Homochiral zinc phosphonates with layered and open framework structures using polycarboxylate as second linkers†

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Reactions of zinc sulfate and (*R*)- or (*S*)-(1-phenylethylamino)methylphosphonic acid (pempH$_2$) in the presence of 1,4-benzenedicarboxylic acid (H$_2$bdc) result in homochiral enantiomers (*R*)- and (*S*)-[Zn$_4$(pempH)$_4$(bdc)$_2$]·2H$_2$O (**1**). When H$_2$bdc is replaced by 1,2,4,5-benzenetetracarboxylic acid (H$_4$btec), enantiomers (*R*)- and (*S*)-[Zn$_3$(pempH)$_2$(btec)(H$_2$O)$_2$]·H$_2$O (**2**) are obtained. Compounds **1** have a layer structure in which the chiral inorganic double chains, made up of corner-sharing {ZnO$_4$} and {PO$_3$C} tetrahedra, are connected by bdc^{2-}. While in compounds **2**, chiral chains of zinc phosphonate are each connected to their four equivalent neighbors through btec^{4-} linkages, resulting in an open framework structure. All these compounds are optically active, exhibiting second harmonic generation (SHG) responses 0.2 or 0.8 times that of urea.

Introduction

Chiral metal-organic frameworks have received considerable attention due to their potential applications in the area of enantiopure catalysis, recognition and separation.[1–3] Metal phosphonates are a class of inorganic-organic hybrid materials that integrate organic and inorganic characteristics within a single molecular composite, thus providing unique chemical and physical properties.[4] Although a number of chiral metal-organic frameworks have been reported so far,[5] few are concerned with metal phosphonates.[6,7] There are two synthetic approaches in preparing chiral metal phosphonates. One is through spontaneous resolution upon crystallization by using achiral or racemic ligands, which usually results in optically inactive conglomerates, *e.g.*, a mechanical and racemic mixture of enantiomeric chiral crystals.[8] Only in one case, as far as we are aware, has nonzero enantiomeric excess through chiral symmetry breaking been achieved when an asymmetrical (2-pyridylmethylamino)methylphosphonate ligand is allowed to react with manganese salt.[9] The more efficient approach is through the employment of enantiopure phosphonate ligands.[6,7,10] A series of homochiral lamellar or pillared layered lanthanide diphosphonates based on derivatives of 1,1′-binaphthalene-6,6′-bisphosphonic acid are reported.[6] Chain compounds Ln[(*S*)-HO$_3$PCH$_2$NHC$_4$H$_7$CO$_2$]$_3$·2H$_2$O (Ln = Tb, Dy, Eu, Gd)[11] and open framework compound Zn$_2$[(S)-O$_3$PCH$_2$NHC$_4$H$_7$CO$_2$]$_2$ [7] are described using 1-phosphonomethylproline as a starting material. Homochiral layered compounds [Zn$_2$(pemp)(pempH)Cl] [12] and [Ln(pempH)(NO$_3$)$_2$(H$_2$O)$_2$] (Ln = Eu, Tb, Ho)[13] are also achieved based on (*S*)- or (*R*)-(1-phenylethylamino)methylphosphonic acid (pempH$_2$).

Another approach that has not been well explored in synthesizing chiral metal phosphonates with open framework structures is to combine the chiral metal phosphonate motif with a second bridging ligand.[14] It is well known that aromatic polycarboxylates are promising candidates for linking metal ions into three-dimensional open frameworks.[15-16] In this paper, we select 1,4-benzenedicarboxylic acid (H$_2$bdc) and 1,2,4,5-benzenetetracarboxylic acid (H$_4$btec) as the second polydentate linker to react with zinc salts and enantiopure (1-phenylethylamino)methylphosphonic acid. Four homochiral zinc complexes, (*R*)-[Zn$_4$(pempH)$_4$(bdc)$_2$]·2H$_2$O (*R*-**1**), (*S*)-[Zn$_4$(pempH)$_4$(bdc)$_2$]·2H$_2$O (*S*-**1**), (*R*)-[Zn$_3$(pempH)$_2$(btec)(H$_2$O)$_2$]·H$_2$O (*R*-**2**) and (*S*)-[Zn$_3$(pempH)$_2$(btec)(H$_2$O)$_2$]·H$_2$O (*S*-**2**), are obtained successfully, where the chiral chains of zinc phosphonate are connected by the carboxylates into a layer (for **1**) or an open framework (for **2**).

Experimental section

Materials and measurements

(*S*)- or (*R*)-(1-phenylethylamino)methylphosphonic acid (pempH$_2$) was prepared by reactions of (*S*)- or (*R*)-1-phenylethylamine, diethyl phosphite and paraformaldehyde according to literature methods.[17] (*S*)- and (*R*)-1-phenylethylamine were purchased from Aldrich without further purification, and all the other starting materials were of reagent grade quality. The elemental analyses were performed in a PE240C elemental analyzer. The infrared spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pellets. The powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-3A X-ray diffractometer. Circular dichroism (CD) spectra were measured on a JASCO J-720W spectrophotometer at room temperature. Approximate estimations of the second-order-nonlinear optical intensity were obtained by comparison of the results obtained from a powder sample (80 ± 150 mm diameter)

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† Electronic supplementary information (ESI) available: Four figures of XRD patterns and thermal analyses for complexes **1** and **2**, Fig. S5: coordinated geometries for zinc in *R*-**2**. CCDC reference numbers 741077–741079. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b914583d

in the form of a pellet (Kurtz powder test[18]) with that obtained for urea. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate the second harmonic generation (SHG) signal. The backward-scattered SHG light was collected using a spherical concave mirror and passed through a filter that transmits only 532 nm radiation. Thermal analyses were performed in nitrogen in the temperature range 25–650 °C with a heating rate of 10 °C min^{-1} on a TGA-DTA V1.1b Inst 2100 instrument. The fluorescent spectra were recorded on an Edinburgh FLS920 fluorescence spectrometer with polycrystalline samples.

Preparation of (*R*)-[$Zn_4(pempH)_4(bdc)_2$]·$2H_2O$ (*R*-1). A mixture of $ZnSO_4·7H_2O$ (0.2 mmol, 0.0564 g), *R*-$pempH_2$ (0.1 mmol, 0.0215 g) and 1,4-H_2bdc (0.1 mmol, 0.0166 g) in 10 mL of H_2O, adjusted to pH 4.8 with 1 mol/L NaOH, was kept in a Teflon-lined autoclave at 180 °C for 5 days. After cooling to room temperature, colorless plate-like crystals of *R*-**1** were obtained. Yield: 55%. Anal. calcd for $C_{52}H_{52}N_4O_{22}P_4Zn_4$: C, 42.47; H, 3.56; N, 3.81%. Found: C, 42.41; H, 3.64; N, 3.78%. IR (KBr, cm^{-1}): 3444(m), 3030(w), 3008(w), 1629(s), 1592(s), 1502(w), 1458(w), 1402(s), 1384(s), 1268(w), 1203(s), 1185(s), 1096(s), 1083(s), 1016(s), 830(w), 766(m), 746(m), 700(m), 606(w), 581(m), 523(w), 495(w), 458(w).

Preparation of (*S*)-[$Zn_4(pempH)_4(bdc)_2$]·$2H_2O$ (*S*-1). Compound *S*-**1** was obtained similarly except that *S*-$pempH_2$ was used. Yield: 51%. Anal. calcd for $C_{52}H_{52}N_4O_{22}P_4Zn_4$: C, 42.47; H, 3.56; N, 3.81%. Found: C, 42.48; H, 3.51; N, 3.73%. IR (KBr, cm^{-1}): 3420(m), 3029(w), 1629(s), 1593(s), 1502(w), 1459(w), 1405(s), 1384(s), 1268(w), 1204(s), 1187(s), 1097(s), 1082(s), 1016(s), 996(s), 829(w), 766(m), 745(m), 699(m), 580(m), 523(w), 496(w), 457(w).

Preparation of (*R*)-[$Zn_3(pempH)_2(btec)(H_2O)_2$]·$H_2O$ (*R*-2). A mixture of $ZnSO_4·7H_2O$ (0.2 mmol, 0.0564 g), *R*-$pempH_2$ (0.1 mmol, 0.0215 g), and H_4btec (0.05 mmol, 0.0127 g) in 10 mL of H_2O, adjusted to pH 4.2 with 1 mol/L NaOH, was kept in a Teflon-lined autoclave at 140 °C for 5 days. After cooling to room temperature, colorless plate-like crystals of *R*-**2** were obtained. Yield: 48%. Anal. calcd for $C_{28}H_{34}N_2O_{17}P_2Zn_3$: C, 36.21; H, 3.69; N, 3.02%. Found: C, 36.17; H, 3.71; N, 3.17%. IR (KBr, cm^{-1}): 3383(m), 2981(m), 1615(s), 1494(m), 1456(m), 1404(s), 1386(s), 1327(m), 1203(w), 1188(w), 1136(s), 1100(s), 1032(m), 1009(m), 821(w), 769(m), 746(w), 699(m), 629(w), 598(m), 563(m), 494(w).

Preparation of (*S*)-[$Zn_3(pempH)_2(btec)(H_2O)_2$]·$H_2O$ (*S*-2). Compound *S*-**2** was obtained similarly to compound *R*-**2** except that *S*-$pempH_2$ was used. Yield: 45%. Anal. calcd for $C_{28}H_{34}N_2O_{17}P_2Zn_3$: C, 36.21; H, 3.69; N, 3.02%. Found: C, 36.19; H, 3.74; N, 3.14%. IR (KBr, cm^{-1}): 3357(m), 2985(m), 1616(s), 1495(m), 1470(m), 1400(s), 1387(s), 1328(m), 1188(w), 1147(s), 1136(s), 1112(s), 1032(m), 1010(m), 821(w), 770(m), 699(m), 630(w), 599(m), 573(m), 495(w).

Crystallographic studies

Data collections for complexes *S*-**1**, *R*-**2** and *S*-**2** were carried out on a Bruker SMART APEX CCD diffractometer equipped with graphite monochromated Mo K_α ($\lambda = 0.71073$ Å) radiation. Hemispheres of data were collected in the θ range of 1.71–26.00° for *S*-**1**, 2.31–25.98° for *R*-**2** and 2.31–26.00° for *S*-**2**, using a narrow-frame method with scan widths of 0.308° in ω and an exposure time of 5 s per frame. The data were integrated using the Siemens SAINT program,[19] with the intensities corrected for the Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. An empirical absorption correction was applied. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL.[20] All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms, except those attached to water molecules, were put in calculated positions. The H atoms of water molecules were found from the Fourier maps.

Table 1 Crystallographic data for compounds *S*-**1**, *R*-**2** and *S*-**2**

	S-**1**	*R*-**2**	*S*-**2**
Formula	$C_{52}H_{64}N_4O_{22}P_4Zn_4$	$C_{28}H_{34}N_2O_{17}P_2Zn_3$	$C_{28}H_{34}N_2O_{17}P_2Zn_3$
M	1482.4	928.62	928.68
Crystal dimensions [mm^3]	0.18 × 0.14 × 0.04	0.22 × 0.12 × 0.06	0.20 × 0.10 × 0.06
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12$	$C2$	$C2$
a [Å]	22.773(3)	31.133(1)	31.147(4)
b [Å]	27.901(4)	7.626 (1)	7.628(8)
c [Å]	9.9919(15)	17.631(2)	17.640(1)
β [°]	90.00	124.5(3)	124.5(1)
V [$Å^3$]	6348.8(1)	3450.2(6)	3454.4(7)
Z	4	4	4
D_c [g cm^{-3}]	1.551	1.788	1.786
μ [mm^{-1}]	1.670	2.242	2.239
$F(000)$	3040	1888	1888
R_{int}	0.033	0.025	0.026
GoF on F^2	1.09	1.10	1.10
R_1, wR_2[a] [$I>2\sigma(I)$]	0.0413, 0.0877	0.0492, 0.113	0.0517, 0.119
(all data)	0.0532, 0.0900	0.0569, 0.115	0.0605, 0.121
Flack parameter	0.03(8)	0.009(4)	0.03(5)
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ [e $Å^{-3}$]	0.32, -0.54	0.43, -0.54	0.40, -0.47

[a] $R_1 = \Sigma \|F_o| - |F_c\| / \Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

All H atoms were refined isotropically with the isotropic vibration parameters related to the non-hydrogen atoms to which they are bonded. Crystallographic and refinement details are listed in Table 1. Selected bond lengths and angles are given in Tables 2 and 3 for *S*-**1**, *R*-**2** and *S*-**2**, respectively.

Results and discussion

Crystal structures of (*R*)-[$Zn_4(pempH)_4(bdc)_2$]·$2H_2O$ (*R*-1) and (*S*)-[$Zn_4(pempH)_4(bdc)_2$]·$2H_2O$ (*S*-1)

Compounds *R*-**1** and *S*-**1** are a pair of optical enantiomers and crystallize in the orthorhombic system, with chiral space group $P2_12_12$.[21] Structure *S*-**1** is solved by single crystal structural analyses. The asymmetric unit of *S*-**1** consists of four independent Zn atoms, four $pempH^-$, two bdc^{2-} and two lattice water molecules (Fig. 1). Each Zn atom adopts a slightly distorted tetrahedral coordination geometry. The four coordination sites around each Zn are provided by three phosphonate oxygen atoms from three $pempH^-$ and one oxygen atom from a bdc^{2-} anion [Zn-O: 1.892(3)-2.005(3)Å, O-Zn-O: 97.1(1)-131.2(1)°].

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

Zn1-O2	1.989(3)	Zn3-O6	2.005(3)
Zn1-O4	1.934(3)	Zn3-O9	1.903(3)
Zn1-O12	1.913(3)	Zn3-O3B	1.909(3)
Zn1-O18	1.944(3)	Zn3-O15A	1.940(3)
Zn2-O5	1.938(3)	Zn4-O1	1.917(3)
Zn2-O7	1.960(3)	Zn4-O10	1.967(3)
Zn2-O11	1.957(3)	Zn4-O14	1.946(3)
Zn2-O19A[a]	1.892(3)	Zn4-O8C	1.981(3)
O2-Zn1-O4	99.4(1)	O6-Zn3-O9	110.9(1)
O2-Zn1-O12	110.8(1)	O3B-Zn3-O6	97.5(1)
O2-Zn1-O18	109.8(1)	O6-Zn3-O15A	105.1(2)
O4-Zn1-O12	112.4(1)	O3B-Zn3-O9	111.3(1)
O4-Zn1-O18	113.2(1)	O9-Zn3-O15A	112.0(1)
O12-Zn1-O18	110.7(1)	O3B-Zn3-O15A	118.7(1)
O5-Zn2-O7	111.7(1)	O1-Zn4-O10	107.2(1)
O5-Zn2-O11	106.7(1)	O1-Zn4-O14	106.2(1)
O5-Zn2-O19A[a]	106.0(1)	O1-Zn4-O8C	111.1(1)
O7-Zn2-O11	104.4(1)	O10-Zn4-O14	131.2(1)
O7-Zn2-O19A[a]	126.8(1)	O8C-Zn4-O10	102.9(1)
O11-Zn2-O19A[a]	98.9(1)	O8C-Zn4-O14	97.1(1)

[a] A: 1/2 – x, 1/2 + y, 1 – z; B: x, y, 1 + z; C: x, y,–1 + z.

Table 3 Selected bond lengths [Å] and angles [°] for *R*-**2** and *S*-**2**

	S-**2**	*R*-**2**
Zn1-O1	1.873(5)	1.874(5)
Zn1-O1w	1.988(5)	1.986(5)
Zn1-O4	1.956(6)	1.944(6)
Zn1-O6C[a]	1.965(5)	1.969(4)
Zn2-O2	1.890(6)	1.892(6)
Zn2-O2w	2.040(5)	2.032(5)
Zn2-O7	1.930(5)	1.942(5)
Zn2-O10A[a]	1.962(5)	1.970(5)
Zn3-O5	1.929(6)	1.942(5)
Zn3-O11	1.920(6)	1.919(5)
Zn3-O14B[a]	1.958(6)	1.950(5)
Zn3-O3D[a]	1.931(5)	1.926(5)
O1-Zn1-O1W	124.2(2)	124.5(2)
O1-Zn1-O4	100.2(2)	99.5(2)
O1-Zn1-O6C[a]	119.0(2)	118.6(2)
O1w-Zn1-O4	109.6(2)	109.4(2)
O1W-Zn1-O6C[a]	97.2(2)	98.0(1)
O4-Zn1-O6C	105.6(2)	105.8(2)
O2-Zn2-O2W	110.1(2)	110.0(2)
O2-Zn2-O7	112.3(2)	112.4(2)
O2-Zn2-O10A[a]	127.6(2)	127.4(2)
O2w-Zn2-O7	110.8(2)	110.4(2)
O2w-Zn2-O10A[a]	96.0(2)	96.7(2)
O7-Zn2-O10A[a]	98.4(2)	98.2(2)
O5-Zn3-O11	122.4(2)	122.0(2)
O5-Zn3-O14B[a]	112.9(3)	113.1(2)
O3D-Zn3-O5[a]	105.0(2)	105.1(2)
O11-Zn3-O14B[a]	99.2(3)	98.3(2)
O3D-Zn3-O11[a]	113.6(2)	114.1(2)
O3D-Zn3-O14B[a]	102.3(2)	102.8(2)

[a] A: x, 1 + y, z; B: x, –1 + y, z; C: 3/2 – x, –1/2 + y, –z; D: 3/2 – x, 1/2 + y, –z.

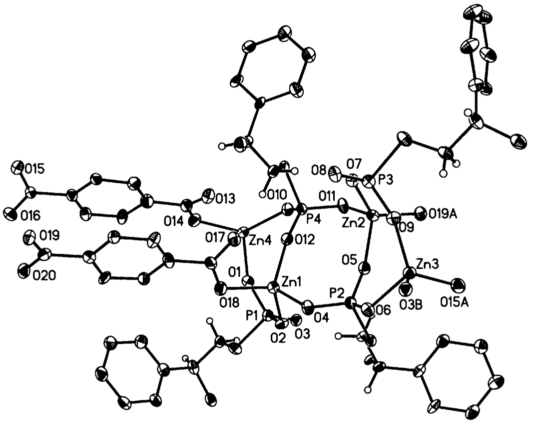
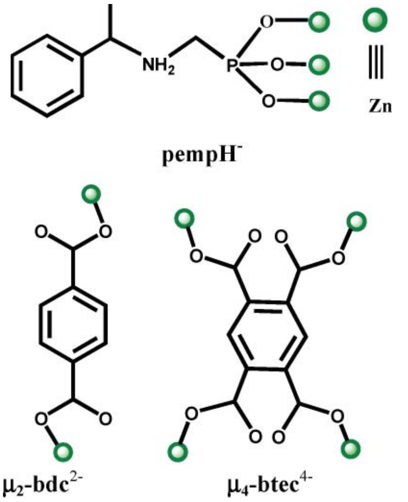


Fig. 1 Coordination geometries of zinc in *S*-**1** with atomic labeling scheme. Thermal ellipsoids are at the 30% probability level. All H atoms except those attached to N and chiral C atoms are omitted for clarity.



Scheme 1 The coordination modes of pempH$^-$, bdc^{2-} and btec^{4-}.

The pempH$^-$ serves as a tridentate ligand, coordinating to three different Zn atoms through its three phosphonate oxygen donors (Scheme 1). Consequently, each {PO$_3$C} tetrahedron is corner-shared with three {ZnO$_4$} tetrahedra and *vice versa*, forming an infinite homochiral double chain along the *c*-axis. Hydrogen bond interactions are found within the chain. The O1W···O8, N1···O6^{i}, N1···O1W^{i}, O1W···O17, N2···O2W, N2···O2, O2W···O11, N3···O20^{ii}, N3···O9, O2W···O16^{iii}, N4···O12 and N4···O7 distances are 3.070(4), 2.874(4), 2.763(4), 2.705(4), 2.712(6), 3.007(4), 3.118(6), 2.719(4), 2.756(4), 2.740(6), 2.806(4) and 2.890(4) Å, respectively (symmetry codes: i, x, y, –1 + z; ii, 1/2 – x, 1/2 + y, 1 – z; iii, 1/2 – x, 1/2 + y, –z). The adjacent chains are connected by μ_2-bdc (Scheme 1), forming a homochiral layer in the *bc* plane. The inter-chain distance within the layer is 13.950 Å (Fig. 2). The organic groups of pempH$^-$ are grafted on the two sides of the layer. The layers are stacked along the *a*-axis and

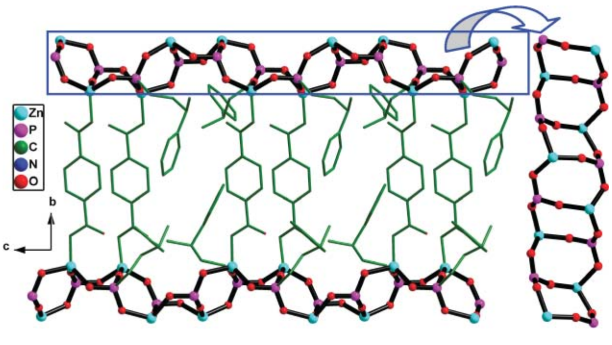


Fig. 2 One layer of structure *S*-**1**.

repeat in an $\cdots$ABAB$\cdots$ sequence with an interlayer distance of 11.386 Å (Fig. 3). No π-π interaction is present between the phenyl rings.

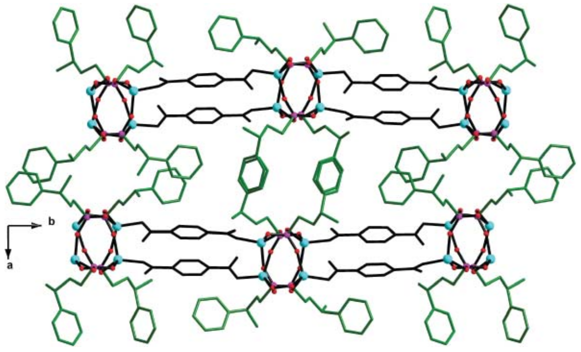


Fig. 3 Structure *S*-**1** packed along the *c*-axis.

Crystal structures of (*R*)-[$Zn_3(pempH)_2(btec)(H_2O)_2$]·$H_2O$ (*R*-2) and (*S*)-[$Zn_3(pempH)_2(btec)(H_2O)_2$]·$H_2O$ (*S*-2)

Single crystal structural analyses reveal that *R*-**2** and *S*-**2** are a pair of optical enantiomers and crystallize in the monoclinic system, with chiral space group *C*2. Take *S*-**2** as an example. The asymmetric unit contains three independent Zn atoms, two pempH$^-$, one btec^{4-} anion, two coordination and one lattice water molecules (Fig. 4). Each Zn atom adopts a slightly distorted tetrahedral geometry. The four coordination sites around Zn1 are provided by three phosphonate oxygen atoms (O1, O4, O6C) from three phosphonate ligands and a water molecule (O1W). Zn2 is coordinated to one phosphonate oxygen atom (O2), one water molecule (O2W), and two carboxylate oxygen atoms (O7, O10A) from different btec^{4-} anions. The four coordinated sites of Zn3 are occupied by two phosphonate oxygen atoms (O3D, O5) and two carboxylate oxygen atoms (O11, O14B). The Zn-O bond distances are in the range of 1.873(5)–2.040(5) Å, while the O-Zn-O bond angles are 96.0(2)–127.6(2)°.

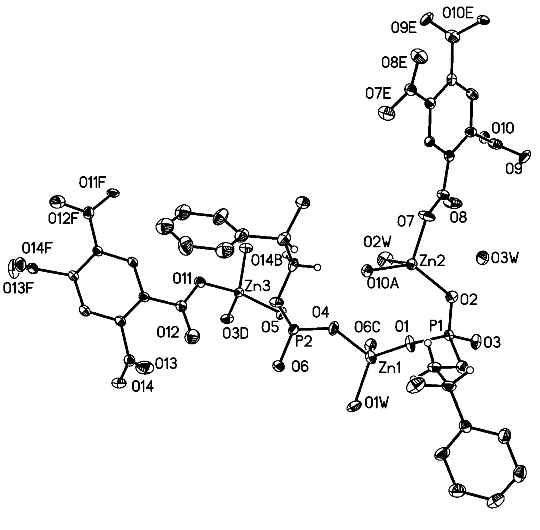


Fig. 4 Coordination geometries of zinc in *S*-**2** with atomic labeling scheme. Thermal ellipsoids are at the 30% probability level. All H atoms except those attached to N and chiral C atoms are omitted for clarity.

The pempH$^-$ again acts as a tridentate ligand, with each of its three phosphonate oxygen atoms coordinated to three different Zn atoms (Zn1, Zn2, Zn3). The {ZnO_4} and {PO_3C} tetrahedra are linked in a corner-sharing manner, forming a zigzag homochiral inorganic chain running along the *b*-axis which contains four-membered rings. Hydrogen bond interactions are found within the chain in *S*-**2**. The O1W$\cdots$O12^{i}, N1$\cdots$O3W^{ii}, N1$\cdots$O9^{ii}, O1W$\cdots$O5^{i}, N2$\cdots$O13^{iii}, N2$\cdots$O10^{ii}, O2W$\cdots$O1W^{i}, O2W$\cdots$O6^{iii} and O3W$\cdots$O8 distances are 2.714(8), 2.855(8), 2.823(9), 2.879(7), 2.704(8), 2.950(8), 2.922(7), 2.933(6) and 2.751(9) Å, respectively (symmetry codes: i, 3/2 − x, −1/2 + y, −z; ii, x, 1 + y, z; iii, x, −1 + y, z). Each chain is surrounded by four equivalent chains, linked by the coordination of carboxylate oxygen atoms from μ_4-btec to Zn2. A three-dimensional homochiral open framework structure is thus constructed, with chiral channels generated along the *b*-axis (Fig. 5). The shortest inter-chain distances are 15.574 Å along the *a*-axis and 8.820 Å along the *c*-axis, respectively. The organic moieties of pempH$^-$ and lattice water fill in the channel spaces.

It would be of interest to compare structures **1** and **2** with those of α-(*S*)- or α-(*R*)-[Zn_2(pemp)(pempH)Cl] and β-(*S*)- or β-(*R*)-[Zn_2(pemp)(pempH)Cl].[12] In the latter cases, chiral inorganic layers made up of corner-sharing {ZnO_3N} (or {ZnO_3Cl}) and {PO_3C} tetrahedra are separated by the organic groups of the phosphonate ligand. While in compounds **1** and **2**, chiral inorganic chains of corner-sharing {ZnO_4} and {PO_3C} are connected by bdc^{2-} to form a layer, and by btec^{4-} to form a 3D open framework. Apparently, the introduction of a rigid polycarboxylate linker provides an efficient route to the formation of chiral metal phosphonates with open framework structures.

Optical properties

Solid-state luminescent properties of *R*-**1** and *S*-**1** were investigated at room temperature. Fig. 6 shows the emission spectra of the two compounds excited at 340 nm. The emission peaks are observed at 425 and 430 nm for complexes *R*-**1** and *S*-**1**, respectively, which can be assigned to the ligand-to-metal charge transfer.[22] No emission is observed for the ligands and compounds **2**, the reasons for which are not clear to us.

Solid-state circular dichroism (CD) spectra were obtained from KBr pellets for compounds **1** and **2**. As shown in Fig. 7, the CD spectra of the (*R*)- and (*S*)-isomers of **1** and **2** are identical mirror images. The results confirm the enantiomeric nature of compounds *R*-**1** and *S*-**1**, and *R*-**2** and *S*-**2**, with the optical activities originating from the chiral phosphonate ligand.[23] Second harmonic generation (SHG) properties of polycrystalline samples of **1** and **2** were also studied. The results indicate that both *R*-**1** and *S*-**1** exhibit SHG responses about 0.2 times that of urea, while *R*-**2** and *S*-**2** exhibit SHG responses about 0.8 times that of urea.

Thermal analyses

For compounds **1**, thermal analyses show a one-step weight loss (2.8% for *R*-**1**, 2.9% for *S*-**1**) in the temperature range 50–165 °C, in agreement with the calculated value of 2.4% for the removal of two H_2O molecules. A plateau appears between 165 and 220 °C, followed by a sharp weight loss (~ 77%) in the range 220–350 °C, indicating the elimination of the organic moieties

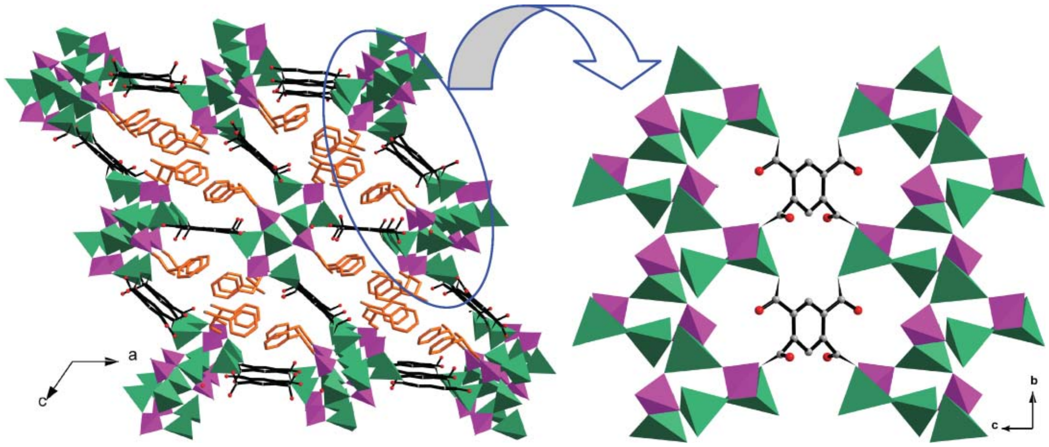


Fig. 5 Left: structure *S*-**2** packed along the *b*-axis; right: chiral inorganic chains linked by μ_4-btec^{4-}.

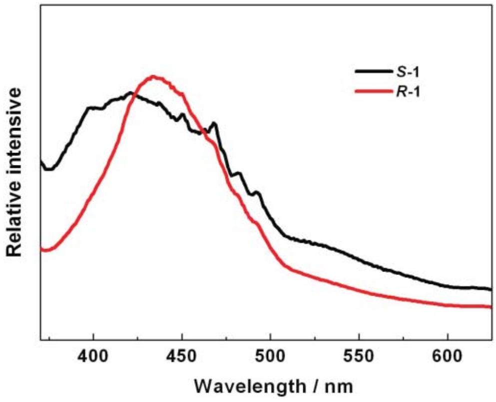


Fig. 6 Solid-state fluorescence emission spectra of *S*-**1** and *R*-**1**.

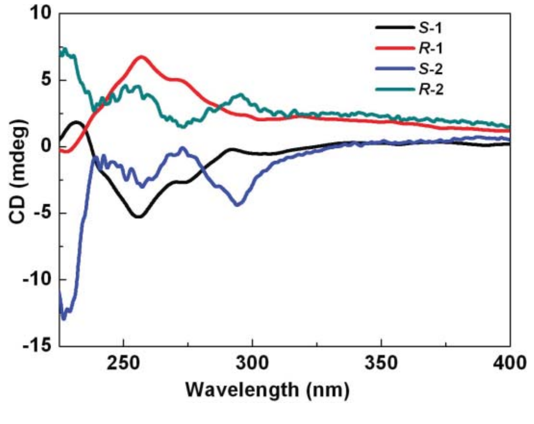


Fig. 7 CD spectra of *S*-**1** (black line), *R*-**1** (red line), *S*-**2** (blue line) and *R*-**2** (green line) in KBr pellets.

and the collapse of the structures. For compounds **2**, a weight loss of 6.7% is observed for both *R*-**2** and *S*-**2** in the temperature range 50–235 °C, which is slightly larger than that expected for the removal of three H_2O molecules (5.8%). The dehydration process is followed immediately by the burning of the organic moieties and the collapse of the structures, with a weight loss of ~ 35% in the range 235–516 °C.

Conclusions

We describe a new synthetic route towards chiral metal phosphonates, *i.e.* through the incorporation of an aromatic polycarboxylate ligand, 1,4-benzenedicarboxylic acid (H_2bdc) or 1,2,4,5-benzenetetracarboxylic acid (H_4btec), to link homochiral chains of zinc phosphonates. Compounds (*R*)- and (*S*)-$[Zn_4(pempH)_4(bdc)_2]\cdot 2H_2O$ (**1**) display a layer structure, made up of chiral inorganic double chains and bdc^{2-} linkages, while compounds (*R*)- and (*S*)-$[Zn_3(pempH)_2(btec)(H_2O)_2]\cdot H_2O$ (**2**) show an open framework structure in which the chiral inorganic chains are connected by btec^{4-} in four directions. Further work is in progress to explore new homochiral metal phosphonates with open framework structures and interesting physical and chemical properties by combining with a second polydentate linker.

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