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Syntheses, structures, and luminescent properties of two cadmium(II) and manganese(II) coordination polymers based on the 11-fluoro-dipyrido[3,2-a:2′,3′-c]-phenazine ligand

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Abstract Two new coordination polymers, namely [Cd(4-nitro-1,2-BDC))(L)] (**1**) and [Mn(1,3-BDC)(L)] (**2**) (4-nitro-1,2-BDC = 4-nitro-1,2-benzenedicarboxylate, 1,3-BDC = 1,3-benzenedicarboxylate, and L = 11-fluoro-dipyrido[3,2-a:2′,3′-c]phenazine), have been synthesized from phen derivative L and dicarboxylates under hydrothermal conditions. Their crystal structures have been determined by single-crystal X-ray diffraction analyses and further characterized by physicochemical and spectroscopic methods. Both compounds **1** and **2** show 1D chain structures. However, neighboring chains of **2** are further joined together by $\pi \cdots \pi$ interactions. Furthermore, the compound **1** shows good fluorescence properties in solid state at room temperature.

Introduction

In the past decades, coordination polymers have been intensely studied because of their various applications including gas storage, ion exchange, catalysis, and fluorescence technology [1–3]. It is well known that judicious selection of ligands as basic building blocks is of great importance during the syntheses of the coordination polymers because slight structural changes in organic building blocks, such as length, flexibility, and symmetry, can dramatically change the structural motifs of coordination polymers [4–6]. So far, a large number of supramolecular architectures have been prepared based on metal ions which can yield various coordination geometries as connecting centers, plus polyfunctional organic ligands such as pyridine-type N-donors and carboxylate-type O-donors as linkers [7–12]. It is well known that 2,2′-bipyridyl-like ligands, for example, 1,10-phenanthroline (phen), are bidentate chelating ligands, which have been widely used in the construction of the polymeric framework. However, its derivative 11-fluoro-dipyrido[3,2-a:2′,3′-c]phenazine (L) (Fig. 1), as a good candidate for construction of supramolecular architectures, has received less attention [13].

In this work, we report the syntheses, crystal structures, elemental analyses, thermogravimetric analysis, and luminescent properties of two novel coordination polymers based on L and different dicarboxylates, [Cd(4-nitro-1,2-BDC))(L)] (**1**) and [Mn(1,3-BDC)(L)] (**2**) (4-nitro-1,2-BDC = 4-nitro-1,2-benzenedicarboxylate and 1,3-BDC = 1,3-benzenedicarboxylate). Their structures have been determined by single-crystal X-ray diffraction analyses, IR spectra, and elemental analyses. In addition, the TGA and luminescent properties of the complexes have also been investigated in the solid state at room temperature.

Experimental

All the materials were of analytical reagent grade and used as received without further purification. Elemental analysis was carried out with a Perkin-Elmer 240C analyzer. Thermal

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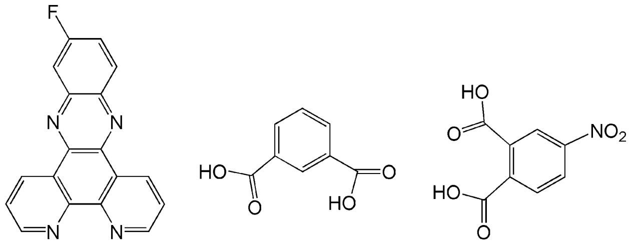


L **1,3-BDC** **4-nitro-1,2-BDC**

Fig. 1 The ligands used in this work

stability experiments were performed on a TG SDT2960 thermal analyzer from room temperature to 800 °C under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The photoluminescent properties were measured on a FLSP920 Edinburgh Fluorescence Spectrometer.

Preparation of [Cd(4-nitro-1,2-BDC)(L)] (**1**)

A mixture of $CdCl_2 \cdot 2H_2O$ (1 mmol, 0.192 g), L (1 mmol, 0.300 g), and 4-nitro-1,4-H_2BDC (1 mmol, 0.211 g) was dissolved in 12 ml distilled water, followed by addition of triethylamine until the pH value of the system was adjusted to between 5 and 6. The resulting solution was sealed in a 23 ml Teflon-lined stainless-steel autoclave and heated at 426 K for 6 d under autogeneous pressure. After the mixture had been cooled to room temperature at a rate of 10 °C h^{-1}, crystals of **1** were obtained. Yield 0.168 g (27 %). Anal. for $C_{26}H_{12}CdFN_5O_6$ (%): calcd. C 50.2, H 2.0, N 11.3; found C 50.4, H 1.3, N 11.3.

Preparation of [Mn(1,3-BDC)(L)] (**2**)

The preparation of **2** was similar to that of **1** except that $MnCl_2 \cdot 4H_2O$ (0.1 mmol, 0.020 g) and 1,3-H_2BDC (0.1 mmol, 0.017 g) were used instead of $CdCl_2 \cdot 2H_2O$ (1 mmol, 0.192 g) and 4-nitro-1,4-H_2BDC (1 mmol, 0.211 g) of **1**. Crystals of **2** suitable for single-crystal X-ray diffraction analysis were collected by filtration, washed several times with distilled water, and dried in air at ambient temperature. Yield 0.009 g (18 %). Anal. for $C_{26}H_{13}FMnN_4O_4$ (%): calcd. C 60.1, H 2.5, N 10.8; found C 60.2, H 2.4, N 10.9.

X-ray crystallography

Single crystal of compounds **1** and **2** was mounted on a Bruker Smart CCD using Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator at room temperature. All structures were solved by the direct method and successive Fourier difference syntheses and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms using SHELXS-97 [14] and SHELXL-97 [15], respectively. Carbon-bound H-atoms were placed in calculated positions (C–H 0.93 Å) and were included in the refinement in the riding model approximation, with U(H) set to 1.2U(C). The F atoms are disordered over two positions in 0.63(1):0.37 ratio for **1** and 0.70(1):0.30 ratio for **2**. The nitro group in **1** is disordered over two positions in a 1:1 ratio in respect of the O atoms. The details of the crystal structures and refinements are summarized in Table 1. Selected bond lengths and angles of **1** and **2** are given in Table 2.

Results and discussion

Crystal structure of compound **1**

As shown in Fig. 2, the asymmetric unit of **1** contains one Cd(II) atom, one L ligand, and one 4-nitro-1,2-BDC anion. The central Cd(II) atom is six-coordinated by four carboxylate atoms from three different 4-nitro-1,4-BDC anions and two nitrogen atoms from one L ligand in an octahedral sphere. The Cd–O distances vary from 2.247(2) to 2.247(2) Å, and the Cd–N distances are 2.405(3) and 2.384(3) Å, respectively (Table 2), which are very close to those found in a similar coordination polymer $[Cd_2(IP)_2(TBZ)_2(H_2O)_2] \cdot (H_2O)$ (IP = isophthalate and TBZ = thiabendazole) [16]. Notably, each 4-nitro-1,2-BDC anion bridges three Cd(II) atoms. In this way, the 4-nitro-1,2-BDC anions bridge neighboring Cd(II) atoms to

Table 1 Crystal data and structure refinements for compounds **1** and **2**

	1	2
Empirical formula	$C_{26}H_{12}CdFN_5O_6$	$C_{26}H_{13}FMnN_4O_4$
Fw	621.81	519.34
Crystal system	Triclinic	Monoclinic
Space group	*P* −1	C 2/c
a [Å]	7.3062(5)	15.6305(16)
b [Å]	12.9494(8)	15.3462(15)
c [Å]	14.0305(9)	18.3424(19)
α [°]	62.905(1)	90
β [°]	75.104(1)	109.256(2)
γ [°]	84.085(1)	90
Volume [Å^3]	1141.89(13)	4153.6(7)
Z	2	8
D_c (g/cm^3)	1.808	1.661
GOF	1.021	0.973
Reflns collected/unique	6229/4418	13092/4084
R_{int}	0.0121	0.0475
R1 [$I > 2\sigma(I)$]	0.0315	0.0553

Table 2 Selected bond lengths [Å] and angles [°] for **1** and **2**

Compound **1**			
Cd(1)–N(2)	2.405(3)	Cd(1)–N(5)	2.384(3)
Cd(1)–O(1)	2.323(2)	Cd(1)–O(2)^{i}	2.247(2)
Cd(1)–O(3)	2.420(3)	Cd(1)–O(4)^{ii}	2.333(3)
O(2)^{i}–Cd(1)–O(1)	90.04(8)	O(2)^{i}–Cd(1)–O(4)^{ii}	80.97(9)
O(1)–Cd(1)–O(4)^{ii}	125.26(9)	O(2)^{i}–Cd(1)–N(5)	116.19(10)
O(1)–Cd(1)–N(5)	146.16(9)	O(4)^{ii}–Cd(1)–N(5)	82.02(10)
O(2)^{i}–Cd(1)–N(2)	92.12(10)	O(1)–Cd(1)–N(2)	89.86(9)
O(4)^{ii}–Cd(1)–N(2)	143.91(10)	N(5)–Cd(1)–N(2)	69.34(10)
O(2)^{i}–Cd(1)–O(3)	165.11(10)	O(1)–Cd(1)–O(3)	77.54(8)
O(4)^{ii}–Cd(1)–O(3)	99.39(9)	N(5)–Cd(1)–O(3)	78.45(10)
N(2)–Cd(1)–O(3)	95.98(9)		
Compound **2**			
Mn(1)–O(1)	2.269(3)	Mn(1)–O(2)	2.221(3)
Mn(1)–O(3)^{i}	2.088(3)	Mn(1)–O(4)^{ii}	2.120(3)
Mn(1)–N(1)	2.304(3)	Mn(1)–N(4)	2.339(3)
O(3)^{i}–Mn(1)–(4)^{ii}	101.51(11)	O(3)^{i}–Mn(1)–O(2)	91.00(11)
O(4)^{ii}–Mn(1)–O(2)	99.62(13)	O(3)^{i}–Mn(1)–O(1)	141.72(11)
O(4)^{ii}–Mn(1)–O(1)	104.32(11)	O(2)–Mn(1)–O(1)	57.26(10)
O(3)^{i}–Mn(1)–N(1)	120.20(11)	O(4)^{ii}–Mn(1)–N(1)	89.49(11)
O(2)–Mn(1)–N(1)	145.18(11)	O(1)–Mn(1)–N(1)	87.94(10)
O(3)^{i}–Mn(1)–N(4)	80.25(11)	O(4)^{ii}–Mn(1)–N(4)	156.88(11)
O(2)–Mn(1)–N(4)	103.41(13)	O(1)–Mn(1)–N(4)	86.65(11)
N(1)–Mn(1)–N(4)	70.34(11)		

Symmetry transformations used to generate equivalent atoms: for **1** (i) $1-x, 1-y, 2-z$; (ii) $2-x, 1-y, 2-z$; for **2** (i) $1-x, 1-y, 1-z$; (ii) $x, 1-y, 1-z$

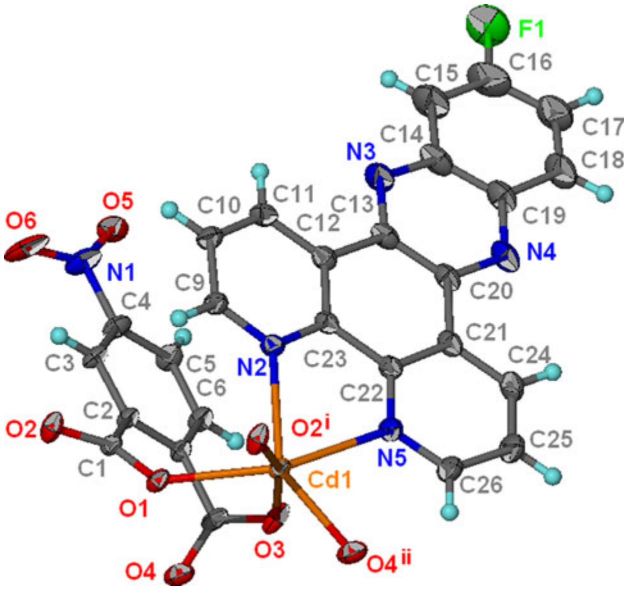


Fig. 2 View of the coordination environment of Cd(II) atom of the complex **1**. All the hydrogen atoms are omitted for clarity

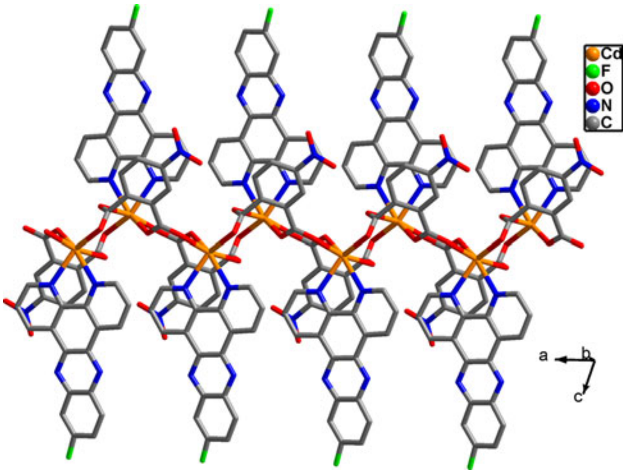


Fig. 3 View of the 1D chain structure of **1**

form a 1D chain structure (Fig. 3). The L ligands are alternately attached on both sides of the chains (Fig. 3).

Crystal structure of compound 2

As illustrated in Fig. 4, the asymmetric unit of **1** contains one Mn(II) atom, one L ligand, and one 1,3-BDC anion. Each Mn(II) atom is five-coordinated by four carboxylate oxygen atoms from two different 1,3-BDC ligands, and two nitrogen atoms from one L ligand in a distorted octahedral coordination sphere. Three carboxylate oxygen atoms (O1, O2, and O3^{i}) and one nitrogen atom (N1) constitute the plane of the octahedra, and the additional carboxylate oxygen atom (O4^{ii}) and the nitrogen atom (N4) are at the axis of the octahedra. The Mn–O bond lengths vary from 2.088(3) to 2.269(3) Å, and the Mn–N distances are 2.304(3) and 2.339(3) Å. Each 1,3-BDC ligand bridges three Mn(II) atoms. In this way, the 1,3-BDC ligands bridge neighboring Mn(II) atoms to form a 1D chain structure (Fig. 5). The L ligands are attached on both sides of the chain in pairs (Fig. 6). In addition, the L ligands from neighboring chains are paired through strong π–π interactions to result in a fascinating 2D supramolecular layer (Fig. 6).

Thermogravimetric analysis (TGA) was performed to examine the thermal stability of compounds **1** and **2** (Fig. 7). The crushed single-crystal samples were heated up to 800 °C under N_2 gas at a heating rate of 10 °C min^{-1}. The compound **1** is thermally stable up to around 288 °C. The first weight loss corresponds to the release of 4-nitro-1,2-BDC anion in the temperature range of 288–400 °C (obsd 31.5 %, calcd 33.6 %). The second weight loss from 405 to 642 °C corresponds to the decomposition of L ligand (obsd 47.6 %, calcd 48.3 %). The remaining weight may be attributed to the formation of CdO (obsd 21.1 %, calcd 20.6 %). The compound **2** begins to decompose at

Fig. 4 View of the coordination environment of Mn(II) atom of the complex **2**. All the hydrogen atoms are omitted for clarity

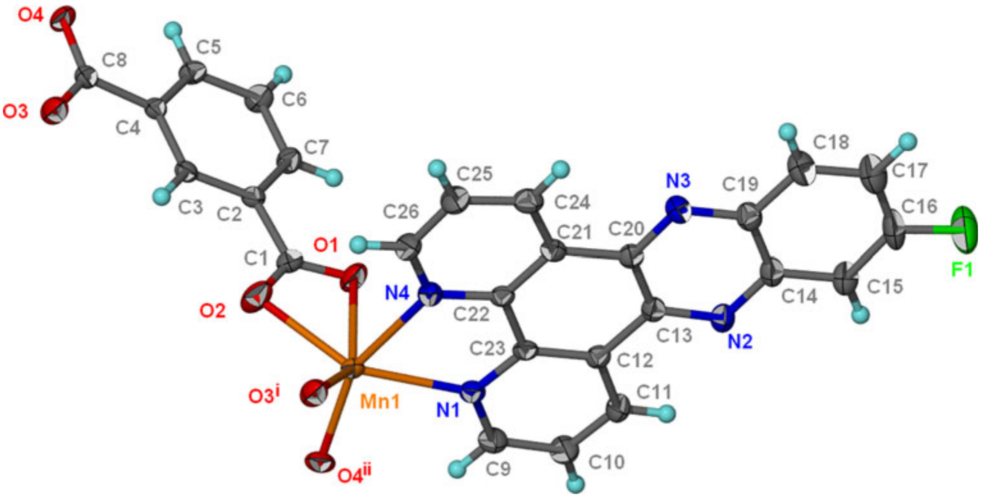
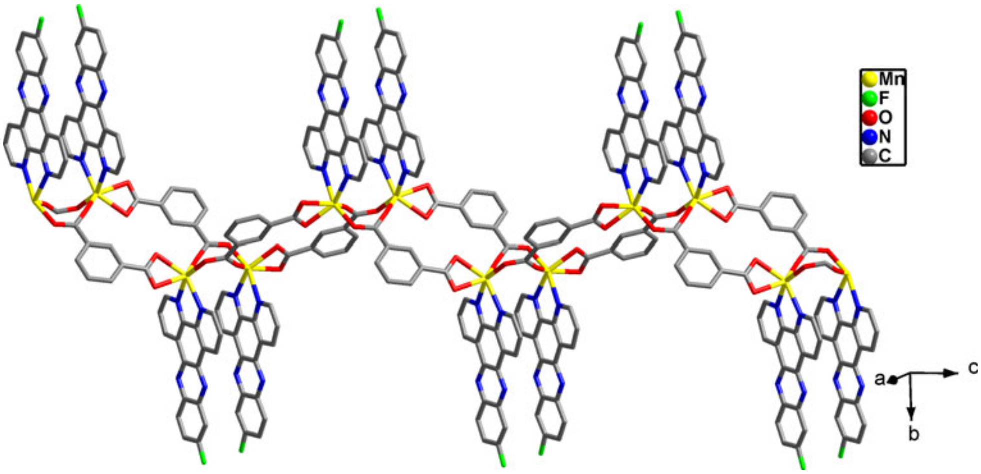


Fig. 5 View of the 1D chain structure of **2**



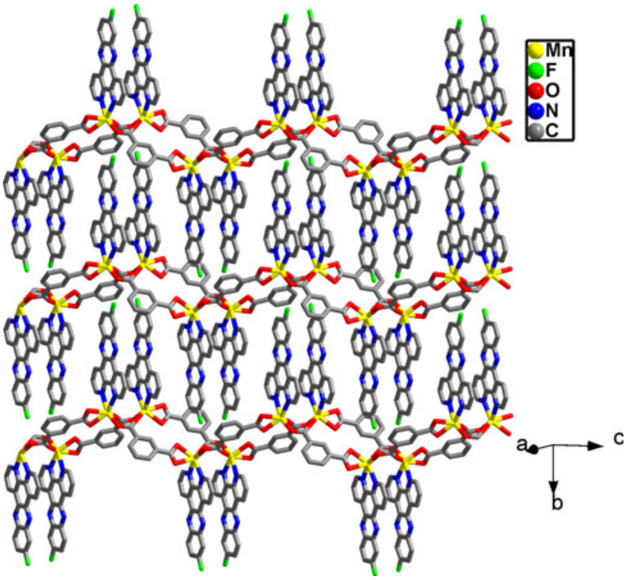


Fig. 6 View of the 2D supramolecular layer constructed by π–π interactions in **2**

175 and ends above 628 °C. The weight loss is attributed to both the 1,3-BDC anion and L ligand (obsd 86.0 %, calcd 89.4 %). However, it is difficult to determine these weight losses accurately as these processes are overlapped with the weight losses due to the dissociation of the 1,3-BDC anion and L ligand. The remaining weight may be attributed to the formation of MnO (obsd 14.0 %, calcd 13.7 %).

It is well known that coordination polymers with d^{10} metals show interesting luminescent properties. Therefore, the luminescent properties of the free organic ligands and compound **1** have been investigated in the solid state at room temperature (Fig. 8). The free L and 4-nitro-1,2-H_2BDC show emission bands centered at 495 and 545 nm, respectively, which can be attributed to the π^*–n or π^*–π transitions as previously reported [4]. Compound **1** shows an emission band at 555 nm ($\lambda_{ex} = 325$ nm). This emission is similar to that of the 4-nitro-1,2-H_2BDC ($\lambda_{em} = 545$ nm). Therefore, the emission of **1** should originate from the 4-nitro-1,2-H_2BDC ligand.

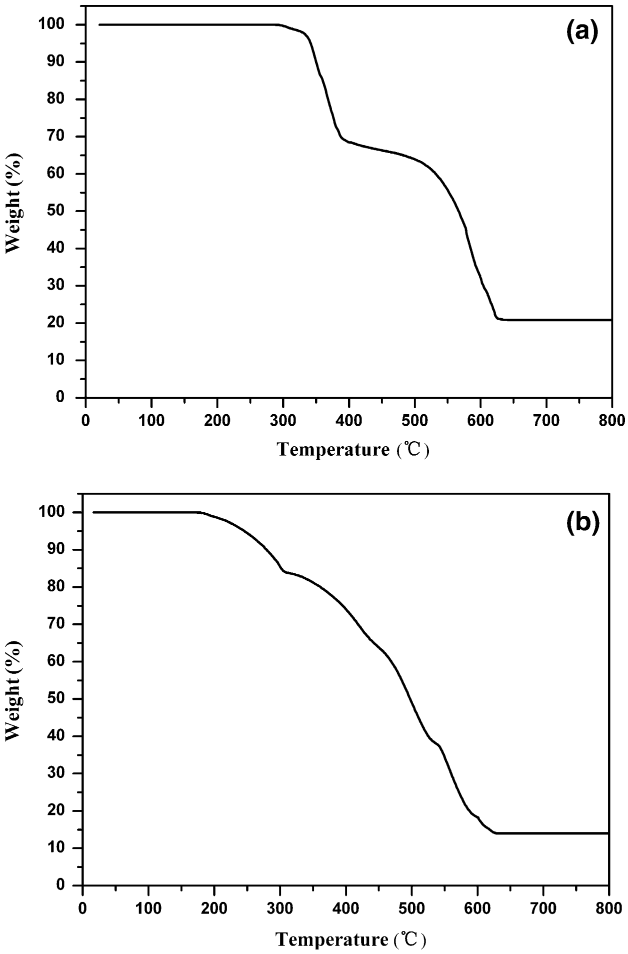


Fig. 7 TG curves of **1** (**a**) and **2** (**b**)

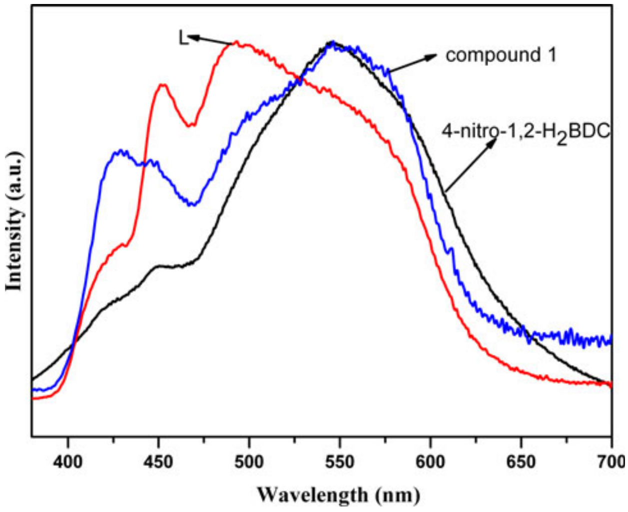


Fig. 8 Emission spectra of L, 4-nitro-1,2-BDC, and compound **1** in solid state at room temperature

Conclusion

Two new Cd(II) and Mn(II) coordination polymers constructed from N-donor ligand L and different aromatic polycarboxylate anions have been prepared under hydrothermal conditions. Both compounds **1** and **2** show 1D chain structures. However, neighboring chains of **2** are further joined together by $\pi \cdots \pi$ interactions. Furthermore, the compound **1** shows good fluorescence properties in the solid state at room temperature. It is anticipated that more metal compounds containing the phen derivatives and aromatic polycarboxylates will be synthesized.

Supplementary materials

CCDC 911677 and 911678 for compounds **1** and **2** contain the supplementary crystallographic data. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via deposit@ccdc.cam.ac.uk.

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