Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Stable Fe(II)-Based Coordination Polymers: Synthesis, Structural Diversity and Catalytic Applications in Homo-coupling Reactions

Qiong Wu,‡[a] Yanbing Han,‡[a] Zhichao Shao,[a] Junxia Li,[b] and Hongwei Hou *[a]

[a]The College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, Henan, 450001, P. R. China

[b]Food and Drug Inspection Institute of Zhengzhou, Henan 450000, P. R. China

*Author for correspondence:

Prof. Hongwei Hou, E-mail: houhongw@zzu.edu.cn.

Contents

Table S1 Crystallographic data and structure refinement details for polymers **1−3**[a,b]

Complex	**1**	**2**	**3**
formula	$C_{79}H_{95}N_{41}O_4S_5Fe_3$	$C_{78}H_{90}N_{42}O_3S_6Fe_3$	$C_{36}H_{64}N_{18}O_{11}Cl_6Fe_3$
f_w	2009.54	2024.01	1305.43
T/K	293(2)	293(2)	293(2)
λ (Mo–Ka), Å	0.71073	1.54178	0.71073
Crystsyst	Monoclinic	Monoclinic	Trigonal
Space group	*C 2*	*C 2*	*R*-3
a (Å)	23.848(13)	23.8508(6)	14.4180(15)
b (Å)	17.081(3)	16.0961(3)	14.4180(15)
c (Å)	16.644(3)	23.6646(4)	21.872(4)
α(°)	90	90	90
β(°)	134.258(16)	90.482(2)	90
γ(°)	90	90	120
V (Å^3)	4856(3)	9084.6(3)	3937.6(9)
Z	2	4	3
D_c (g×cm^{-3})	1.319	1.440	1.537
μ (mm^{-1})	0.614	5.643	1.183
F(000)	2000	4080	1872
GOF on F^2	0.888	1.044	1.068
R1 (I > 2σ(I))	0.0550	0.0634	0.0509
wR2(I > 2σ(I))	0.1357	0.1734	0.1138

$^aR_1 = \sum||F_o|-|F_c||\sum/|F_o|$. $^bwR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table S2 Bond lengths and angels of **1**-**3**

	Polymer 1		
Fe(1)-N(20)	2.190(12)	Fe(2)-N(6)#3	2.262(7)
Fe(1)-N(9)#1	2.176(5)	Fe(2)-N(6)#4	2.262(7)
Fe(1)-N(9)	2.176(5)	Fe(3)-N(21)	2.155(8)
Fe(1)-N(10)#1	2.174(5)	Fe(3)-N(21)#2	2.155(8)
Fe(1)-N(10)	2.174(5)	Fe(3)-N(3)#5	2.217(6)
Fe(1)-O(1)	2.290(14)	Fe(3)-N(3)#6	2.217(6)
Fe(2)-N(15)	2.168(6)	Fe(3)-N(18)#2	2.220(6)
Fe(2)-N(15)#2	2.168(6)	Fe(3)-N(18)	2.220(6)
Fe(2)-N(19)	2.164(8)		
Fe(2)-N(19)#2	2.164(8)		
N(20)-Fe(1)-N(9)#1	87.10(18)	N(15)#2-Fe(2)-N(6)#3	84.6(2)
N(20)-Fe(1)-N(9)	87.10(18)	N(19)-Fe(2)-N(6)#3	177.2(3)
N(9)#1-Fe(1)-N(9)	174.2(4)	N(19)#2-Fe(2)-N(6)#3	90.8(3)
N(20)-Fe(1)-N(10)#1	87.17(17)	N(15)-Fe(2)-N(6)#4	84.6(2)
N(9)#1-Fe(1)-N(10)#1	88.5(2)	N(15)#2-Fe(2)-N(6)#4	92.3(2)
N(9)-Fe(1)-N(10)#1	91.2(2)	N(19)-Fe(2)-N(6)#4	90.8(3)
N(20)-Fe(1)-N(10)	87.17(17)	N(19)#2-Fe(2)-N(6)#4	177.2(3)
N(9)#1-Fe(1)-N(10)	91.2(2)	N(6)#3-Fe(2)-N(6)#4	87.3(4)
N(9)-Fe(1)-N(10)	88.5(2)	N(21)-Fe(3)-N(21)#2	90.3(5)
N(10)#1-Fe(1)-N(10)	174.3(3)	N(21)-Fe(3)-N(3)#5	92.4(3)
N(20)-Fe(1)-O(1)	180.0	N(21)#2-Fe(3)-N(3)#5	90.9(2)
N(9)#1-Fe(1)-O(1)	92.90(18)	N(21)-Fe(3)-N(3)#6	90.9(2)
N(9)-Fe(1)-O(1)	92.90(18)	N(21)#2-Fe(3)-N(3)#6	92.4(3)
N(10)#1-Fe(1)-O(1)	92.83(17)	N(3)#5-Fe(3)-N(3)#6	175.2(4)
N(10)-Fe(1)-O(1)	92.83(17)	N(21)-Fe(3)-N(18)#2	176.9(3)
N(15)-Fe(2)-N(15)#2	175.7(4)	N(21)#2-Fe(3)-	91.8(3)
N(15)-Fe(2)-N(19)	89.7(3)	N(18)#2	85.3(2)
N(15)#2-Fe(2)-N(19)	93.4(3)	N(3)#5-Fe(3)-N(18)#2	91.2(2)
N(15)-Fe(2)-N(19)#2	93.4(3)	N(3)#6-Fe(3)-N(18)#2	91.8(3)
N(15)#2-Fe(2)-	89.7(3)	N(21)-Fe(3)-N(18)	176.9(3)
N(19)#2	91.2(4)	N(21)#2-Fe(3)-N(18)	91.2(2)
N(19)-Fe(2)-N(19)#2	92.2(2)	N(3)#5-Fe(3)-N(18)	85.3(2)
N(15)-Fe(2)-N(6)#3	132.1(5)	N(3)#6-Fe(3)-N(18)	86.2(4)
C(34)-N(9)-Fe(1)	122.4(5)	N(18)#2-Fe(3)-N(18)	127.9(5)
C(35)-N(9)-Fe(1)	131.6(5)	C(17)-N(15)-Fe(2)	127.7(5)
C(13)-N(10)-Fe(1)	123.9(5)	C(18)-N(15)-Fe(2)	180.0
C(14)-N(10)-Fe(1)	131.1(5)	C(21)-N(20)-Fe(1)	148.0(7)
C(16)-N(18)-Fe(3)	149.8(7)	C(20)-N(21)-Fe(3)	

C(19)-N(19)-Fe(2)	

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+2   #2 -x,y,-z+1   #3 x-1/2,y-1/2,z

#4 -x+1/2,y-1/2,-z+1   #5 -x+1/2,y+1/2,-z+1

#6 x-1/2,y+1/2,z   #7 x+1/2,y-1/2,z

#8 x+1/2,y+1/2,z

Polymer 2			
Fe(1)-N(15)	2.186(2)	Fe(2)-N(19)#4	2.224(3)
Fe(1)-N(15)#1	2.186(2)	Fe(2)-N(19)	2.224(3)
Fe(1)-N(3)#2	2.196(3)	Fe(3)-N(11)#4	2.135(3)
Fe(1)-N(3)#3	2.196(3)	Fe(3)-N(11)	2.135(3)
Fe(1)-N(9)#1	2.199(3)	Fe(3)-N(8)#4	2.206(3)
Fe(1)-N(9)	2.199(3)	Fe(3)-N(8)	2.206(3)
Fe(2)-N(16)	2.150(3)	Fe(3)-N(12)	2.226(3)
Fe(2)-N(16)#4	2.151(3)	Fe(3)-N(12)#4	2.227(3)
Fe(2)-N(4)#5	2.209(2)		
Fe(2)-N(4)#6	2.209(2)		
N(15)-Fe(1)-N(15)#1	180.0	N(4)#5-Fe(2)-N(19)	85.20(10)
N(15)-Fe(1)-N(3)#2	92.80(9)	N(4)#6-Fe(2)-N(19)	91.58(9)
N(15)#1-Fe(1)-N(3)#2	87.20(9)	N(19)#4-Fe(2)-N(19)	90.72(14)
N(15)-Fe(1)-N(3)#3	87.20(9)	N(11)#4-Fe(3)-N(11)	90.78(16)
N(15)#1-Fe(1)-N(3)#3	92.80(9)	N(11)#4-Fe(3)-N(8)#4	89.41(11)
N(3)#2-Fe(1)-N(3)#3	180.0(2)	N(11)-Fe(3)-N(8)#4	178.97(11)
N(15)-Fe(1)-N(9)#1	88.36(10)	N(11)#4-Fe(3)-N(8)	178.97(11)
N(15)#1-Fe(1)-N(9)#1	91.64(10)	N(11)-Fe(3)-N(8)	89.41(11)
N(3)#2-Fe(1)-N(9)#1	91.88(10)	N(8)#4-Fe(3)-N(8)	90.42(15)
N(3)#3-Fe(1)-N(9)#1	88.12(10)	N(11)#4-Fe(3)-N(12)	94.07(10)
N(15)-Fe(1)-N(9)	91.64(10)	N(11)-Fe(3)-N(12)	90.34(10)
N(15)#1-Fe(1)-N(9)	88.36(10)	N(8)#4-Fe(3)-N(12)	90.65(9)
N(3)#2-Fe(1)-N(9)	88.12(10)	N(8)-Fe(3)-N(12)	84.91(10)
N(3)#3-Fe(1)-N(9)	91.88(10)	N(11)#4-Fe(3)-	90.34(10)
N(9)#1-Fe(1)-N(9)	180.0	N(12)#4	94.08(10)
N(16)-Fe(2)-N(16)#4	89.68(16)	N(11)-Fe(3)-N(12)#4	84.91(10)
N(16)-Fe(2)-N(4)#5	92.98(10)	N(8)#4-Fe(3)-	90.66(9)
N(16)#4-Fe(2)-N(4)#5	90.27(10)	N(12)#4	173.72(13)
N(16)-Fe(2)-N(4)#6	90.27(10)	N(8)-Fe(3)-N(12)#4	130.3(2)
N(16)#4-Fe(2)-N(4)#6	92.98(10)	N(12)-Fe(3)-N(12)#4	126.7(2)
N(4)#5-Fe(2)-N(4)#6	175.42(13)	C(2)-N(3)-Fe(1)#7	128.3(2)
N(16)-Fe(2)-N(19)#4	89.83(11)	C(1)-N(3)-Fe(1)#7	127.8(2)
N(16)#4-Fe(2)-	178.11(10)	C(15)-N(4)-Fe(2)#8	124.4(2)
N(19)#4	91.58(9)	C(16)-N(4)-Fe(2)#8	131.5(2)

N(4)#5-Fe(2)-N(19)#4	85.20(10)	C(17)-N(8)-Fe(3)	145.5(3)
N(4)#6-Fe(2)-N(19)#4	178.11(10)	C(12)-N(8)-Fe(3)	149.4(3)
N(16)-Fe(2)-N(19)	89.83(11)	C(23)-N(9)-Fe(1)	129.3(2)
N(16)#4-Fe(2)-N(19)	150.2(3)	C(19)-N(11)-Fe(3)	127.9(2)
C(38)-N(16)-Fe(2)	123.8(2)	C(21)-N(12)-Fe(3)	128.6(2)
C(35)-N(19)-Fe(2)	132.1(2)	C(25)-N(15)-Fe(1)	
C(36)-N(19)-Fe(2)		C(24)-N(15)-Fe(1)	

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+1/2,-z *#2 -x+1,-y+1,-z*

#3 x-1/2,y-1/2,z *#4 -x+1,y,-z+1/2*

#5 -x+1,y-1,-z+1/2 *#6 x,y-1,z* *#7 x+1/2,y+1/2,z*

#8 x,y+1,z

Polymer 3			
Fe(1)-O(1)#1	2.128(2)	Fe(1)-N(1)#1	2.170(2)
Fe(1)-O(1)	2.128(2)	Fe(1)-Cl(1)	2.5148(8)
Fe(1)-N(1)	2.170(2)	Fe(1)-Cl(1)#1	2.5148(9)
O(1)#1-Fe(1)-O(1)	180.0	N(1)-Fe(1)-Cl(1)	89.74(7)
O(1)#1-Fe(1)-N(1)	85.77(9)	N(1)#1-Fe(1)-Cl(1)	90.26(7)
O(1)-Fe(1)-N(1)	94.23(9)	O(1)#1-Fe(1)-Cl(1)#1	90.73(7)
O(1)#1-Fe(1)-N(1)#1	94.23(9)	O(1)-Fe(1)-Cl(1)#1	89.26(7)
O(1)-Fe(1)-N(1)#1	85.77(9)	N(1)-Fe(1)-Cl(1)#1	90.26(7)
N(1)-Fe(1)-N(1)#1	180.0	N(1)#1-Fe(1)-Cl(1)#1	89.74(7)
O(1)#1-Fe(1)-Cl(1)	89.27(7)	Cl(1)-Fe(1)-Cl(1)#1	180.0
O(1)-Fe(1)-Cl(1)	90.74(7)	Fe(1)-O(1)-H(1A)	110.0
C(7)-N(1)-Fe(1)	129.8(2)	Fe(1)-O(1)-H(1B)	126.3
C(10)-N(1)-Fe(1)	125.8(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+4/3,-y+5/3,-z+2/3 *#2 -x+y+1,-x+2,z*

#3 -y+2,x-y+1,z

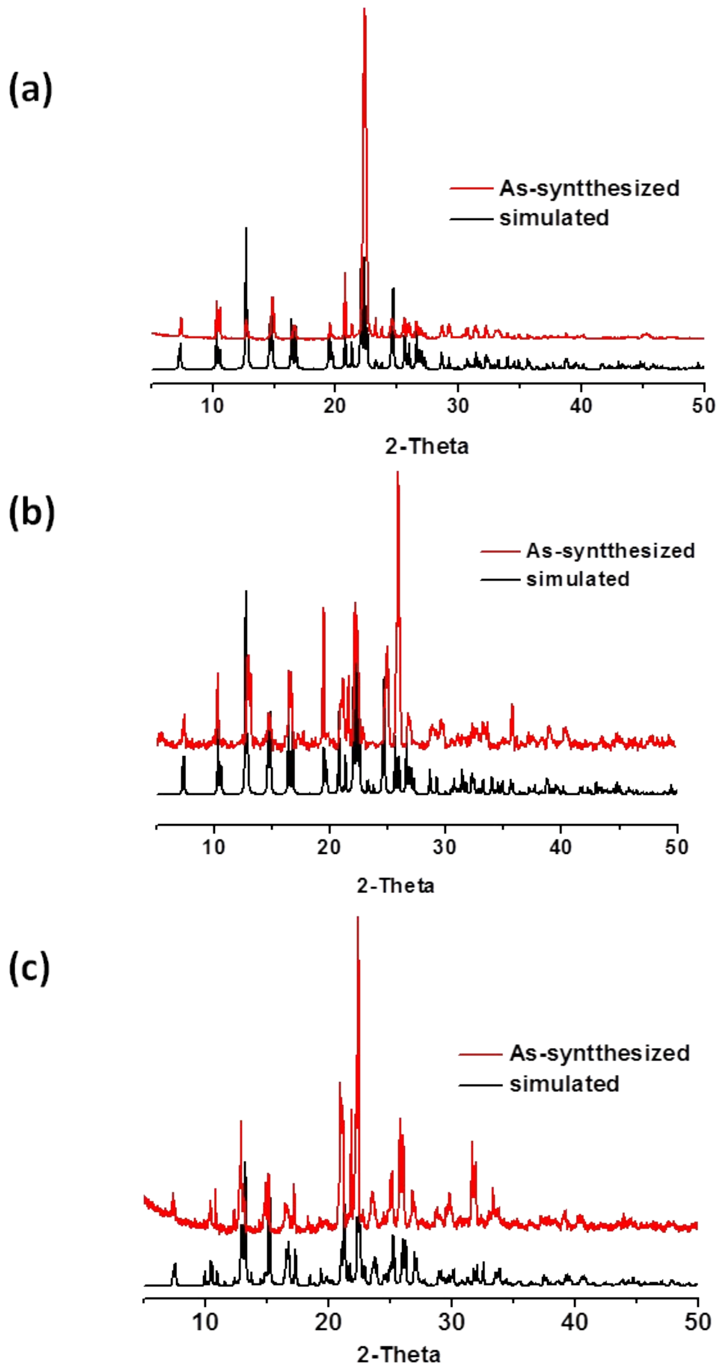

Fig S1. Experimental (red) and simulated (black) PXRD patterns of Polymer **1−3 (a-c)**

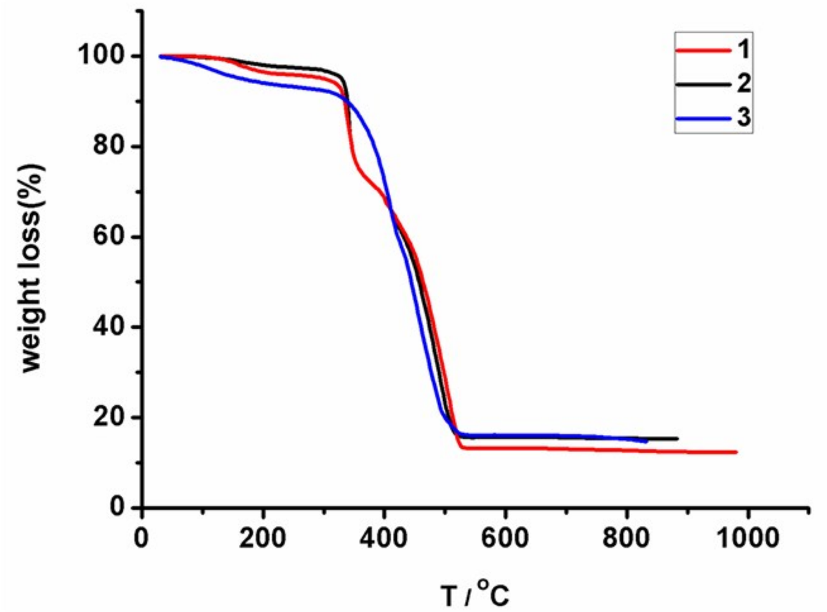

Fig S2. Thermogravimetric curve of Polymer **1**−**3**.

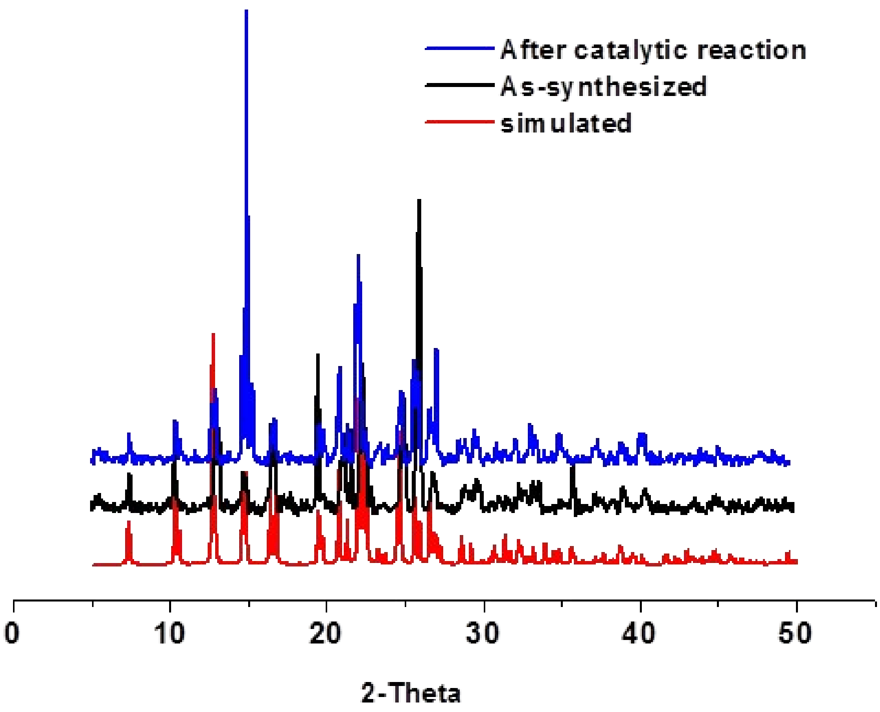

Fig S3. The PXRD diagram before and after the catalyst reaction for **1**

Table S3. ^{1}H NMR data of biphenyl compound **5a**-**5c**

Compounds	^{1}H NMR (400 MHz, $CDCl_3$)
Dipheny l (**5a**)	δ 7.44-7.58 (m, 6H, CHar), 7.78 (d, 4H, J = 8.1 Hz, CHar).
4, 4'-Dimethoxybiphenyl (**5b**)	δ3.81 (s, 6H, OCH_3), 6.88 (d, 4H, J = 8.5 Hz, CHar), 7.71 (d, 4H, J = 8.5 Hz, CHar).
4, 4'-Diethoxybiphenyl (**5c**)	δ1.37 (t, 6H, J = 7.0 Hz, CH_3), 4.03 (q, 4H, J = 7.0 Hz, CH_2), 6.86 (d, 4H, J = 8.5 Hz, CHar), 7.69 (d, 4H, J = 8.5 Hz, CHar).