetraethylbenzidine-bridged ligands (entries 4-6, Table 3) and Fe-7 to Fe-9 from tetra(isopropyl)benzidine-bridged ligands (entries 7–9, Table 3), the catalytic activities of the binuclear iron complexes decreased when using bulkier substituents at the aniline, indicating that the ethylene coordination and insertion (catalytic activity) became slower when bulky-substituents surrounded the metal.^{8f} It is difficult to rationalize a general trend for the catalytic performance in terms of the influence of the ligands. For Fe-10 with an additional methyl substituent, higher activity was observed versus Fe-1, which is probably caused by the better solubility of the complex.²⁰ However, Fe-11 with an additional methyl-substituent showed

Table 3 Ethylene polymerization by iron complexes ^a						
Entry	Cat.	PE (g)	Activity ^b	$M_{\rm w}^{c}$ (kg mol ⁻¹)	$M_{\rm w}/M_{\rm n}^{\ c}$	$T_{\rm m}^{\ \ d} (^{\circ} {\rm C})$
1	Fe-1	8.50	8.50	88.7	11.1	131.9
2	Fe-2	13.1	13.1	66.1	9.50	132.5
3	Fe-3	8.00	8.00	51.6	7.00	134.3
4	Fe-4	12.5	12.5	240	27.1	133.0
5	Fe-5	11.9	11.9	232	18.6	133.1
6	Fe-6	7.40	7.40	225	16.4	133.6
7	Fe-7	12.6	12.6	283	30.6	132.6
8	Fe-8	9.30	9.30	181	24.4	133.2
9	Fe-9	8.10	8.10	174	18.6	133.3
10	Fe-10	11.4	11.4	73.7	7.50	132.8
11	Fe-11	5.37	5.37	22.8	3.90	131.8

^{*a*} General conditions: 1.0 μmol of Fe; 1500 of Al/Fe; 100 mL toluene for 10 atm ethylene; 60 °C; 30 min. ^{*b*} 10^6 g mol⁻¹ (Fe) h⁻¹. ^{*c*} Determined by GPC. ^{*d*} Determined by DSC.

lower activity than did the analog **Fe-8**; such an observation makes more sense if the net charge of metal ion is positively affecting its catalytic activity.¹⁹ In all cases, the binuclear iron complexes exhibited higher activity and better thermo-stability than did the mono-nuclear analogs¹ and related binuclear analogs.¹³

Conclusion

Binuclear iron complexes ligated by *N*,*N*'-bis(1-(3-(1-aryliminoethyl)pyridin-2-yl)ethylidene)tetraalkylbenzidine derivatives have been synthesized, characterized and screened as ethylene polymerization pre-catalysts. Upon activation with MAO or MMAO, all the binuclear iron complex pre-catalysts exhibited high activities towards ethylene polymerization. The resultant polyethylenes revealed a wide polydispersity, though the polyethylene was highly linear. As well as the high activity [up to $1.3 \times 10^7 \text{ g mol}^{-1}$ (Fe) h⁻¹], the current complex pre-catalysts performed with better thermo-stability than did related monometallic complexes¹ and other binuclear analogs.¹³ The title binuclear iron complex pre-catalysts are currently under further investigation in our laboratory, in order that their behaviour can more closely match that required for industrial consideration.

Experimental

General considerations

All manipulations of air and/or moisture sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium-benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane, 3A) were purchased from Akzo Nobel Corp. High-purity ethylene was purchased from Beijing Yansan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Acros, or local suppliers. NMR spectra were recorded on Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard. High temperature NMR spectra were recorded on Bruker DMX 300 MHz instrument at ambient temperature using TMS as an internal standard and d-1,2dichlorobenzene as the solvent. FT-IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using an HPMOD 1106 microanalyzer. MALDI-TOF spectra were detected on autoflex III Bruker, using CCA as the substrate. Molecular weights (M_w) and molecular weight distribution (M_w/M_n) of polyethylenes were determined by a PL-GPC220 at 150 °C with three PLgel 10 µm MIXED-B columns, with 1,2,4-trichlorobenzene as the solvent. Melting points of polyethylenes were obtained from the second scanning run on Q2000 DSC-7 at a heating rate of 10 $^{\circ}$ C min⁻¹ to 150 $^{\circ}$ C.

Synthesis and characterization of *N*,*N*'-bis(1-(3-(1-aryliminoethyl)pyridin-2-yl)ethylidene)tetraalkylbenzidine derivatives

3,3′,5,5′-Tetraethylbenzidine derivatives were synthesized according to the literature,¹⁵ meanwhile 2-acetyl-6-aryliminopyridine was prepared by our previously reported method.¹⁶ Further reaction of 3,3',5,5'-tetraethylbenzidine with two equivalent of 2-acetyl-6-aryliminopyridine formed the desired N,N'-bis(1-(3-(1-aryliminoethyl)pyridin-2-yl)ethylidene)tetraalkylbenzidine derivatives. As a typical example, the synthesis of N, N'-bis(1-(3-(1-(2,6-diethylphenylimino)ethyl)pyridin-2-yl) ethylidene)tetraethylbenzidine (L5) was conducted as follows: 2-acetyl-6-(1-((2,6-diethylphenyl)imino)ethyl)pyridine (0.75 g, 2.5 mmol) and 3,3',5,5'-tetraethylbenzidine (0.28 g, 1.25 mmol) were mixed in 100 mL toluene in the presence of a catalytic amount 4-methylbenzenesulfinic acid. The mixture was refluxed for 24 h, then cooled to room temperature. The solution was evaporated at reduced pressure, the residue was then separated by a column chromatography to collect the product, N,N'-bis(1-(3-(1-(2,6-diethylphenylimino)ethyl)pyridin-2-yl)ethylidene)tetra-ethylbenzidine (L5) in 0.24 g as a yellow solid, yield 22.6% (mp: 272 °C). ¹H NMR (400 MHz, CDCl₃, ppm): 8.51 (d, *J* = 8.0 Hz, 4H, Py-*H*), 7.95 (t, *J* = 8.0 Hz, 2H, Py-*H*), 7.13 (d, J = 7.6 Hz, 4H, Ph-H), 7.05 (t, J = 8.0 Hz, 2H, Ph-H), 6.29 (s, 4H, Ph-H), 2.40–2.53 (m, 8H, $4 \times CH_2$), 2.24 (s, 6H, $2 \times CH_3$), 2.10 (s, 6H, $2 \times CH_3$), 1.14 (t, J = 7.6 Hz, 12H, $4 \times CH_3$). ¹³C NMR: (100 MHz, CDCl₃, ppm): 167.5, 166.9, 155.2, 155.0, 147.9, 136.9, 136.0, 131.2, 126.4, 126.0, 125.8, 123.4, 122.3, 24.7, 18.2, 16.9, 16.7, 13.8. FT-IR (cm⁻¹): 2964 (m), 1637 ($\nu_{C=N}$, s), 1567 (m), 1450 (s), 1362 (s), 1321 (w), 1296 (w), 1243 (m), 1200 (s), 1119 (m), 1098 (m), 857 (w), 828 (m), 769 (m), 689 (w). Anal. calcd for C₅₈H₆₈N₆ (848): N, 9.90; C, 82.03; H, 8.07. Found: N, 9.65; C, 81.96; H, 8.12%.

N,N′-Bis(1-(3-(1-(2,6-dimethylphenylimino)ethyl)pyridin-2-yl)ethylidene)tetramethylbenzidine (L1)

Using a similar procedure to L5, L1 was also prepared as a yellow solid, yield 0.45 g, 49.3% (mp: 235 °C). ¹H NMR: (400 MHz, CDCl₃, ppm): 8.53 (d, J = 8.0 Hz, 2H, Py–H), 7.96 (t, J = 8.0 Hz, 1H, Py–H), 7.37 (d, J = 8.0 Hz, 2H, Ph–H), 7.09 (t, J = 8.0 Hz, 1H, Ph–H), 6.96 (s, 2H, Ph–H), 2.31 (s, 3H, CH₃), 2.26 (s, 3H, CH₃), 2.14 (s, 6H, $2 \times CH_3$), 2.07 (s, 6H, $2 \times CH_3$). ¹³C NMR (100 MHz, CDCl₃, ppm): 167.5, 167.3, 155.2, 155.1, 148.8, 148.7, 136.9, 136.0, 128.0, 126.4, 125.8, 125.5, 123.1, 122.4, 18.2, 18.0, 16.7, 16.5. FT-IR (cm⁻¹): 2913 (m), 1639 ($\nu_{C=N}$, s), 1569 (m), 1461 (s), 1429 (s), 1362 (s), 1324 (w), 1296 (w), 1247 (m), 1200 (s), 1120 (m), 1083 (m), 857 (m), 814 (m), 769 (s), 689 (w). Anal. calcd for C₅₀H₅₂N₆ (736): N, 11.40; C, 81.49; H, 7.11. Found: N, 10.99; C, 81.36; H, 6.92%.

N,N'-Bis(1-(3-(1-(2,6-diethylphenylimino)ethyl)pyridin-2-yl)-ethylidene)tetramethylbenzidine (L2)

Prepared as a yellow solid, yield 0.41 g, 42.6% (mp: 238 °C). ¹H NMR (400 MHz, CDCl₃, ppm): 8.51 (d, J = 8.0 Hz, 4H, Py–H), 7.95 (t, J = 8.0 Hz, 2H, Py–H), 7.13 (d, J = 7.6 Hz, 4H, Ph–H), 7.05 (t, J = 8.0 Hz, 2H, Ph–H), 6.29 (s, 4H, Ph–H), 2.29–2.44 (m, 8H, 4 × CH₂), 2.24 (s, 6H, 2 × CH₃), 2.10 (s, 6H, 2 × CH₃), 1.14 (t, J = 7.6 Hz, 12H, 4 × CH₃). ¹³C NMR (100 MHz, CDCl₃, ppm): 167.5, 166.9, 155.2, 155.0, 147.9, 136.9, 136.0, 131.2, 126.4, 126.0, 125.8, 123.4, 122.3, 24.7, 18.2, 16.9, 16.7, 13.8. FT-IR (cm⁻¹): 2964 (m), 1637 ($\nu_{C=N}$, s), 1567 (s), 1450 (m), 1362 (s), 1321 (w), 1296 (w), 1243 (s), 1200 (m), 1119 (m), 1098 (w), 857 (w), 828 (m),

769 (s), 689 (w). Anal. calcd for $C_{56}H_{60}N_6$ (792): N, 10.60; C, 81.78; H, 7.63. Found: N, 10.69; C, 81.95; H, 7.39%.

N,N′-Bis(1-(3-(1-(2,6-diisopropylphenylimino)ethyl)pyridin-2-yl)ethylidene)tetramethylbenzidine (L3)

Prepared as a yellow solid, yield 0.28 g, 26.8% (mp: 245 °C). ¹H NMR (400 MHz, CDCl₃, ppm): 8.56 (d, J = 8.0 Hz, 4H, Py–H), 7.96 (t, J = 8.0 Hz, 2H, Py–H), 7.36 (s, 4H, Ph–H), 7.19 (d, J = 7.6 Hz, 4H, Ph–H), 7.11 (t, J = 8.0 Hz, 2H, Ph–H), 2.71–2.83 (m, 4H, 2 × CH₂), 2.31 (s, 6H, 2 × CH₃), 2.29 (s, 6H, 2 × CH₃), 2.14 (s, 12H, 4 × CH₃), 1.18 (d, 12H, J = 2.0 Hz, 4 × CH₃), 1.16 (d, 12H, J = 2.0 Hz, 4 × CH₃), 1.16 (d, 12H, J = 2.0 Hz, 4 × CH₃). ¹³C NMR (100 MHz, CDCl₃, ppm): 167.5, 166.5, 155.3, 155.2, 152.6, 137.4, 136.4, 131.2, 126.9, 126.0, 125.7, 124.5, 123.2, 122.1, 28.4, 25.6, 23.3, 23.0, 18.2, 17.9. FT-IR (cm⁻¹): 2957 (m), 2015 (w), 1641 ($\nu_{C=N}$, s), 1570 (w), 1460 (m), 1361 (s), 1322 (w), 1243 (m), 1204 (s), 1117 (m), 859 (w), 824 (m), 766 (s), 692 (w). Anal. calcd for C₅₈H₆₈N₆ (848): N, 9.90; C, 82.03; H, 8.07. Found: N, 9.55; C, 81.86; H, 8.15%.

N,N[']-Bis(1-(3-(1-(2,6-dimethylphenylimino)ethyl)pyridin-2-yl)ethylidene)tetraethylbenzidine (L4)

Prepared as a yellow solid, yield 0.43 g, 43.6% (mp: 283 °C). ¹H NMR (400 MHz, CDCl₃, ppm): 8.51 (d, J = 8.0 Hz, 4H, Py–H), 7.95 (t, J = 8.0 Hz, 2H, Py–H), 7.13 (d, J = 7.6 Hz, 4H, Ph–H), 7.05 (t, J = 8.0 Hz, 2H, Ph–H), 6.29 (s, 4H, Ph–H), 2.29–2.43 (m, 8H, 4 × CH₂), 2.24 (s, 6H, 2 × CH₃), 2.10 (s, 6H, 2 × CH₃), 1.14 (t, J =7.6 Hz, 12H, 4 × CH₃). ¹³C NMR (100 MHz, CDCl₃, ppm): 167.5, 166.9, 155.2, 155.0, 147.9, 136.9, 136.0, 131.2, 126.4, 126.0, 125.8, 123.4, 122.3, 24.7, 18.2, 16.9, 16.7, 13.8. FT-IR (cm⁻¹): 2964 (m), 1637 ($\nu_{C=N}$, s), 1567 (w), 1450 (m), 1362 (s), 1321 (w), 1296 (w), 1243 (m), 1200 (s), 1119 (s), 1098 (m), 857 (m), 828 (m), 769 (s), 689 (w). Anal. calcd for C₅₄H₆₀N₆ (792): N, 10.60; C, 81.78; H, 7.63. Found: N, 10.65; C, 81.95; H, 7.39%.

N,N′-Bis(1-(3-(1-(2,6-diisopropylphenylimino)ethyl)pyridin-2-yl)ethylidene)tetraethylbenzidine (L6)

Prepared as a yellow solid, yield 0.34 g, 30.5% (mp: 270 °C). ¹H NMR (400 MHz, CDCl₃, ppm): 8.53 (d, J = 8.0 Hz, 4H, Py–H), 7.96 (t, J = 8.0 Hz, 2H, Py–H), 7.40 (s, 4H, Ph–H), 7.17 (d, J = 7.6 Hz, 4H, Ph–H), 7.11 (t, J = 8.0 Hz, 2H, Ph–H), 2.78–2.91 (m, 4H, 4 × CH), 2.34–2.51 (m, 8H, 4 × CH₂), 2.29 (s, 6H, 2 × CH₃), 2.26 (s, 6H, 2 × CH₃), 1.22 (t, 12H, J = 7.6 Hz, 4 × CH₃), 1.16 (d, 24H, J = 5.6 Hz, 8 × CH₃). ¹³C NMR (100 MHz, CDCl₃, ppm): 167.2, 167.0, 155.3, 155.2, 146.8, 146.6, 136.9, 136.6, 135.9, 131.7, 124.7, 123.6, 123.1, 122.3, 28.4, 25.0, 23.3, 23.0, 17.2, 17.0, 14.0. FT IR (cm⁻¹): 2962 (m), 1635 ($\nu_{C=N}$, s), 1569 (w), 1454 (m), 1362 (s), 1322 (w), 1241 (m), 1196 (s), 1120 (s), 1103 (m), 869 (w), 824 (m), 766 (s), 692 (m). Anal. calcd for C₆₂H₇₆N₆ (904): N, 9.28; C, 82.26; H, 8.46. Found: N, 8.89; C, 81.95; H, 8.43%.

N,N′-Bis(1-(3-(1-(2,6-dimethylphenylimino)ethyl)pyridin-2-yl)ethylidene)tetraisopropylbenzidine (L7)

Prepared as a yellow solid, yield 0.36 g, 34.4% (mp: 279 °C). ¹H NMR (400 MHz, CDCl₃, ppm): 8.57 (d, J = 8.0 Hz, 4H, Py–H), 7.97 (t, J = 8.0 Hz, 2H, Py–H), 7.42 (s, 4H, Ph–H), 7.10 (d, J = 7.6

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Hz, 4H, Ph–*H*), 6.97 (t, J = 7.6 Hz, 2H, Ph–*H*), 2.79–2.90 (m, 4H, 4 × C*H*), 2.35 (s, 6H, 2 × C*H*₃), 2.28 (s, 6H, 2 × C*H*₃), 2.10 (s, 12H, 4 × C*H*₃), 1.41 (d, J = 7.2 Hz, 24H, 8 × C*H*₃). ¹³C NMR (100 MHz, CDCl₃, ppm): 167.3, 167.2, 155.2, 155.0, 148.8, 137.3, 137.0, 136.1, 128.0, 125.5, 123.1, 122.4, 122.3, 121.8, 28.6, 23.4, 23.0, 18.1, 17.4, 16.6. FT-IR (cm⁻¹): 2958 (m), 1636 ($\nu_{C=N}$, s), 1569 (w), 1460 (m), 1362 (s), 1321 (w), 1244 (w), 1200 (m), 1117 (s), 868 (w), 822 (m), 760 (m). Anal. calcd for C₅₈H₆₈N₆ (848): N, 9.90; C, 82.03; H, 8.07. Found: N, 9.59; C, 81.93; H, 8.05%.

N,*N*'-Bis(1-(3-(1-(2,6-diethylphenylimino)ethyl)pyridin-2-yl)ethylidene)tetraisopropylbenzidine (L8)

Prepared as a yellow solid, yield 0.36 g, 31.9% (mp: 276 °C). ¹H NMR (400 MHz, CDCl₃, ppm): 8.53 (d, J = 8.0 Hz, 4H, Py–H), 7.96 (t, J = 8.0 Hz, 2H, Py–H), 7.42 (s, 4H, Ph–H), 7.13 (d, J = 7.6 Hz, 4H, Ph–H), 7.05 (d, J = 8.0 Hz, 2H, Ph–H), 2.73–2.81 (m, 4H, 4 × CH), 2.40–2.54 (m, 8H, 4 × CH₂), 2.36 (s, 6H, 2 × CH₃), 2.28 (s, 6H, 2 × CH₃), 1.24 (d, J = 7.2 Hz, 24H, 8 × CH₃), 1.16 (t, J = 7.6 Hz, 12H, 4 × CH₃). ¹³C NMR (100 MHz, CDCl₃, ppm): 167.5, 167.0, 155.3, 155.0, 145.6, 139.3, 137.3, 136.1, 131.3, 128.3, 126.0, 123.4, 122.4, 121.8, 28.6, 24.7, 23.4, 23.0, 16.9, 13.8. FT-IR (cm⁻¹): 2960 (m), 2015 (w), 1636 ($\nu_{C=N}$, s), 1582 (w), 1444 (m), 1362 (s), 1322 (w), 1240 (m), 1196 (w), 1117 (s), 868 (m), 823 (m), 783 (m), 762 (s). Anal. calcd for C₆₂H₇₆N₆ (904): N, 9.28; C, 82.26; H, 8.46. Found: N, 8.97; C, 82.03; H, 8.43%.

N,N'-Bis(1-(3-(1-(2,6-diisopropylphenylimino)ethyl)pyridin-2yl)ethylidene)tetraisopropylbenzidine (L9)

Prepared on 0.42 g scale as a yellow solid, yield 35.0% (mp: 202 °C). ¹H NMR (400 MHz, CDCl₃, ppm): 8.60 (d, J = 8.0 Hz, 4H, Py–H), 7.99 (t, J = 8.0 Hz, 2H, Py–H), 7.43 (s, 4H, Ph–H), 7.17 (d, J = 7.6 Hz, 4H, Ph–H), 7.12 (t, J = 8.0 Hz, 2H, Ph–H), 2.71–2.89 (m, 8H, 4 × CH₂), 2.30 (s, 6H, 2 × CH₃), 2.27 (s, 6H, 2 × CH₃), 1.25 (d, J = 5.6 Hz, 24H, 8 × CH₃), 1.19 (d, J = 5.6 Hz, 24H, 8 × CH₃), 1.19 (d, J = 5.6 Hz, 24H, 8 × CH₃), 1.17 (d, J = 16.6, 146.3, 145.6, 137.4, 137.3, 136.9, 136.1, 135.8, 135.7, 124.6, 123.8, 123.6, 123.1, 123.1, 122.6, 122.3, 121.8, 28.6, 28.4, 23.4, 23.3, 23.3, 23.0, 22.9, 17.3, 17.2, 17.1. FT-IR (cm⁻¹): 2960 (m), 2158 (w), 2015 (w), 1639 ($\nu_{C=N}$, s), 1570 (m), 1455 (s), 1361 (s), 1323 (w), 1239 (m), 1194 (s), 1117 (m), 961 (w), 868 (m), 823 (m), 763 (s), 691 (m). Anal. calcd for C₆₆H₈₄N₆ (960): N, 8.74; C, 82.45; H, 8.81. Found: N, 8.59; C, 82.15; H, 8.66%.

N,N′-Bis(1-(3-(1-mesityliminoethyl)pyridin-2-yl)ethylidene)tetramethylbenzidine (L10)

Prepared on 0.30 g scale as a yellow solid, yield 32% (mp: 228 °C). ¹H NMR (400 MHz, CDCl₃, ppm): 8.49 (d, J = 7.6 Hz, 2H, Py–H), 7.93 (t, J = 8.0 Hz, 1H, Py–H), 7.36 (s, 2H, Ph–H), 6.91 (s, 2H, Ph–H), 2.31 (s, 6H, 2 × CH₃), 2.29 (s, 3H, CH₃), 2.27 (s, 6H, 2 × CH₃), 2.10 (s, 6H, 2 × CH₃). ¹³C NMR: (100 MHz, CDCl₃, ppm): 167.5, 167.3, 155.3, 148.8, 147.8, 137.0, 136.0, 131.1, 128.0, 126.5, 126.3, 125.8, 125.5, 122.5, 18.2, 18.0, 16.7, 16.5. FT-IR (cm⁻¹): 2964 (m), 2030 (w), 1643 ($\nu_{C=N}$, s), 1574 (m), 1454 (s), 1362 (s), 1322 (w), 1205 (s), 1150 (w), 1120 (m), 859 (m), 817 (m), 741 (w), 694 (w). Anal. calcd for C₅₃H₅₈N₆ (764): N, 10.79; C, 81.71; H, 7.50. Found: N, 10.59; C, 82.15; H, 7.66%.

N,N′-Bis(1-(3-(1-(2,6-diethyl-4-methylphenyl)imino)ethyl)pyridin-2-yl)ethylidene tetraisopropylbenzidine (L11)

Prepared on 0.25 g scale as a yellow solid, yield 22.1% (mp: 265 °C). ¹H NMR (400 MHz, CDCl₃, ppm): 8.50 (d, J = 7.6 Hz, 2H, Py–H), 7.94 (t, J = 8.0 Hz, 1H, Py–H), 7.41 (s, 1H, Ph–H), 7.27 (s, 1H, Ph–H), 6.94 (s, 2H, Ph–H), 2.78–2.87 (m, 2H, 2 × CH), 2.36–2.43 (m, 4H, 2 × CH₂), 2.35 (s, 3H, CH₃), 2.27 (s, 3H, CH₃), 1.26 (d, J = 1.6 Hz, 12H, 4 × CH₃), 1.15 (t, J = 7.6 Hz, 6H, 2 × CH₃). ¹³C NMR: (100 MHz, CDCl₃, ppm): 167.2, 155.4, 155.2, 145.6, 145.4, 137.3, 136.9, 136.1, 132.5, 131.2, 126.8, 122.3, 121.9, 121.8, 28.6, 24.7, 23.4, 23.4, 23.1, 23.0, 21.1, 17.3, 16.8, 13.9. FT-IR (cm⁻¹): 2964 (m), 1643 ($\nu_{C=N}$, m), 1577 (m), 1456 (s), 1365 (s), 1325 (w), 1254 (m), 1195 (s), 1121 (w), 857 (m), 814 (m), 779 (w), 694 (w). Anal. calcd for C₆₄H₈₀N₆ (932): N, 9.00; C, 82.36; H, 8.64. Found: N, 8.71; C, 82.03; H, 8.59%.

Synthesis and characterization of binuclear iron complexes

The formation of the iron complexes is illustrated by the procedure for complex **Fe-1** as follows: N,N'-Bis(1-(3-(1-(2, 6-dimethylphenylimino)ethyl)pyridin-2-yl)ethylidene)tetramethyl benzidine (**L1**) (0.074 g, 0.10 mmol) and FeCl₂·4H₂O (0.040 g, 0.20 mmol) were mixed in CH₂Cl₂ (5 mL) and EtOH (5 mL) for 8 h at room temperature. The precipitate was collected by filtration and washed with diethyl ether (3 × 5 mL), then dried under vacuum to afford **Fe-1** as a blue solid (0.050 g, 67.7% yield). FT-IR (cm⁻¹): 2908 (w), 1624 ($\nu_{C=N}$, m), 1591 (m), 1498 (w), 1466 (s), 1365 (m), 1265 (s), 1224 (s), 1095 (s), 858 (m), 823 (s), 775 (m), 738 (m), 689 (w). Anal. calcd for C₅₀H₅₂N₆Fe₂Cl₄ (990): N, 8.48; C, 60.63; H, 5.29. Found: N, 8.80; C, 60.43; H, 5.37%. MS (MALDI-TOF, *m/z*): 990.17. Found: *m/z* 981.2 [M – FeCl₄ + CCA]⁺, 837.1 [M – FeCl₃]⁺, 747.1 [M – Fe₂Cl₄]⁺.

Fe-2. A mixture of *N*,*N'*-bis(1-(3-(1-(2,6-diethylphenylimino) ethyl)pyridin-2-yl)ethylidene)tetramethylbenzidine (**L2**) (0.079 g, 0.10 mmol) and FeCl₂·4H₂O (0.040 g, 0.20 mmol) in CH₂Cl₂ (5 mL) and EtOH (5 mL) was stirred for 8 h at room temperature. The precipitate was collected by filtration and washed with diethyl ether (3 × 5 mL), then dried under vacuum to afford **Fe-2** as a blue solid (0.026 g, 33.6% yield). FT-IR (cm⁻¹): 2966 (s), 1619 ($\nu_{C=N}$, w), 1584 (m), 1465 (s), 1370 (s), 1263 (s), 1209 (m), 1104 (m), 1033 (m), 865 (s), 806 (m), 766 (m), 738 (w). Anal. calcd for C₅₆H₆₀N₆Fe₂Cl₄ (1046): N, 7.62; C, 63.17; H, 6.22. Found: N, 7.49; C, 63.48; H, 6.07%. MS (MALDI-TOF, *m*/*z*): 1046.23. Found: *m*/*z* 1037.1 [M – FeCl₄ + CCA]⁺, 884.0 [M – FeCl₃]⁺, 794.0 [M – Fe₂Cl₄]⁺.

Fe-3. A mixture of *N*,*N*'-bis(1-(3-(1-(2,6-diisopropylphenylimino)ethyl)pyridin-2-yl)ethylidene)tetramethylbenzidine (L3) (0.084 g, 0.10 mmol) and FeCl₂·4H₂O (0.040 g, 0.20 mmol) in CH₂Cl₂ (5 mL) and EtOH (5 mL) was stirred for 8 h at room temperature. The precipitate was collected by filtration and washed with diethyl ether (3 × 5 mL), then dried under vacuum to afford **Fe-3** as a blue solid (0.079 g, 94.0% yield). FT-IR (cm⁻¹): 2963 (s), 2018 (w), 1616 ($\nu_{C=N}$, w), 1584 (m), 1466 (s), 1372 (s), 1324 (m), 1263 (s), 1210 (m), 1103 (m), 867 (m), 804 (s), 762 (w), 734 (w), 692 (w). Anal. calcd for C₅₈H₆₈N₆Fe₂Cl₄ (1102): N, 7.62; C, 63.17; H, 6.22. Found: N, 7.92; C, 63.09; H, 5.97%. MS

(MALDI-TOF, m/z): 1102.29. Found: m/z 1093.2 [M - FeCl₄ + CCA]⁺, 940.1 [M - FeCl₃]⁺, 850.1 [M - Fe₂Cl₄]⁺.

Fe-4. A mixture of *N*,*N*'-bis(1-(3-(1-(2,6-dimethylphenylimino) ethyl)pyridin-2-yl)ethylidene)tetraethylbenzidine (**L4**) (0.079 g, 0.10 mmol) and FeCl₂·4H₂O (0.040 g, 0.20 mmol) in CH₂Cl₂ (5 mL) and EtOH (5 mL) was stirred for 8 h at room temperature. The precipitate was collected by filtration and washed with diethyl ether (3 × 5 mL), then dried under vacuum to afford **Fe-4** as a blue solid (0.091 g, 87.5% yield). FT-IR (cm⁻¹): 2968 (s), 1616 ($\nu_{C=N}$, m), 1585 (s), 1448 (s), 1367 (s), 1266 (s), 1212 (s), 1161 (w), 1096 (m), 871 (m), 831 (s), 748 (w), 699 (w). Anal. calcd for C₅₄H₆₀N₆Fe₂Cl₄ (1046): N, 8.03; C, 61.97; H, 5.78. Found: N, 8.24; C, 62.06; H, 5.50%. MS (MALDI-TOF, *m*/*z*): 1046.23. Found: *m*/*z* 1037.1 [M – FeCl₄ + CCA]⁺, 884.0 [M – FeCl₃]⁺, 794.0 [M – Fe₂Cl₄]⁺.

Fe-5. A mixture of *N*,*N*'-bis(1-(3-(1-(2,6-diethylphenylimino) ethyl)pyridin-2-yl)ethylidene)tetraethylbenzidine (L5) (0.084 g, 0.10 mmol) and FeCl₂·4H₂O (0.040 g, 0.20 mmol) in CH₂Cl₂ (5 mL) and EtOH (5 mL) was stirred for 8 h at room temperature. The precipitate was collected by filtration and washed with diethyl ether (3 × 5 mL), then dried under vacuum to afford **Fe-5** as a blue solid (0.070 g, 64.3% yield). FT-IR (cm⁻¹): 2964 (s), 2166 (w), 1621 ($\nu_{C=N}$, m), 1584 (m), 1447 (s), 1368 (s), 1325 (m), 1296 (s), 1206 (s), 1107 (m), 868 (s), 805 (s), 765 (w), 698 (w). Anal. calcd for C₅₈H₆₈N₆Fe₂Cl₄ (1102): N, 7.62; C, 63.17; H, 6.22. Found: N, 7.68; C, 63.35; H, 6.07. MS (MALDI-TOF, *m/z*): 1102.29. Found: *m/z* 1093.2 [M - FeCl₄ + CCA]⁺, 850.1 [M - Fe₂Cl₄]⁺.

Fe-6. A mixture of *N*,*N*'-bis(1-(3-(1-(2,6-diisopropylylphenylimino)ethyl)pyridin-2-yl)ethylidene)tetraethylbenzidine (L6) (0.090 g, 0.10 mmol) and FeCl₂·4H₂O (0.040 g, 0.20 mmol) in CH₂Cl₂ (5 mL) and EtOH (5 mL) was stirred for 8 h at room temperature. The precipitate was collected by filtration and washed with diethyl ether (3 × 5 mL), then dried under vacuum to afford **Fe-6** as a blue solid (0.065 g, 56.3% yield). FT-IR (cm⁻¹): 2963 (s), 1621 ($\nu_{C=N}$, m), 1584 (s), 1447 (m), 1367 (s), 1321 (m), 1262 (s), 1206 (m), 1103 (m), 866 (w), 833 (s), 798 (s), 764 (w). Anal. calcd for C₆₂H₇₆N₆Fe₂Cl₄ (1158): N, 7.25; C, 64.26; H, 6.61. Found: N, 7.45; C, 64.19; H, 6.58%. MS (MALDI-TOF, *m/z*): 1158.36. Found: *m/z* 1149.3 [M – FeCl₄ + CCA]⁺, 996.1 [M – FeCl₃]⁺, 906.2 [M – Fe₂Cl₄]⁺.

Fe-7. A mixture of N,N'-bis(1-(3-(1-(2,6-dimethylphenylimino) ethyl)pyridin-2-yl)ethylidene)tetraisopropylbenzidine (L7) (0.084 g, 0.10 mmol) and FeCl₂·4H₂O (0.040 g, 0.20 mmol) in CH₂Cl₂ (5 mL) and EtOH (5 mL) was stirred for 8 h at room temperature. The precipitate was collected by filtration and washed with diethyl ether (3 × 5 mL), then dried under vacuum to afford **Fe**-7 as a blue solid (0.030 g, 27.3% yield). FT-IR (cm⁻¹): 2962 (s), 1621 ($\nu_{C=N}$, w), 1587 (m), 1465 (s), 1368 (s), 323 (m), 1263 (s), 1213 (m), 1098 (m), 868 (w), 815 (s), 770 (w). Anal. calcd for C₅₈H₆₈N₆Fe₂Cl₄ (1102): N, 7.62; C, 63.17; H, 6.22. Found: N, 7.43; C, 63.60; H, 6.01. MS (MALDI-TOF, *m*/*z*): 1102.29. Found: *m*/*z* 1093.2 [M - FeCl₄ + CCA]⁺, 940.1 [M - FeCl₃]⁺, 850.1 [M - Fe₂Cl₄]⁺.

Fe-8. A mixture of N,N'-bis(1-(3-(1-(2,6-diethylphenylimino)) ethyl)pyridin-2-yl)ethylidene)tetraisopropylbenzidine (L8) (0.090 g, 0.10 mmol) and FeCl₂·4H₂O (0.040 g, 0.20 mmol) in

CH₂Cl₂ (5 mL) and EtOH (5 mL) was stirred for 8 h at room temperature. The precipitate was collected by filtration and washed with diethyl ether (3 × 5 mL), then dried under vacuum to afford **Fe-8** as a blue solid (0.080 g, 69.2% yield). FT-IR (cm⁻¹): 2965 (s), 2107 (w), 1627 ($\nu_{C=N}$, w), 1587 (s), 1441 (m), 1372 (s), 1322 (m), 1258 (s), 1207 (m), 1107 (m), 869 (w), 810 (s), 763 (s), 696 (s). Anal. calcd for C₆₂H₇₆N₆Fe₂Cl₄ (1158): N, 7.25; C, 64.26; H 6.61. Found: N, 6.97; C, 64.65; H, 6.45%. MS (MALDI-TOF, *m/z*): 1158.36. Found: *m/z* 1149.4 [M – FeCl₄ + CCA]⁺, 996.3 [M – FeCl₃]⁺, 906.3 [M – Fe₂Cl₄]⁺.

Fe-9. A mixture of *N*,*N'*-bis(1-(3-(1-(2,6-diisopropylphenylimino)ethyl)pyridin-2-yl)ethylidene)tetraisopropylbenzidine (**L9**) (0.096 g, 0.10 mmol) and FeCl₂·4H₂O (0.040 g, 0.20 mmol) in CH₂Cl₂ (5 mL) and EtOH (5 mL) was stirred for 8 h at room temperature. The precipitate was collected by filtration and washed with diethyl ether (3 × 5 mL), then dried under vacuum to afford **Fe-9** as a blue solid (0.056 g, 45.8% yield). FT-IR (cm⁻¹): 2962 (s), 2162 (w), 2017 (w), 1618 ($\nu_{C=N}$, w), 1586 (s), 1461 (s), 1368 (s), 1264 (s), 1208 (s), 1101 (m), 1028 (m), 941 (w), 836 (s), 804 (s), 764 (w). Anal. calcd for C₆₆H₈₄N₆Fe₂Cl₄ (1214): N, 6.92; C, 65.25; H, 6.97. Found: N, 6.87; C, 65.17; H, 7.07%. MS (MALDI-TOF, *m*/*z*): 1214.42. Found: *m*/*z* 1205.5 [M – FeCl₄ + CCA]⁺, 1052.4 [M – FeCl₃]⁺, 962.4 [M – Fe₂Cl₄]⁺.

Fe-10. A mixture of *N*,*N'*-bis(1-(3-(1-mesityliminoethyl)pyridin-2-yl)ethylidene)tetramethylbenzidine (L10) (0.076 g, 0.10 mmol) and FeCl₂·4H₂O (0.040 g, 0.20 mmol) in CH₂Cl₂ (5 mL) and EtOH (5 mL) was stirred for 8 h at room temperature. The precipitate was collected by filtration and washed with diethyl ether (3 × 5 mL), then dried under vacuum to afford **Fe-10** as a blue solid (0.078 g, 76.6% yield). FT-IR (cm⁻¹): 2964 (m), 1638 ($\nu_{C=N}$, w), 1569 (m), 1454 (m), 1364 (s), 1322 (w), 1247 (w), 1206 (s), 1119 (s), 852 (s), 816 (s), 790 (m), 762 (w), 692 (w). Anal. calcd for C₅₂H₅₆ N₆ Fe₂Cl₄ (1018): N, 8.25; C, 61.32; H, 5.54. Found: N, 8.09; C, 61.17; H, 5.34%. MS (MALDI-TOF, *m/z*): 1018.2. Found: *m/z* 1009.3 [M – FeCl₄ + CCA]⁺, 856.1 [M – FeCl₃]⁺, 766.1 [M – Fe₂Cl₄]⁺.

Fe-11. A mixture of *N*,*N*'-bis(1-(3-(1-(2,6-diethyl-4-methylphenyl)imino)ethyl)pyridin-2-yl)ethylidene tetraisopropylbenzidine (**L11**) (0.092 g, 0.10 mmol) and FeCl₂· 4H₂O (0.040 g, 0.20 mmol) in CH₂Cl₂ (5 mL) and EtOH (5 mL) was stirred for 8 h at room temperature. The precipitate was collected by filtration and washed with diethyl ether (3 × 5 mL), then dried under vacuum to afford **Fe-11** as a blue solid (0.070 g, 59.0% yield): FT-IR (cm⁻¹): 2962 (m), 2017 (w), 1618 ($\nu_{C=N}$, w), 1586 (m), 1464 (m), 1368 (s), 1322 (w), 1264 (s), 1208 (m), 1101 (w), 836 (s), 804 (s), 764 (w), 696 (w). Anal. calcd for C₆₄H₈₀N₆Fe₂Cl₄ (1186): N, 7.08; C: 64.77, H: 6.79. Found: N, 6.68; C, 65.15; H, 6.62%. MS (MALDI-TOF, *m*/*z*): 1186.39. Found: *m*/*z* 1177.5 [M – FeCl₄ + CCA]⁺, 932.4 [M – Fe₂Cl₄]⁺.

X-ray crystallographic studies

The X-ray diffraction study was conducted using graphitemonochromatic Mo-K α radiation ($\lambda = 0.71073$ Å) at 173(2) K. Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption.

Table 4 Crystal data and structure refinement details for L5

CCDC	938522
Empirical formula	$C_{58}H_{68}N_{6}$
Fw	849.18
$T(\mathbf{K})$	173(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.2594(17)
b (Å)	12.235(2)
c (Å)	13.770(3)
α (deg)	74.30(3)
β (deg)	81.22(3)
γ (deg)	73.35(3)
$V(\text{\AA}^3)$	1279.1(4)
Z	1
$D_{\text{calcd}} (\text{mg m}^{-3})$	1.102
$\mu (\mathrm{mm}^{-1})$	0.065
F(000)	458
Crystal size (mm)	0.27 imes 0.15 imes 0.08
θ range (deg)	1.54-27.49
Limiting indices	$-10 \le h \le 10, -15 \le k \le 15,$
	$-17 \leq l \leq 17$
No. of reflections collected	11 474
No. unique reflections [R(int)]	5816 (0.0509)
Completeness to θ (%)	99.0%
Goodness of fit on F^2	1.152
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.1360, wR2 = 0.3521
<i>R</i> indices (all data)	R1 = 0.2238, wR2 = 0.4188
Largest diff. peak and hole $(Å^{-3})$	0.343 and -0.186
No. of reflections collected	

The structure was solved by direct methods and refined by fullmatrix least squares on F2. All hydrogen atoms were placed in calculated positions. Using the SHELXL-97 package,²¹ structure solution and refinement was performed.† Details of the X-ray structure determinations and refinements are provided in Table 4.

General procedure for ethylene polymerization

Ethylene polymerization under 10/5 atm ethylene. A 300 mL stainless steel autoclave, equipped with a mechanical stirrer and a temperature controller, was employed for the reaction. Firstly, 50 mL toluene (freshly distilled) was injected to the clave which was full of ethylene. When the required temperature was reached, another 30 mL toluene which dissolved the complex and the required amount of co-catalyst (MAO, MMAO), and the residual toluene was added by successively by syringe. The reaction mixture was intensely stirred for the desired time under the corresponding pressure of ethylene through the entire experiment. The reaction was terminated and analyzed using the same procedure as above for ethylene polymerization at ambient pressure.

Ethylene polymerization under 1 atm ethylene

The pre-catalyst was dissolved in toluene using standard Schlenk techniques, and the reaction solution was stirred with a magnetic stir bar under ethylene atmosphere (1 atm) with a steam bath for controlling the temperature. Finally, the

required amount of co-catalyst was added by a syringe. After the reaction was carried out for the required period, the reaction was immediately terminated by the addition of 10% aqueous hydrogen chloride. The precipitated polymer was collected, washed with water and ethanol, and finally dried.

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