Side-chain coordination polymers containing redox-active pendants: complexation of ferrocene-based bidentate ligands with $M(hfac)_2$ (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate, M = Mn, Ni, Cu, Zn) and CuX (X = I, Br)

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Coordination polymers with redox active pendants, {5-ferrocenylpyrimidine·$M(hfac)_2$}$_n$ [M = Mn (**1a**), Ni (**1b**), Cu (**1c**), Zn (**1d**)] and {5-ferrocenylpyrimidine·CuX}$_n$ [X = I (**2a**), Br (**2b**)], have been prepared and characterized. In complex **1c**, the Cu(II) ions are linked by the bridging ligands to form one-dimensional chains. This complex was shown to exhibit an antiferromagnetic intra-chain interaction, which was analyzed by the Bonner–Fisher model ($2J/k_B = -6.3$ K). Complex **2a** shows a two-dimensional sheet-like structure, in which one-dimensional chains, consisting of the Cu(I) ions and the ligands, are further bridged by iodide anions. These compounds show quasi-reversible redox processes of the ferrocenyl groups in the solid state.

Introduction

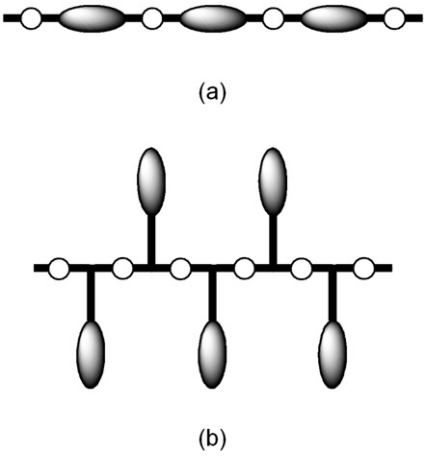
Syntheses of metallocene-based polymers or oligomers with conjugated or non-conjugated backbones have been extensively explored.[1] Metallocenes[1b] play important roles in the field of materials science, as components of catalysts,[2] molecular magnets,[3] and non-linear optical materials.[4] In particular, the redox activity of metallocenes leads to a variety of interesting electrical and photophysical phenomena.[5] Thus, metallocene-based polymers are interesting, but they are generally difficult to characterize structurally. We propose a method to construct well-defined, metallocene-based coordination *polymers* by applying the self-assembly approach. The design and synthesis of supramolecular coordination compounds constructed from multifunctional ligands and transition metals have been explored over the past decade.[6] Several intriguing coordination polymers involving ferrocenes have also been reported recently.[7]

Functional polymers can generally be classified, by reference to the positions of the functional groups, as either main-chain polymers or side-chain polymers (Scheme 1). Previously, we reported the synthesis of main-chain coordination polymers involving ferrocene units by using bidentate ligands of 1,1′-(4-dipyridinethio)ferrocene (**L3**) and 1,1′-(2-dipyridinethio)-ferrocene (**L4**) (Scheme 2).[8] In order to produce side-chain coordination polymers carrying ferrocene units as pendants, we designed simple ligands of 5-ferrocenylpyrimidine (**L1**) and ferrocenylpyrazine (**L2**) (Scheme 2), which are expected to act as bidentate ligands. In particular, the pyrimidine derivative **L1** may be interesting from the viewpoint of molecular magnetism.[9] However, we could isolate only *molecular* complexes of 1:2 M:L stoichiometry for both ligands in a previous study.[10] In the present study, ferrocene-containing 1:1 coordination polymers, {**L1**·$M(hfac)_2$}$_n$ (M = Mn, Ni, Cu, Zn, hfac = hexafluoroacetylacetonate) and {**L1**·CuX}$_n$ (X = I, Br), have been synthesized (Scheme 3). We report in this paper the preparation, structures, electrochemical properties and magnetic properties of these side-chain coordination polymers.

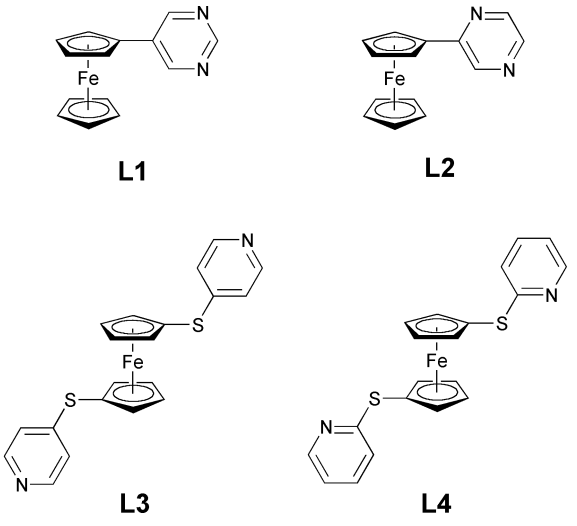
Results and discussion

Side-chain coordination polymer complexes {L1 · $M(hfac)_2$}$_n$

Reactions of ligand **L1** with equimolar amounts of $M(hfac)_2$ in heptane produced the 1:1 coordination polymers {**L1**·$M(hfac)_2$}$_n$ [M = Mn (**1a**), Ni (**1b**), Cu (**1c**), Zn (**1d**)]. Compounds **1a**–**1d** were confirmed to be isomorphous by comparing X-ray diffraction patterns. We have chosen $M(hfac)_2$ units in order to synthesize coordination polymers, although their reactions in diethyl ether result in the formation of 1:2 M:L stoichiometry *molecular* complexes.[10] We have found that performing the reaction in heptane leads to the formation of coordination polymers. Fig. 1 shows the structure of {**L1**·$Cu(hfac)_2$}$_n$ (**1c**), consisting of one-dimensional zigzag chains, which are extended along the *a* axis. Crystal data are given in Table 1



Scheme 1 Schematic illustrations of the two main architectures for functional polymers: main-chain polymers (a) and side-chain polymers (b). The open and closed circles represent functional moieties and linkers, respectively.

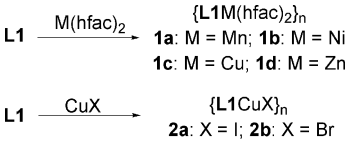


Scheme 2 Structural formula of ferrocene-based ligands **L1**–**L4**.

and selected bond distances and angles in Table 2. There are two crystallographically independent $Cu(hfac)_2$ units within the chain, which are joined alternatingly by the ligands: ···L···Cu(1)···L···Cu(2)···L···. The ligand acts as a bidentate ligand and coordinates to the trans positions of $Cu(hfac)_2$. Thus, the chain structure can be regarded as a one-dimensional polymer carrying ferrocene pendant groups. The dihedral angle between the Cp ring and the pyrimidine ring of the ligand is 29.0(2)°. The intra-chain and inter-chain Cu···Cu separations are *ca.* 6.0 and 11.4 Å, respectively, and there are no inter-chain interactions of any note.

The coordination geometries around the two crystallographically independent metal centers in **1c** are slightly different, although both coordination environments are distorted octahedral. Around Cu(1), elongation of the Cu(1)–O(1) [2.189(3) Å] bond relative to the Cu(1)–O(2) [2.042(3) Å] bond is observed; the Jahn–Teller distortion occurs along the O(1)–Cu(1)–O(1*) axis. Similar coordination environments with elongated O–Cu–O geometries have been reported for several $Cu(hfac)_2$ derivatives.[8a,11] Consistent with this, the IR spectrum of **1c** shows two carbonyl stretching bands of the hfac moieties at 1651 and 1639 cm^{-1}. On the other hand, around the metal center of Cu(2), the Jahn–Teller distortion occurs along the N(2)–Cu(2)–N(2*) axis. The Cu(2)–N(2) bond length of 2.497(3) Å is rather long, while the Cu(1)–N(1) bond length of 2.026(3) Å is a typical value.[8a,11] The Cu(2)–O(3) and Cu(2)–O(4) bonds have similar lengths, 1.957(3) and 1.949(2) Å, respectively. Local coordination environments similar to this are found in $Cu(hfac)_2$(pyrazine)[12] and $[Cu(hfac)_2]_3$-(μ-tmpyz) (tmpyz = 2,3,5-trimethylpyrazine)[9e] in which Cu–N = 2.529(4) and 2.537(10) Å, respectively. It is interesting to note that the local structure of **1c** is similar to that of $[\{Cu(hfac)_2\}_3(\mu\text{-mpym})_2]$ (mpym = 5-methylpyrimidine), which is a trinuclear *molecular* complex.[13] The mpym complex involves three trans-coordinated $Cu(hfac)_2$ moieties that are linked by two mpym ligands, and hence the complex can be regarded as a partial structure of **1c**.

From the viewpoint of molecular magnetism, the coordination polymers of pyrimidine derivatives have been a focus of attention, because the pyrimidine unit can act as a ferromagnetic linker.[9] Thus, the magnetic behavior of the present com-



Scheme 3 General reaction scheme.

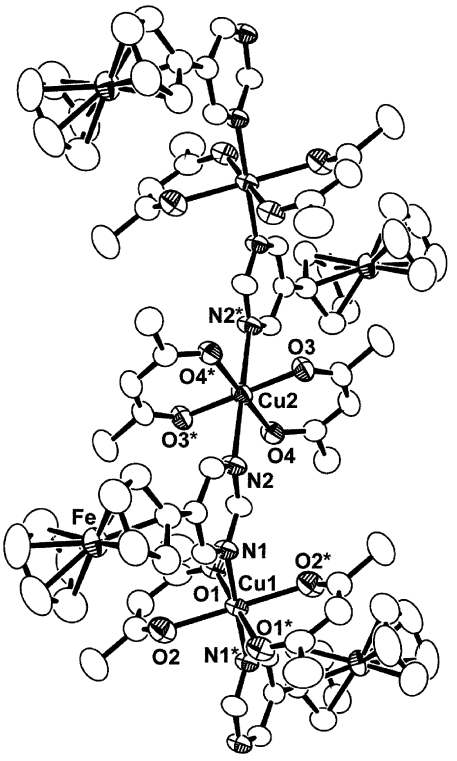


Fig. 1 ORTEP representation (50% thermal probability ellipsoids) of the one-dimensional zigzag chain in complex **1c**. Hydrogen and fluorine atoms are omitted for clarity.

plex, involving one-dimensional chains of Cu(II) ions, is of interest. The magnetic susceptibility was measured using a SQUID susceptometer. Plots of χ and χT *vs.* T are shown in Fig. 2. At room temperature, χT has a value that is consistent with magnetically isolated $S = 1/2$ spins. The χT value decreases monotonically down to 10 K, which indicates the presence of weak antiferromagnetic interactions between the Cu(II) ions. Since the magnetic interaction operates between equally spaced Cu^{II} ions in the polymeric chain, the Bonner–Fisher model was employed to analyze the data. The spin Hamiltonian is expressed as eqn. (1) and the theoretical molar susceptibility is given in eqn. (2) where $x = |J|/k_BT$.

Table 1 Crystallographic data for **1a** and **2a**

Compound	**1c**	**2a**
Chemical formula	$C_{24}H_{14}N_2O_4F_{12}CuFe$	$C_{14}H_{12}N_2FeCuI$
Formula weight	741.76	454.56
Crystal system	Triclinic	Monoclinic
a/Å	11.437(6)	12.515(2)
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
b/Å	12.002(4)	9.537(2)
c/Å	10.862(7)	12.683(2)
α/°	90.70(4)	
β/°	90.22(5)	112.54(1)
γ/°	112.06(3)	
U/Å^3	1381(1)	1398.1(4)
T/K	296	296
Z	2	4
μ/cm^{-1}	14.10	47.51
Measured reflections	6649	3559
Observed reflections	6330	3213
R_{int}	0.016	0.014
R_1[a]	0.045	0.068
R_w[a]	0.144	0.097

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2 Selected bond lengths (Å) and bond angles (°) in **1c** and **2a** with estimated standard deviations in parentheses

1c			
Cu(1)–O(1)	2.189(3)	Cu(1)–O(2)	2.042(3)
Cu(1)–N(1)	2.026(3)	Cu(2)–O(3)	1.957(3)
Cu(2)–O(4)	1.949(2)	Cu(2)–N(2)	2.497(3)
N(1)–Cu(1)–N(1)$^{\#1}$	180	N(1)–Cu(1)–O(1)	88.9(1)
N(1)–Cu(1)–O(2)	90.4(1)	N(2)–Cu(2)–N(2)$^{\#2}$	180
N(2)–Cu(2)–O(3)	81.3(1)	N(2)–Cu(2)–O(4)	90.2(1)
2a			
Cu–I	2.6213(7)	Cu$^{\#3}$–I	2.6621(6)
Cu–N(1)	2.079(3)	Cu–N(2)$^{\#4}$	2.082(3)
Cu–I–Cu$^{\#3}$	67.44(2)	I–Cu–I$^{\#3}$	112.56(2)
I–Cu–N(1)	107.7(1)	I–Cu–N(2)$^{\#4}$	111.9(1)
N(1)–Cu–N(2)$^{\#4}$	111.3(1)		

Symmetry codes: $^{\#1}$ $-x+2, -y+1, z+2$; $^{\#2}$ $-x+2, -y+2, z+2$; $^{\#3}$ $-x+1, -y, -z+2$; $^{\#4}$ $-x+1, y+1/2, -z+3/2$.

$$\hat{H} = -2J\sum_i S_i \cdot S_{i+1} \quad (1)$$

$$\chi = \frac{Ng^2\mu_B^2}{k_B T}\frac{0.25 + 0.14995x + 0.30094x^2}{1 + 1.9862x + 0.68854x^2 + 6.0626x^3} \quad (2)$$

The best-fit parameters are $g = 2.037$ and $2J/k_B = -6.3$ K. The antiferromagnetic behavior is consistent with the crystal structure in which there are two crystallographically independent Cu(hfac)$_2$ molecules in the unit cell; the pyrimidine moiety coordinates to the Cu(1) and Cu(2) ions in equatorial-equatorial and axial-axial fashions, respectively (*vide ante*). It has been shown that the magnetic interaction between the copper ions becomes antiferromagnetic for equatorial-equatorial coordination, whereas it becomes ferromagnetic for axial-axial or axial-equatorial coordinations.[9] For example, a copper(II)-pyrimidine coordination polymer, [(pyrimidine)$_2$·Cu(NO$_3$)$_2$]$_n$, shows ferromagnetic interactions of $2J/k_B = +1.8$ K,[9e] whereas [{9-(5-pyrimidinyl)anthracene}·Cu(NO$_3$)$_2$·(solvent)]$_n$, with only equatorial-equatorial coordination, shows strong antiferromagnetic interactions between copper(II) ions of $2J/k_B = -55$ K.[9b] Thus, the origin of the small antiferromagnetic interaction in **1c** can be attributed to the alternation of equatorial-equatorial and axial-axial coordination. However, it is noteworthy that an intra-chain interaction, although small, could be observed in the present complex, because the main-chain coordination polymer [**L3**·Cu(hfac)$_2$]$_n$ exhibited only negligible intermolecular magnetic interactions (Weiss temperature $\theta = -0.06$ K).[8a]

Extended side-chain coordination polymer complexes {L1 · CuX}$_n$

Reaction of **L1** with equimolar amounts of CuX produced the 1:1 coordination polymers {**L1**·CuX}$_n$ [X = I (**2a**), Br (**2b**)].

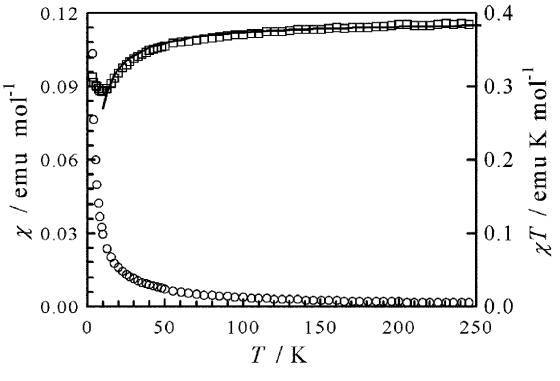


Fig. 2 Temperature dependence of χT (○) and χ (△) for complex **2c**; the solid line is the best fit using the Bonner–Fisher model.

We have chosen copper(I) halides because they often lead to extended coordination structures.[14] An ORTEP view of **2a** is shown in Fig. 3, with selected bond lengths and angles being listed in Table 2. Compound **2a** is an extended side-chain type coordination polymer. In this complex, the copper ions are linked by the **L1** ligands to form one-dimensional units carrying ferrocene pendant groups. These chains are further bridged by iodide anions, to form a two-dimensional extended structure. We could not carry out a structure determination of **2b** but it is most likely to be a coordination polymer as well, because of the 1:1 stoichiometry.

The coordination around the copper atom in **2a** is tetrahedral with an N(1)–Cu–I angle of 107.7(1)°, and Cu–N(1) and Cu–I bond lengths of 2.079(3) and 2.6213(7) Å, respectively. The copper atom lies on the inversion center. The two ferrocenyl rings are located *ca.* 1.64 Å away from the iron atom and show a synclinal (eclipsed) conformation. The dihedral angle between the cyclopentadienyl ring and the pyrimidine ring of the ligand is 28.5(2)°. The two-dimensional sheet extends along the *bc* plane. The distances between the copper ions *via* the ligand and *via* the halide bridge are *ca.* 5.97 and 2.93 Å, respectively. The distance between the nearest iron ions in the sheet is *ca.* 7.59 Å.

Among the many CuX coordination polymers reported to date, assembled structures similar to the present case are found in a few complexes, such as [CuBr(3,4′-bpy)] (bpy = bipyridine),[15] [Cu$_2$I$_2$(dtpcp)$_2$·THF] (dtpcp = 2,11-dithia[3,3]-paracyclophane)[16] and [(CuBr)$_2$(μ-pym)$_2$] (pym = pyrimidine).[14c] The CuI complex of pyrimidine, [(CuI)$_2$(μ-pym)], shows a structure that is very different from that of complex **1c**. The complex exhibits 2:1 stoichiometry and contains parallel stair-step polymeric chains interlinked by pyrimidines.[17] In complex **1c**, the bulky ferrocenyl moiety may prevent the CuI moieties from linking to each other.

Solid-state electrochemistry

The coordination complexes were shown to exhibit redox processes in the solid state based on the redox activities of the

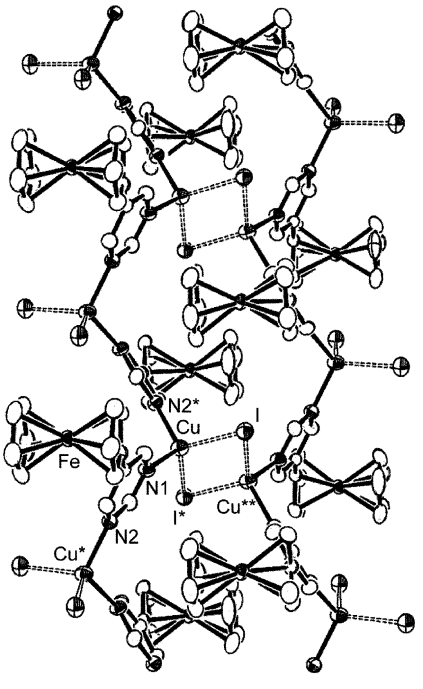


Fig. 3 ORTEP representation (50% thermal probability ellipsoids) of the expanded side-chain complex **2a**. Hydrogen atoms are omitted for clarity.

Table 3 Solid-state redox potentials from cyclic voltammetry (in V *vs.* $FeCp_2/FeCp_2^+$)

Compound	$E_{1/2}$	E_{pa}	E_{pc}
L1	0.10	0.31	−0.11
1a	0.06	0.09	0.02
1b	0.06	0.13	0.01
1c	0.05	0.07	0.03
1d	0.07	0.11	0.04
2a	0.06	0.10	0.02
2b	0.08	0.24	−0.10

ferrocenyl group. Compound **L1** shows a half-wave potential in the solid state at $E_{1/2} = 0.10$ (*vs.* solid state $FeCp_2/FeCp_2^+$), which is slightly shifted from that in solution.[8a,10] As listed in Table 3, the $E_{1/2}$ values for **1a**–**1d** and **2a**–**2b** are observed at around 0.06 V, which corresponds to the redox processes of the ferrocenyl moiety. These potentials show negative shifts with respect to those of **L1** in the solid state, which may be attributable to the relative stabilization of the oxidized state in the complexes. Similar tendencies have been reported for the redox processes of $[\mathbf{L3}{\cdot}M(hfac)_2]_n$ (M = Mn, Cu, Zn).[8a] Thus, no significant differences could be observed in the redox properties between the molecular complexes[10] and the coordination polymers. In addition to the redox waves of the ferrocenyl groups, the copper(II) derivatives **1c** show another redox wave at $E_{1/2} \sim -0.2$ V in the solid state, which is assignable to the redox processes of the $Cu(hfac)_2$ unit.

Conclusion

Complexation of the ferrocene-based ligand **L1** with $M(hfac)_2$ produces one-dimensional compounds, while an extension of the dimensionality is further achieved by the use of copper halides. As we have demonstrated here, incorporating functional groups into the pendants of coordination polymers by designing appropriate ligands is a promising approach to the synthesis of functional assembled complexes. Structurally well-defined coordination polymers obtained by the self-assembly method will be good models of relevant oligomers or polymers, for which structure determinations are generally difficult.

Experimental

General

All reagents and solvents were commercially available except for 5-ferrocenylpyrimidine, which was synthesized by following the literature procedure.[10] Infrared spectra were recorded on a JASCO FT-IR 230 spectrometer as KBr pellets in the 4000–400 cm^{-1} range. Cyclic voltammograms were recorded with an ALS/chi electrochemical-analyzer model 600A. Solid-state voltammograms[8] were measured by using a carbon-paste working electrode; well-ground mixtures of each bulk sample and carbon paste (graphite and mineral oil) were placed in a cavity on a Teflon rod and connected to a platinum wire. A platinum-wire counter electrode and an Ag/AgCl reference electrode were used. Measurements were performed by using a three-electrode system in 0.1 mol dm^{-3} $NaClO_4$ aqueous solutions at a scan rate of 0.2 V s^{-1}, in the range of −0.3 to 0.8 V. Magnetic susceptibilities were measured by means of a Quantum Design MPMS-2 SQUID susceptometer in the 2–300 K temperature range at a constant field of 1 T. Elemental analyses were performed on a Perkin–Elmer 2400CHN Elemental Analyzer.

Syntheses

$\{\mathbf{L1}\cdot Mn(hfac)_2\}_n$ (1a). A mixture of **L1** (26 mg, 1.0×10^{-2} mmol) and $Mn(hfac)_2{\cdot}2H_2O$ (50 mg, 1.0×10^{-2} mmol) was refluxed for 1 h in heptane (20 mL). After cooling the red solution to room temperature, an orange-red powder of **1a** formed (57 mg, yield *ca.* 70%). FT-IR (cm^{-1}): 3129 w, 3097 w, 1647 s, 1560 m, 1533 m, 1491 s, 1255 s, 1211 s, 1147 s, 800 m, 665 s, 586 s. Anal. calcd. (%) for $C_{24}H_{14}N_2O_4F_{12}FeMn$: C, 39.32; H, 1.92; N, 3.82; found: C, 41.33; H, 1.74; N 4.21. The sample was contaminated by **L1**. Calc. (%) for $(\mathbf{1a})_{0.8}(\mathbf{L1})_{0.2}$: C, 40.95; H, 2.06; N, 4.17. Ligand **L1** was hard to remove from the reaction product because of their similar solubility.

$\{\mathbf{L1}\cdot Ni(hfac)_2\}_n$ (1b). 1b was prepared as for **1a** using **L1** (26 mg, 1.0×10^{-2} mmol) and $Ni(hfac)_2{\cdot}2H_2O$ (50 mg, 1.0×10^{-2} mmol). An orange-red powder was obtained in 67% yield (51 mg). FT-IR (cm^{-1}): 3129 w, 3097 w, 1645 s, 1556 m, 1531 m, 1259 s, 1209 s, 1149 s, 1101 m, 798 m, 673 s, 588 m. Anal. calcd. (%) for $C_{24}H_{14}N_2O_4F_{12}NiFe$: C, 39.12; H, 1.91; N, 3.80; found: C, 39.39; H, 1.50; N 3.59.

$\{\mathbf{L1}\cdot Cu(hfac)_2\}_n$ (1c). 1c was prepared as for **2a** using **L1** (26 mg, 1.0×10^{-2} mmol) and $Cu(hfac)_2{\cdot}H_2O$ (50 mg, 1.0×10^{-2} mmol). Reddish-brown crystals in 75% yield (57 mg) were obtained. FT-IR (cm^{-1}): 3129 w, 3097 w, 1651 m, 1639 m, 1532 m, 1496 m, 1481 m, 1260 s, 1216 s, 1181 m, 1159 s, 1141 s, 1107 m, 801 m, 668 m, 595 m. Anal. calcd. (%) for $C_{24}H_{14}N_2O_4F_{12}CuFe$: C, 38.86; H, 1.90; N, 3.78; found: C, 38.87; H, 1.98; N 3.72.

$\{\mathbf{L1}\cdot Zn(hfac)_2\}_n$ (1d). 1d was prepared as for **1a** using **L1** (26 mg, 1.0×10^{-2} mmol) and $Zn(hfac)_2{\cdot}2H_2O$ (50 mg, 1.0×10^{-2} mmol). An orange-red powder was obtained in 84% yield (64 mg). FT-IR (cm^{-1}): 3129 w, 3097 w, 1651 m, 1639 m, 1532 m, 1496 m, 1481 m, 1260 s, 1216 s, 1181 m, 1159 s, 1141 s, 1107 m, 801 m, 668 m, 595 m. Anal. calcd. (%) for $C_{24}H_{14}N_2O_4F_{12}FeZn$: C, 38.77; H, 1.90; N, 3.77; found: C, 38.96; H, 1.56; N 3.65.

$\{\mathbf{L1}\cdot CuI\}_n$ (2a). To a solution of CuI (20 mg, 1.0×10^{-2} mmol) in 2 mL of acetonitrile, a solution of **L1** (26 mg, 1.0×10^{-2} mmol) in 4 mL of methanol was added. After standing for a few days, orange-red crystals were formed, which were suitable for X-ray analysis. The product was obtained in 65% yield (30 mg). FT-IR (cm^{-1}): 3099 w, 3078 w, 3062 w, 3036 w, 1579 s, 1481 m, 1433 m, 1404 s, 1174 m, 1101 w, 837 m, 816 m, 706 m, 509 m, 492 m, 476 m. Anal. calcd. (%) for $C_{14}H_{12}N_2FeCuI$: C, 36.99; H, 2.66; N, 6.16; found: C, 37.09; H, 2.71; N, 6.10.

$\{\mathbf{L1}\cdot CuBr\}_n$ (2b). 2b was prepared as for **2a** using **L1** (26 mg, 1.0×10^{-2} mmol) and CuBr (14 mg, 1.0×10^{-2} mmol). A golden-yellow powder in 72% yield (29 mg) was obtained. FT-IR (cm^{-1}): 3076 m, 3035 w, 1577 m, 1559 m, 1478 m, 1436 s, 1404 s, 1387 m, 1174 s, 1104 m, 1000 m, 849 m, 820 m, 705 s, 492 m, 479 m, 433 m. Anal. calcd. (%) for $C_{14}H_{12}N_2BrFeCu$: C, 41.26; H, 2.97; N, 6.87; found: C, 41.51; H, 3.02; N, 6.86.

Crystallographic measurements

X-Ray diffraction data for single crystals were collected on a Rigaku AFC-5S four-circle diffractometer equipped with a graphite crystal and incident beam monochromator using Mo Kα radiation ($\lambda = 0.71073$ Å) at 296 K. Crystal data, data collection parameters and analysis statistics for **1c** and **2a** are listed in Table 1. Selected bond angles and bond lengths are given in Table 2. Powder X-ray measurements were performed on a Rigaku RAD-IIB. Compounds **1a**–**1d** were confirmed to

be isomorphous by comparing X-ray diffraction patterns, while compounds **2a** and **2b** show different powder patterns. All calculations were performed using the teXsan crystallographic software package.[18] These structures were solved by the direct method (SIR 92[19]) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and an absorption correction was applied (ψ-scan). The hydrogen atoms were inserted at the calculated positions and allowed to ride on their respective parent atoms. Structures were drawn using ORTEP software.[20]

CCDC reference numbers 191984 (**1c**) and CCDC 198076 (**2a**). See http://www.rsc.org/suppdata/nj/b2/b212518h/ for crystallographic files in CIF or other electronic format.

Acknowledgements

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