Synthesis, Crystal Structure and Magnetic Properties of a Mn(II) Fluorenedicarboxylate Complex

Xiu-Hua Zhao[a], Ya-Yun Zhao[b], Mei-Qin Zha[b], and Xing Li[a,b]

[a] Faculty of Science, Ningbo University, Ningbo, Zhejiang 315211, P. R. China

[b] Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo, Zhejiang 315211, P. R. China

Reprint requests to Prof. Dr. Xing Li. Fax: Int. +574/87600869. E-mail: lix905@126.com or lixing@nbu.edu.cn

A new Mn(II) metal-organic framework, $[Mn(DFDC)(phen)]_n$ (**1**) (where $H_2DFDC = 9,9$-diethylfluorene-2,7-dicarboxylic acid, phen = 1,10-phenanthroline), was solvothermally synthesized and characterized by single-crystal and powder X-ray diffraction (PXRD), elemental and thermal analysis, IR, UV/Vis spectroscopy, fluorescence and magnetic measurements. Single-crystal X-ray analysis reveals that **1** exhibits a three-dimensional coordination polymer structure. The compound crystallizes in the orthorhombic space group *Pnna* with $a = 9.1215(9)$, $b = 26.436(3)$, $c = 10.2428(10)$ Å, $V = 2469.9(4)$ Å^3, $Z = 4$, final $wR2 = 0.1323$ for 2825 reflections. The Mn(II) ion is coordinated by four oxygen atoms from four different H_2DFDC ligands and two nitrogen atoms from one phen ligand in an octahedral coordination geometry. The compound shows ferromagnetic coupling behavior and has high thermal stability up to 420 °C.

Key words: Solvothermal Synthesis, Crystal Structure, Fluorenedicarboxylate, Mn(II) Complex

Introduction

In recent years, much interest has been focused on design and synthesis of metal-organic frameworks (MOFs) with novel structural motifs due to not only their fascinating topological diversities [1 – 5], but also their potential applications for luminescence [6], magnetic effects [7], catalysis [8], and gas storage and separation [9]. It has been documented that π-conjugated systems containing carboxylate groups are versatile ligands for the fabrication of MOFs, in which the carboxylates can exhibit different coordination geometries [10 – 12].

A fluorene with rigid biphenyl moieties possesses active hydrogen atoms on 2-, 7- and 9- positions, which are easily replaced by chromophoric functional groups for connection to metal ions [13 – 15]. Previous studies have shown that fluorene or its derivatives functionalized by carboxyl groups can form a vast variety of metal-organic coordination compounds [16 – 20]. However, there are still many insurmountable challenges involving the preparation of the complexes with directed dimensional networks, and the choice of inorganic or organic components exhibiting distinct physical or chemical properties. In the work discussed in this paper we have synthesized 9,9-diethylfluorene-2,7-dicarboxylic acid (H_2DFDC) as an organic linker and used 1,10-phenanthroline (phen) as a terminal ligand to construct MOFs. A manganese complex has been prepared, namely, $[Mn(DFDC)(phen)]_n$ (**1**), which has been characterized by IR, TGA, fluorescence, and powder and single-crystal X-ray diffraction studies.

Experimental Section

Materials and methods

All starting materials were of analytical grade and used without further purification. Elemental analyses of C, H and N were performed with an EA1110CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectrum was recorded ($400 – 4000$ cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. UV/Vis spectra were recorded ($200 – 800$ nm region) on a TU-1901 UV/Vis spectrophotometer. Thermal analyses were carried out in air with a heating rate of

$10\,^{\circ}\text{C min}^{-1}$ on a STA449C integration thermal analyzer. The solid-state fluorescence spectra were measured on a LS 50B luminescence spectrometer (Perkin-Elmer). The magnetic susceptibility measurement was performed on a Quantum Design SQUID magnetometer (Quantum Design Model MPMS-7) in the temperature range $2 - 300$ K.

*Synthesis of 2,7-dibromo-9,9-diethylfluorene (**L1**, Scheme 1)*

To 2,7-dibromofluorene (Aldrich, 1.30 g, 4.0 mmol) were added powdered potassium hydroxide (1.12 g, 20.0 mmol), potassium iodide (0.068 g), and dimethyl sulfoxide (DMSO, 25 mL), and the mixture was cooled to $0\,^{\circ}\text{C}$; ethyl bromide (1.0 mL, 1.17 g, 10 mmol) was added dropwise over 30 min. The mixture turned from light-green to red and light-purple. After the temperature had increased to $20\,^{\circ}\text{C}$, the mixture was left overnight with stirring, and then poured into water to precipitate the crude product; 1.39 g (yield 90 %). The product was purified by column chromatography on silica gel by elution with petroleum ether (**L1**, 1.08 g, 70 %). – ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 7.53$ (dd, $J = 2$, 7.2 Hz, 2H, PhH), 7.47 (d, $J = 2$ Hz, 2H, PhH), 7.46 (d, $J = 1.6$ Hz, 2H, PhH), 2.00 (q, 4H, CH$_2$), 0.32 (t, 6H, CH$_3$). – IR (KBr, cm^{-1}): $v = 3071$(w), 2954(s), 2916(s), 2869(m), 2848(m), 2359(s), 2333(m), 1888(w), 1732(m), 1596 (s), 1573(s), 1453(s), 1444(vs), 1216(s), 1398(m), 1375(s), 1339(w), 1247(s), 1217(w), 1185 (w), 1130(w), 1107(m), 1051(s), 1004(m), 924(m), 888(m), 868(vs), 815(vs), 772(s), 734 (m), 665(m).

*Synthesis of 9,9-diethylfluorene-2,7-dicarboxylic acid (**L2**, Scheme 1)*

The sample of **L1** (4.6 g, 12 mmol) was dissolved in 140 mL of dry THF, and the solution was cooled to $-78\,^{\circ}\text{C}$. *n*-Butyllithium (15 mL of a 36 mmol solution) was added over a period of 30 min, and then the reaction mixture was allowed to warm to $-50\,^{\circ}\text{C}$; a large excess of dry CO$_2$ gas was introduced for 60 min, and then the cooling bath was removed. The suspension was stirred for 24 h at room temperature; then it was acidified with a 10 % HCl solution. After separation, the aqueous layer was extracted with dichloromethane (3×50 mL). The combined organic layers
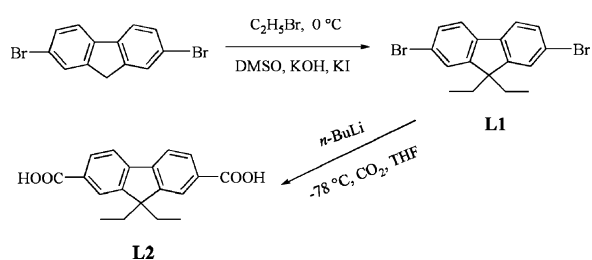
were washed with brine and dried over Na$_2$SO$_4$. After removal of the solvent, the residue was purified by column chromatography on silica gel by elution with hexane (**L2**, 3.4 g, 92 %). – ^{1}H NMR (DMSO, 400 MHz): $\delta = 7.99$ (m, $J = 8.4$, 7.6, 1.2 Hz, 6H, PhH), 2.09 (q, $J = 7.2$, 14.4 Hz, 4H, CH$_2$), 0.16 (t, $J = 7.6$ Hz, 6H, CH$_3$). – ^{13}C NMR (DMSO, 400 MHz): $\delta = 168.16$ (COOH), 151.16, 144.82, 131.11, 129.54, 124.52, 121.45, 56.66 (CH$_2$), 32.16 (CH$_3$), 8.96. – IR (KBr, cm^{-1}): $v = 3080$(w), 2978(m), 2957(s), 2876(m), 2667(s), 2552(s), 2361(s), 1681(vs), 1611 (s), 1582(w), 1470(s), 1447(vs), 1409(vs), 1378(m), 1343(w), 1322 (w), 1282(s), 1255(m), 1141 (m), 1086(m), 928 (m), 905(m), 835(s), 761(vs), 743(s), 659(m), 599 (m).

*Preparation of [Mn(DFDC)(phen)]$_n$ (**1**)*

A mixture of MnCl$_2$·4H$_2$O (0.01 mmol), 1,10-phen (0.01 mmol) and H$_2$DFDC (0.005 mmol) was placed in a vial containing H$_2$O (0.1 mL), EtOH (0.1 mL) and MeOH (0.5 mL). The vial was sealed, heated at $80\,^{\circ}\text{C}$ for 72 h, and allowed to cool to room temperature. Crystals suitable for X-ray diffraction were collected by filtration, washed with diethyl ether and dried in air. Yield: 45 % (based on Mn). – Elemental anal. for **1** (C$_{31}$H$_{24}$MnN$_2$O$_4$): calcd. C 68.51, H 4.46, N 5.15; found C 68.56, H 4.41, N 5.28. – IR (KBr, cm^{-1}): $v = 3434$(m), 3049(w), 2967(s), 2934(w), 2911(m), 2878(w), 2847(w), 1591(vs), 1559 (vs), 1514(s), 1497(w), 1479(w), 1456(m), 1424(vs), 1384(vs), 1348(w), 1313(w), 1253(s), 1143 (vs), 1100(s), 1081(m), 1046(w), 915(s), 864(vs), 846(vs), 780(vs), 756(s), 728(vs), 666(w), 634(w), 609(w).

X-Ray diffraction data collection and refinement

Data collection for **1** was performed on a Bruker-AXS diffractometer with graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using the program S ADABS [21]. The structure was solved by Direct Methods, the metal atoms were located from the E-maps, and the other non-hydrogen atoms were derived from the successive difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters by full-matrix least-squares techniques and all hydrogen atoms with isotropic displacement parameters on F^2 using S HELXTL [22]. The crystallographic data of complex **1** are listed in Table 1 and selected bond lengths and angles in Table 2.

Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Focus X-ray diffractometer using CuK_α radiation. The calculated PXRD patterns were produced using the program S HELXTL-X POW.

CCDC 794221 contains the supplementary crystallographic data for this paper. These data can be obtained free

Scheme 1. Synthetic route to the organic ligands **L1** and **L2**.

Table 1. Crystal structure data for **1**.

Formula	$C_{31}H_{24}MnN_2O_4$
M_r	543.46
Crystal size, mm^3	$0.28 \times 0.16 \times 0.11$
Crystal system	orthorhombic
Space group	*Pnna*
a, Å	9.1215(9)
b, Å	26.436(3)
c, Å	10.2428(10)
V, Å^3	2469.9(4)
Z	4
$D_{calcd.}$, g cm^{-3}	1.46
$\mu(MoK_\alpha)$, mm^{-1}	0.6
$F(000)$, e	1124
hkl range	$-11 \le h \le 11$, $-33 \le k \le 34$, $-13 \le l \le 11$
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.652
Refl. measured / unique / R_{int}	11295 / 2825 / 0.0394
Param. refined	173
$R(F)/wR(F^2)$ (all refls.)	0.0584 / 0.1323
GoF (F^2)	1.116
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.62 / -0.41

Table 2. Selected bond lengths (Å) and bond angles (deg) for **1** with estimated standard deviations in parentheses[a].

Distances			
Mn1–O1	2.1197(16)	Mn1–O2^{ii}	2.1355(15)
Mn1–N1	2.3568(19)		
Angles			
O1–Mn1–N1^i	82.24(7)	O1–Mn1–N1	93.80(7)
O2^{ii}–Mn1–N1^i	166.22(6)	O2^{ii}–Mn1–N1	95.66(6)
O1^i–Mn1–O1	175.18(10)	N1^i–Mn1–N1	70.58(9)
O1^i–Mn1–O2^{ii}	84.80(6)	O1–Mn1–O2^{ii}	98.38(6)

[a] Symmetry codes: i $= -x + 1/2$, $-y + 1$, z; ii $= -x$, $-y + 1$, $-z + 1$.

Results and Discussion

Crystal and molecular structure

Compound **1** is stable in air and insoluble in common solvents. The homogeneity of samples of **1** were checked by powder X-ray diffraction (see below).

Single-crystal X-ray diffraction revealed a three-dimensional framework in orthorhombic crystals of space group *Pnna* with $Z = 4$. As shown in Fig. 1, complex **1** is composed of one DFDC dianion, one phen ligand and one Mn(II) cation. The coordination environment around the Mn(II) ion is shown in Fig. 2. It exhibits an octahedral coordination geometry of four oxygen atoms from four different DFDC^{2-} ligands and
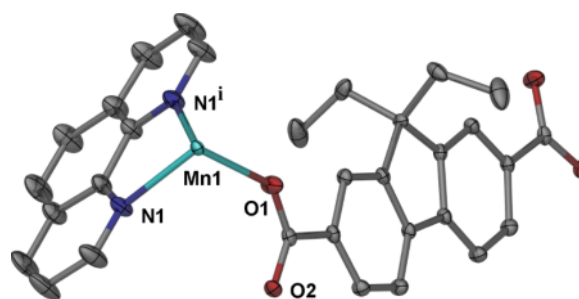

Fig. 1 (color online). The structural unit of **1** with displacement ellipsoids at 50 % probability level.

two nitrogen atoms from one phen ligand. O1, O1^i occupy the axial positions, N1, N1^i, O2^{ii}, O2^{iii} are located in the equatorial plane. Mn–O distances range from 2.120(2) to 2.136(2) Å, and the Mn–N distance is 2.357(2) Å.

In complex **1**, the DFDC^{2-} ligand acts as tetradentate unit connecting four Mn (II) ions by its carboxylate groups (Fig. 3). The centroid-to-centroid separation of the nearest two benzene rings of the phen ligands is 3.933 Å, which implies weak π-π stacking interactions.

Powder X-ray diffraction (PXRD)

In an attempt to confirm the homogeneity of the material synthesized, we have measured the PXRD pattern and compared the results with the powder pattern as calculated on the basis of the single-crystal data. As shown in Fig. 4, the experimental diffraction peaks of
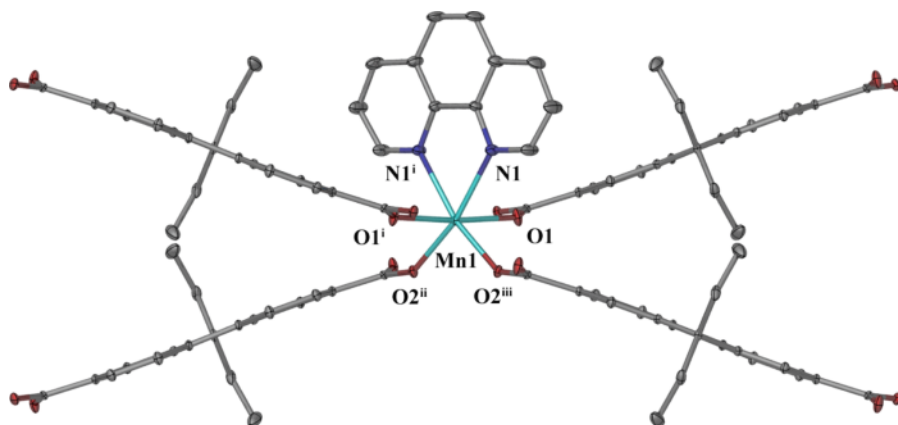
Fig. 2 (color online). The full coordination environment of the Mn(II) ions in **1**. Symmetry codes: i = −x + 1/2, −y + 1, z; ii = −x, −y + 1, −z + 1; iii = x + 1/2, y, −z + 1.
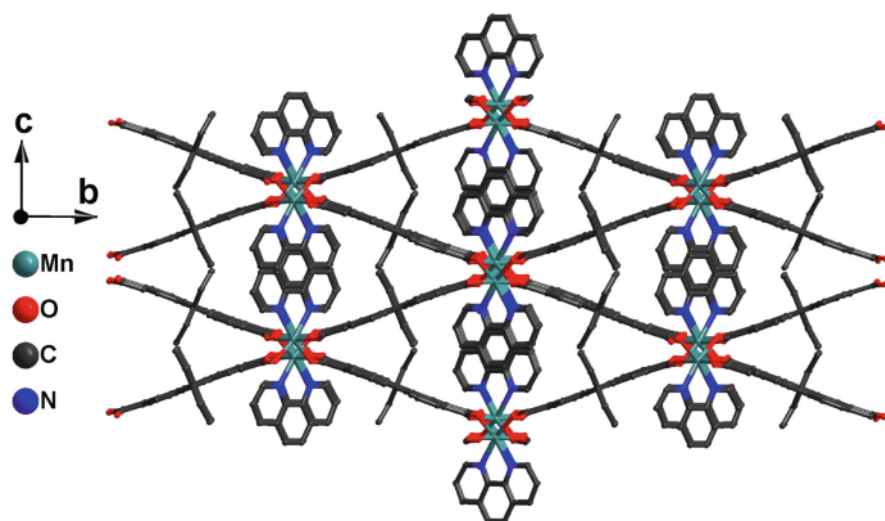

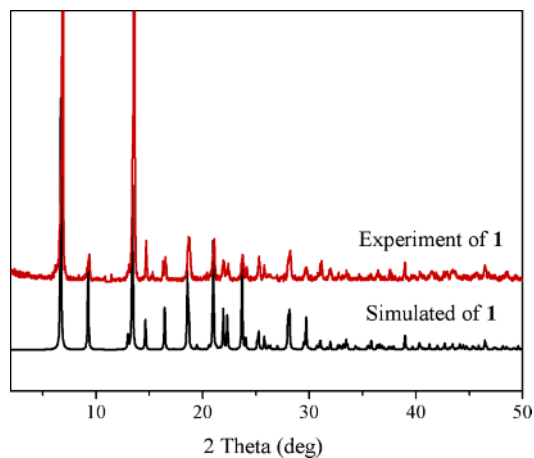Fig. 3 (color online). A view of the 3D structure of compound **1**.

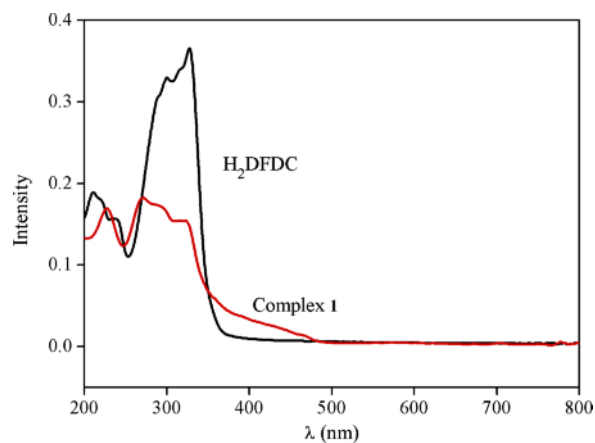Fig. 4 (color online). Experimental and simulated powder XRD patterns of **1**.

Fig. 5 (color online). UV/Vis absorption spectra of the H_2DFDC ligand and **1** (solid state).

the bulk samples are almost consistent with those of the single-crystal data indicating that the product obtained is almost pure on the level of X-ray powder diffraction.

UV/Vis absorption and photoluminescence spectra

The UV/Vis spectra of **1** and H_2DFDC at room temperature (solid state) are shown in Fig. 5. The ligand exhibits high-energy bands at 220 and 327 nm due to π-π* transitions. The less intense absorptions at 220 and 327 nm are tentatively ascribed to the admixture of metal-to-ligand transitions [17].

The solid-state photoluminescence spectra of **1** and H_2DFDC have been measured at room temperature. As shown in Fig. 6, the H_2DFDC ligand exhibits strong fluorescence emission at 400 nm upon photoexcitation at 300 nm, while complex **1** hardly exhibits any photoluminescence, indicating that the auxiliary ligand (phen) and the Mn(II) ion quench the excited state of **1** [18].

Thermal analysis

The thermal analysis experiment was carried out to determine the thermal stability of the complex, which is an important aspect for metal-organic frameworks [15, 16]. The experiment was performed in air from room temperature to 800 °C at a heating rate of 10 °C min^{-1} (Fig. 7). The DTA curve shows two exothermic peaks centered at 459 and 497 °C [23], corresponding to combustion of part of the organic component. The weight loss of 38.6 % (calcd: 33.2 %) corresponds to one phen ($C_{12}H_8N_2$) molecule per formula
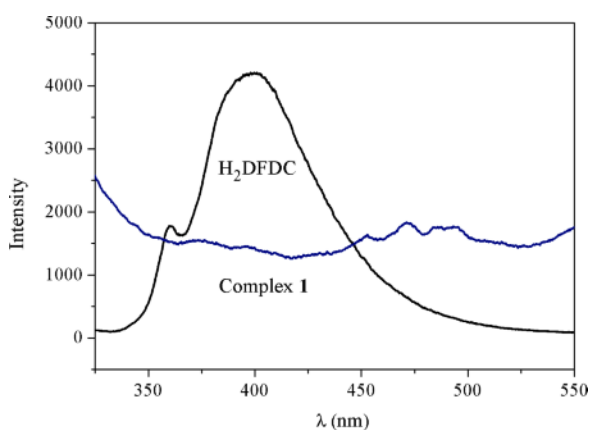
unit [Mn(DFDC)(phen)] from 420 to 494 °C, along with the decomposition of the DFDC. The final decomposed product (at 800 °C) was presumably MnO_2 based on the remaining weight (observed: 15.8 %; calcd: 16.0 %). TG-DTA shows that complex **1** has high thermal stability up to 420 °C.

Magnetic properties

The temperature-dependent susceptibility of **1** was measured on a SQUID magnetometer in the 2 – 300 K temperature range. The $\chi_m T$ and χ_m *vs.* T plots for **1** are shown in Fig. 8. Upon increasing the temperature, from 2 to 50 K the χ_m value sharply drops and slowly decreases from 50 to 300 K. The effective moment (μ_{eff}) of 4.94 μ_B at room temperature is lower than the expected one (5.92 μ_B) for high-spin uncoupled Mn(II) ions [24 – 30]. The $\chi_m T$ value increases
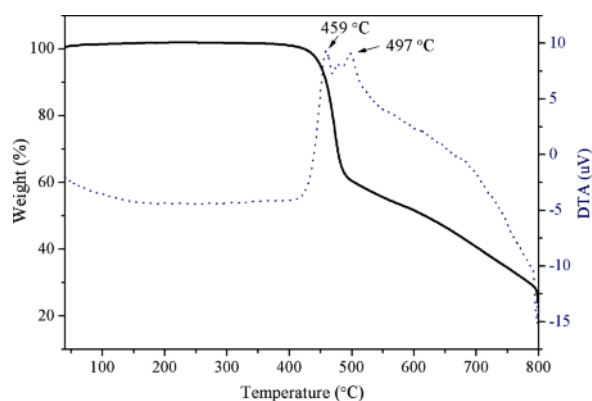

Fig. 7 (color online). TG-DTA curve of the title complex **1** (weight: solid line; DTA: dotted line).
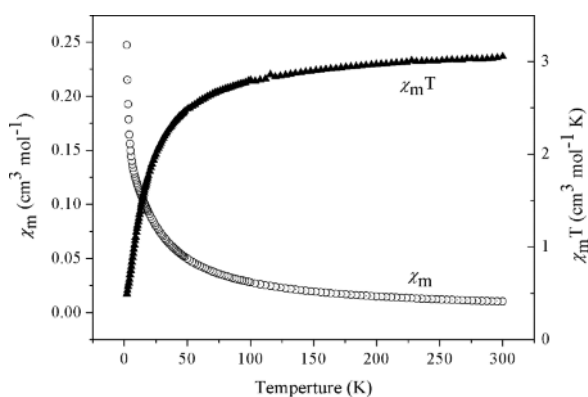

Fig. 8. Temperature dependence of the magnetic susceptibility of **1**.

Fig. 6 (color online). The photoluminescence emission spectra of the H_2DFDC ligand and **1** (solid state).

sharply from 28 to 51.8 K, and then more slowly reaching a maximum of 3.05 cm^3·mol^{-1}·K at 300 K showing ferromagnetic coupling [24].

Conclusion

In this work, a three-dimensional metal-organic framework containing Mn(II) ions, 9,9-diethylfluorene-2,7-dicarboxylate ligands (DFDC^{2-}) and 1,10-phenanthroline as auxilliary ligand has been synthesized by solvothermal reaction. The DFDC^{2-} ligand acts as tetradentate unit bridging four Mn

(II) ions by its carboxylate groups. Compound **1** shows high thermal stability (up to 420 °C) and has ferromagnetic coupling. These features enable it to be an excellent candidate for functional materials.

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