



## Research paper

## Spontaneous resolution of non-centrosymmetric coordination polymers of zinc(II) with achiral imidazole-biphenyl-carboxylate ligands



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## ARTICLE INFO

## Keywords:

Coordination polymer

Carboxylate-imidazole linkers

Crystal structure

Topology

## ABSTRACT

A convenient synthesis and a full characterization of imidazole- and benzimidazole-biphenyl-carboxylic acid ligands and two zinc coordination polymers are presented. The crystal structure of two precursors 1-(4-iodophenyl)-1*H*-imidazole (**1**), 1-(4-iodophenyl)-1*H*-benzo[*d*]imidazole (**2**), of 4'-(1*H*-benzo[*d*]imidazol-1-yl)biphenyl-4-carboxylic acid (**HL2**), as bimodal linker and of two coordination polymers [Zn(L1)<sub>2</sub>] and [Zn<sub>2</sub>(L2)<sub>2</sub>(Ac)<sub>2</sub>], have been determined by X-ray crystallography. Compounds **1** and **2** exhibit a supramolecular crystal structure consolidated by a system of π-π and C-H...π interactions, respectively. The Zn atoms of the same absolute configuration in [Zn(L1)<sub>2</sub>] and [Zn<sub>2</sub>(L2)<sub>2</sub>(Ac)<sub>2</sub>] are assembled into a homochiral two-dimensional (4, 2) coordination network and a one-dimensional coordination polymeric double strand, respectively.

## 1. Introduction

Coordination polymers (CPs) are a class of compounds which have been intensively studied over the past decade due to their applications and the structural arrangements. Coordination polymeric structures are of interest regarding crystal engineering with the aim to improve the design of extended structures [1,2]. Non-porous coordination polymers are often investigated for their structural topologies in the context of crystal engineering [3–10], luminescence [11–19], magnetism [20–22], spin-crossover [23–26] or catalysis [27–29]. For coordination polymers it is still a great challenge to predict the composition and crystal structures [30], the more so, when the synthesis involves the combination of two or more ligands into a mixed-ligand coordination polymer [1,31–36] or bi- or mixed-functional linkers such as azolate-carboxylate [37] or phosphonate-carboxylate [38].

Metal Organic Frameworks (MOFs), a class of porous organic-inorganic hybrid materials, have established themselves as promising candidates for gas storage and separation [39–40], controlled drug release [41] or heterogeneous catalysis [42]. They comprise an inorganic part – the secondary building unit, containing metals or metal clusters – and an organic part – a linker containing donor atoms (e.g. O, S, P, N, etc.) [43]. Particularly, the imidazole ring is an important moiety that is

used in the synthesis of zeolitic imidazolate frameworks (ZIFs) [44–47] or various other coordination polymers (CPs) [48–51]. Although not as common, linkers containing both imidazole and carboxylate groups are also known to form coordination compounds with various transition metals [52–56]. In one particular case, when transition metals Cu, Zn and Cd were used, linkers containing imidazole derivatives and carboxylate functions grafted on a phenyl core, lead to the formation of interesting 2D and 3D structures [57].

Our work comes as an extension of these results, presenting the synthesis of two unsymmetrical organic linkers, containing imidazole/benzimidazole rings and carboxylate groups grafted on a biphenyl core. These unsymmetrical ligands and their precursors were synthesized using known coupling methods [58–60]. Their synthesis using *N*-arylation of heteroatomic compounds, such as azole or indole derivatives, is well established as an important organic reaction [61–64] with significant pharmaceutical industry applications (e.g. sertidole, midazolam), agrochemical industry, or natural product synthesis [65,66].

This study designs, prepares and characterizes, two unsymmetrical imidazole-biphenyl-carboxylate linkers, one of which is being reported for the first time (Scheme 1). These ligands were used in the synthesis of two new two-dimensional Zn coordination polymers. Moreover, the X-ray structures of one of the linkers, two of the precursors, as well as the

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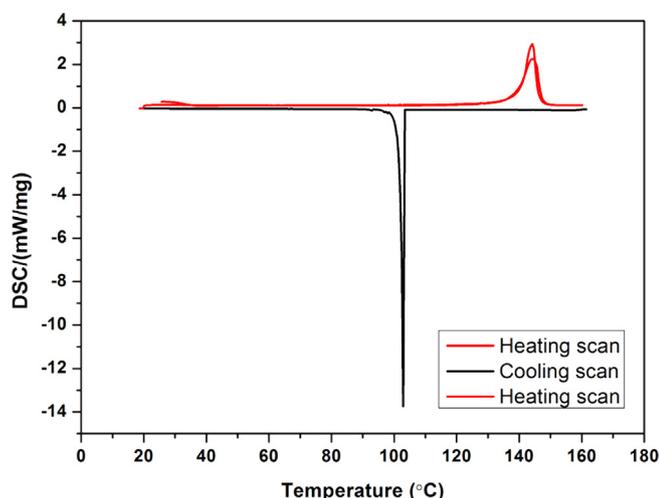
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<https://doi.org/10.1016/j.ica.2018.05.024>

Received 16 February 2018; Received in revised form 14 May 2018; Accepted 19 May 2018

Available online 26 May 2018

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**Scheme 1.** Coupling reactions of imidazole derivatives to the imidazole-bi-phenyl-carboxylic acid target ligands **HL1** and **HL2**.

two coordination polymers are presented. All synthesized compounds were characterized by NMR, MS, IR and X-ray spectroscopy and thermogravimetric analysis.

## 2. Experimental section

### 2.1. General consideration

All reactions were performed using standard Schlenk techniques under a nitrogen atmosphere. Solvents were dried by standard procedures. All materials were purchased from commercial suppliers and used as received. Yields reported in the publication are isolated yields and represent an average of at least two independent runs.

The NMR spectra have been recorded on a BRUKER AVANCE III 400 instrument operating at 400.1 and 100.6 MHz for  $^1\text{H}$  and  $^{13}\text{C}$  nuclei respectively. Unambiguous 1D NMR signal assignments were made based on 2D NMR homo- and heteronuclear correlations such as H,H-COSY, H,C-HSQC and H,C-HMBC experiments, recorded using standard pulse sequences in the version with  $z$ -gradients, as delivered by Bruker with TopSpin 2.1 PL6 spectrometer control and the processing software was used MestReNova 9.01. For the NMR analysis, all the compounds were dissolved in  $\text{DMSO-}d_6$  or  $\text{CDCl}_3$ . Chemical shifts are reported in ppm, multiplicity as  $s$  = singlet,  $d$  = doublet,  $t$  = triplet,  $q$  = quartet,  $m$  = multiplet, coupling constant in Hz and referred to residual solvent peak ( $\text{DMSO-}d_6$   $^1\text{H}$ : 2.51 ppm and  $^{13}\text{C}$ : 39.47 ppm).

Thermo-analytical measurements were performed with a DSC 200 F3 MAIA and a STA 449 F1 JUPITER (Netzsch, Germany) device. Temperature and sensitivity calibrations in the temperature range of 30–600 °C were carried out with indium. About 25–60 mg of solid samples were weighed and sealed in a DSC aluminium crucible or placed in alumina pans for TG measurements. The temperature range used for measurements was between 30 and 700 °C with a heating rate of 5 to 10 °C  $\text{min}^{-1}$ , under an atmosphere of dry nitrogen at a flow rate of 50  $\text{mL min}^{-1}$ . The data were processed with the NETZSCH PROTENS 4.2 software.

Infra-red spectra were recorded on BURUKER VERTEX 70 FTIR spectrometer (Bruker Optics, Germany). The measurements were performed in ATR Golden Gate® (Attenuated Total Reflectance) mode in the 600–4000  $\text{cm}^{-1}$  range at room temperature with a resolution of 4  $\text{cm}^{-1}$  and accumulation of 64 scans.

CHN elemental analysis was performed on a VARIO-EL-III elemental analyzer

Mass spectrometry data were obtained using an AGILENT 6520 Series Accurate-Mass Quadrupole Time-of-Flight (Q-TOF) LC/MS. The

samples dissolved in methanol were introduced into the electrospray ion source (ESI) via a syringe pump at a flow-rate of 0.1  $\text{mL/min}$ . After optimization of the Q/TOF MS parameters, they were set as follows: electrospray ionisation (positive and negative ion mode), drying gas ( $\text{N}_2$ ) flow rate 9.0  $\text{L/min}$ ; drying gas temperature 325 °C; nebulizer pressure 25 psig, capillary voltage 4200 V; fragmentation voltage 200 V; the full-scan mass spectra of the investigated compounds were acquired in the  $m/z$  range of 100–3000. The mass scale was calibrated using the standard calibration procedure and compounds provided by the manufacturer. Data were collected and processed using MassHunter Workstation Software Data Acquisition for 6200/6500 Series, version B.01.03

### 2.2. General procedure for *N*-arylation

The compounds were prepared according to a previously published procedure [67], adapted as follows: A round bottom flask equipped with a glass valve with PTFE stopcock (Young, London) was charged with a magnetic stir bar, imidazole derivative (1 mol), 1,4-diiodobenzene (1.2 mol), salicylaldehyde (20 mol%),  $\text{Cu}_2\text{O}$  (5 mol%) and  $\text{Cs}_2\text{CO}_3$  (3 eqv.). Under a flow of  $\text{N}_2$ , a minimum amount of dry MeCN was added by syringe. The reaction mixture was heated to the indicated temperature for the required time. It was then cooled to room temperature, diluted with MeCN and filtered through a plug of silica. The solvent was removed on a rotary evaporator and the resulting residue was purified by flash chromatography on silica gel ( $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ ) to provide the pure desired product. Copies of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of all products are provided in [Supp. Inf.](#)

#### 2.2.1. Synthesis of 1-(4-iodophenyl)-1H-imidazole – 1

The general procedure was followed using imidazole (0.34 g, 5 mmol), 1,4-diiodobenzene (1.98 g, 6 mmol), salicylaldehyde (0.137 g, 1 mmol),  $\text{Cu}_2\text{O}$  (0.035 g, 0.25 mmol),  $\text{Cs}_2\text{CO}_3$  (4.86 g, 15 mmol) and MeCN (9.0 mL) as solvent for 24 h at 82 °C. After cooling down to room temperature, MeCN (30 mL) was added and the suspension was filtered through a plug of silica. The solvent was removed on a rotary evaporator and the brown crude mixture was separated by column chromatography (Yield 58%, yellowish powder; M.p. 144 °C).

$^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400.1 MHz):  $\delta$  = 8.26 (1H, s, H-2'); 7.83 (2H, d,  $^3J$  = 8.7 Hz, H-3); 7.75 (1H, s, H-5'); 7.49 (2H, d,  $^3J$  = 8.7 Hz, H-2, H-6); 7.10 (1H, s, H-4') ppm.

$^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 100.6 MHz):  $\delta$  = 138.9 (C-3, C-5); 137.1 (C-1); 136.1 (C-2'); 130.6 (C-4'); 122.8 (C-2, C-6); 118.3 (C-5'); 92.2 (C-4) ppm.

Elemental analysis calcd. (%) for  $\text{C}_9\text{H}_7\text{N}_2\text{I}$  ( $M$  = 270.07 g/mol): C 40.03, H 2.61, N 10.37; found: C 40.22, H 2.98, N 10.62.

IR (ATR):  $\nu$  ( $\text{cm}^{-1}$ ) = 3050w, 3046w, 3025w, 3020w, 1610vw, 1586w, 1496vs, 1477w, 1467 m, 1455 m, 1431w, 1405w, 1376w, 1316 m, 1299w, 1289 m, 1269w, 1229 s, 1207 m, 1161vw, 1141vw, 110004vw, 1058w, 1006 m, 974 m, 970 m, 932w, 889w, 869w, 851w, 840 m, 823 m, 780w, 764 m, 741 s, 722w, 706w, 638w, 616w.

#### 2.2.2. Synthesis of 1-(4-iodophenyl)-1H-benzo[d]imidazole – 2

A mixture of benzimidazole (0.24 g, 2.0 mmol), 1,4-diiodobenzene (0.79 g, 2.3 mmol), salicylaldehyde (0.05 g, 0.36 mmol),  $\text{Cu}_2\text{O}$  (0.015 g, 0.1 mmol) and  $\text{Cs}_2\text{CO}_3$  (1.9 g, 5.8 mmol) and dry MeCN (3.0 mL) was stirred for 24 h at 86 °C and then cooled down to room temperature. The mixture was filtered through a plug of silica. The filtrate was concentrated on a rotary evaporator and the resulting residue was purified by column chromatography on silica gel to provide the desired product as a yellow powder (Yield 50%, M.p. 125 °C).

$^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400.1 MHz):  $\delta$  = 8.58 (1H, s, H-2'); 7.98 (2H, d,  $^3J$  = 8.6, H-3, H-5); 7.79 (1H, d,  $^3J$  = 8.6 Hz, H-4'); 7.63 (1H, d,  $^3J$  = 8.6 Hz, H-7'); 7.52 (2H, d,  $^3J$  = 8.6 Hz, H-2, H-6); 7.30–7.36 (2H, m, H-5', H-6') ppm.

$^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 100.6 MHz):  $\delta$  = 144.3 (C-9'); 143.5 (C-2');

139.2 (C-3, C-5); 136.9 (C-1); 133.2 (C-8'); 126.1 (C-2, C-6); 124.0 (C-6'); 123.0 (C-5'); 120.5 (C-4'); 111.1 (C-7'); 93.5 (C-4) ppm.

Elemental analysis calcd. (%) for  $C_{13}H_9N_2I$  ( $M = 320.13$  g/mol): C 48.77, H 2.83, N 9.96; found: C 48.52, H 2.98, N 10.02.

**IR (ATR):**  $\nu$  ( $cm^{-1}$ ) = 3128 m, 2989w, 2901w, 1588 m, 1506 s, 1497 s, 1466 m, 1410 m, 1366w, 1301 s, 1257 m, 1246 m, 1105 m, 1051 s, 1004 m, 959 m, 903 m, 817 s, 810 s, 736 m, 649 m.

### 2.2.3. Synthesis of 4'-(1H-imidazol-1-yl)biphenyl-4-carboxylic acid – HL1

Procedure A

An oven-dried 100 mL 2-neck flask equipped with a magnetic stirrer was charged with **1** (0.54 g, 2 mmol) dissolved in degassed  $C_6H_5CH_3$  (20 mL), 4-carboxyphenylboronic acid (0.365 g, 2.2 mmol) in EtOH (10 mL) and  $Na_2CO_3$  (4.24 g, 40 mmol) in deionized water (15 mL) and  $Pd[P(C_6H_5)_3]_4$  (0.115 g, 0.1 mmol) in degassed  $C_6H_5CH_3$  (20 mL). This mixture was degassed by bubbling  $N_2$  for 30 min. The flask was fitted with a reflux condenser and heated at 92 °C for 24 h. After the desired reaction time, the mixture was filtered and the filtrate was concentrated on a rotary evaporator. Water (30 mL) was then added and the mixture was acidified (pH  $\approx$  2) with diluted chlorhidric acid (1N) to give a precipitate. The desired product was isolated by centrifugation and washed several times with water (Yield 83%, yellow powder).

#### Procedure B

A 250 mL 2-neck flask equipped with a mechanical stirring bar, condenser and a nitrogen gas inlet was charged with **1** (3 g, 11.1 mmol), 4-carboxyphenylboronic acid (2.02 g, 12.1 mmol) and *n*-propanol (15 mL) under nitrogen purge. The mixture was stirred at room temperature for 30 min, allowing the reactants to dissolve. To this mixture, a solution of  $Pd(OAc)_2$  (0.25 g, 1.1 mmol) and  $P(C_6H_5)_3$  (0.867 g, 3.3 mmol) in *n*- $C_3H_7OH$  (5 mL) and a solution of  $Na_2CO_3$  (1.41 g, 13.3 mmol) in deionized water (4 mL) were added. After refluxing for 24 h, the mixture was filtered and then acidified with diluted HCl (1N). The precipitate was isolated by centrifugation and washed several times with deionized water (yield 85%).

$^1H$  NMR (DMSO- $d_6$ , 400.1 MHz):  $\delta$  = 13 (1H, brs, COOH), 9.23 (1H, s, H-2''); 8.18 (1H, s, H-5''); 8.08 (2H, d,  $^3J$  = 8.3 Hz, H-3, H-5); 8.0 (2H, d,  $^3J$  = 8.6 Hz, H-2', H-6'), 7.93–7.90 (4H, m, H-2, H-6, H-3', H-5') 7.6 (1H, s, H-4'') ppm.

$^{13}C$  NMR (DMSO- $d_6$ , 100.6 MHz):  $\delta$  = 167.5 (COOH); 143.2 (C-1); 139.3 (C-1'); 136.1 (C-4); 135.4 (C-2''); 130.5 (C-3, C-5); 130.4 (C-4), 128.9 (C-2, C-6); 127.4 (C-2, C-6); 125.3 (C-4''); 122.2 (C-3, C-5); 120.0 (C-5'') ppm.

Elemental analysis calcd. (%) for  $C_{16}H_{12}N_2O_2$  ( $M = 264.28$  g/mol): C 72.72, H 4.58, N 10.6; found: C 72.69, H 4.52, N 10.53.

**IR (ATR):**  $\nu$  ( $cm^{-1}$ ) = 3122w, 2921w, 2401vw, 1928w, 1679 s, 1606 m, 1534 m, 1504 m, 1469w, 1425w, 1402w, 1369vw, 1294vs, 1236 m, 1180 m, 1114 s, 1051 s, 1012 m, 961 m, 935 m, 872 m, 825 s, 765vs, 727 m, 702w, 648 m, 622vw.

### 2.2.4. Synthesis of 4'-(1H-benzimidazol-1-yl)biphenyl-4-carboxylic acid – HL2

**HL2** was prepared according to the same synthetic procedure reported for **HL1**, using the same ratio of reagents. Isolated yields (yellow to brown powder) of **HL2** are 62% (procedure 1) and 72% (procedure 2).

$^1H$  NMR (DMSO- $d_6$ , 400.1 MHz):  $\delta$  = 13.06 (1H, brs, COOH); 8.86 (1H, s, H-2''); 8.08 (2H, d,  $^3J$  = 8.3 Hz, H-3, H-5); 8.01 (2H, d,  $^3J$  = 8.5 Hz, H-2', H-6'); 7.92 (2H, d,  $^3J$  = 8.3, H-2, H-6); 7.84 (2H, d,  $^3J$  = 8.5 Hz, H-3', H-5'), 7.81 (1H, d,  $^3J$  = 8.3, H-4''), 7.71 (1H, d,  $J$  = 8.3, H-7''), 7.40–7.33 (2H, m, H-5'', H-6'') ppm.

$^{13}C$  NMR (DMSO- $d_6$ , 100.6 MHz):  $\delta$  = 167.5 (COOH); 144.3 (C-9''); 143.7 (C-2''); 143.6 (C-1); 138.7 (C-1'); 136.4 (C-4); 133.3 (C-8''); 130.5 (C-3, C-5); 130.4 (C-4), 129.0 (C-2, C-6); 127.3 (C-2, C-6); 124.6 (C-3, C-5); 124.1 (C-6''); 123.0 (C-5''); 120.5 (C-4''); 111.2 (C-7'') ppm.

Elemental analysis calcd. (%) for  $C_{20}H_{14}N_2O_2$  ( $M = 314.38$  g/mol): C 76.42, H 4.49, N 8.91; found: C 76.52, H 4.58, N 8.82.

**IR (ATR):**  $\nu$  ( $cm^{-1}$ ) = 2926w, 1906vw, 1689 s, 1605 s, 1501 s, 1458 m, 1431 m, 1400 m, 1373w, 1301 s, 1263 s, 1229 s, 1182 m, 1110 m, 1006 m, 980 m, 899w, 875w, 831vs, 806 m, 761vs, 688 m, 630w.

### 2.2.5. Synthesis of compound $[Zn(L1)_2]$

$Zn(NO_3)_2 \cdot 6H_2O$  (0.02 g, 0.075 mmol) and **HL1** (0.01 g, 0.037 mmol) were dissolved in DMF (1 mL) at room temperature. The clear solution was transferred into a 30 mL culture tube and kept under static conditions for 2 days at 120 °C. After cooling, the colourless crystalline product was collected by centrifugation and washed with DMF and methanol. Finally, the crystals were dried at room temperature (0.004g, Yield 40%).

Elemental analysis calcd. (%) for  $C_{32}H_{22}N_4O_4Zn$  ( $M = 591.91$  g/mol): C 64.93, H 3.75, N 9.47; found: C 64.82, H 3.78, N 9.52.

**IR (ATR):**  $\nu$  ( $cm^{-1}$ ) = 3169vw, 3140w, 3121w, 3049vw, 2922w, 1950vw, 1663 m, 1620vs, 1553 m, 1526 s, 1352vs, 1308 m, 1234w, 1180w, 1124 s, 1099 m, 1065 s, 1009 m, 968 m, 645 m, 870w, 840vs, 827vs, 781vs, 754 s, 731 s, 706 m, 687 m, 660 s, 616w.

### 2.2.6. Synthesis of compound $[Zn_2(L2)_2(Ac)_2]$

$Zn(NO_3)_2 \cdot 6H_2O$  (0.0352 g, 0.1 mmol) and **HL2** (0.0186 g, 0.05 mmol) were dissolved in DMF (1.5 mL) at room temperature. Then, acetic acid (0.1 mL) was added and the mixture was transferred into a 30 mL culture tube and kept under static conditions for 4 days at 120 °C. The colourless crystalline product thus formed was collected by centrifugation and washed with DMF and methanol. Finally, the crystals were dried at room temperature (0.007g, Yield 32%).

Elemental analysis calcd. (%) for  $C_{44}H_{32}N_4O_8Zn_2$  ( $M = 875.48$  g/mol): C 60.36, H 3.68, N 6.40; found: C 60.42, H 3.58, N 6.52.

**IR (ATR):**  $\nu$  ( $cm^{-1}$ ) = 3146vw, 3078vw, 2924w, 2854w, 1672w, 1645w, 1597vs, 1533 s, 1510 s, 1460 m, 1404vs, 1336 m, 1302 m, 1238 s, 1151w, 1144w, 1111w, 997 m, 937w, 914w, 864 s, 783vs, 750vs, 692 s, 621w.

## 2.3. X-ray crystallography

X-ray diffraction measurements for the five compounds were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated  $MoK\alpha$  radiation. Single crystals were positioned at 40 mm from the detector and 160, 265, 454, 242 and 467 frames were measured each for 3, 8, 30, 30 and 25 s over 1° scan width for 1–5, respectively. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction [68]. The structures were solved by direct methods using Olex2 [69] and refined by full-matrix least-squares on  $F^2$  with SHELXL-97 [70] using an anisotropic model for non-hydrogen atoms. All H atoms were introduced in idealised positions ( $d_{CH} = 0.96$  Å) using the riding model with their isotropic displacement parameters fixed at 120% of their riding atom. The molecular plots were obtained using the Olex2 program. The crystallographic data and refinement details are quoted in Table 1, while bond lengths are summarised in Table S3 (Supp. Inf.). CCDC – 1,819,555 (1), CCDC – 1,819,557 (2), CCDC – 1,819,560 (**HL1**), CCDC – 1,819,558  $\{[Zn(L1)_2]\}$  and CCDC – 1,819,559  $\{[Zn_2(L2)_2(Ac)_2]\}$  contain the supplementary crystallographic data for this contribution. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or [deposit@ccdc.ca.ac.uk](mailto:deposit@ccdc.ca.ac.uk))

## 3. Results and discussion

### 3.1. Synthesis of ligands

*N*-arylation of 1*H*-imidazole or 1*H*-benzimidazole with 1,4-diodobenzene was carried out to obtain 1-(4-iodophenyl)-1*H*-imidazole (1)

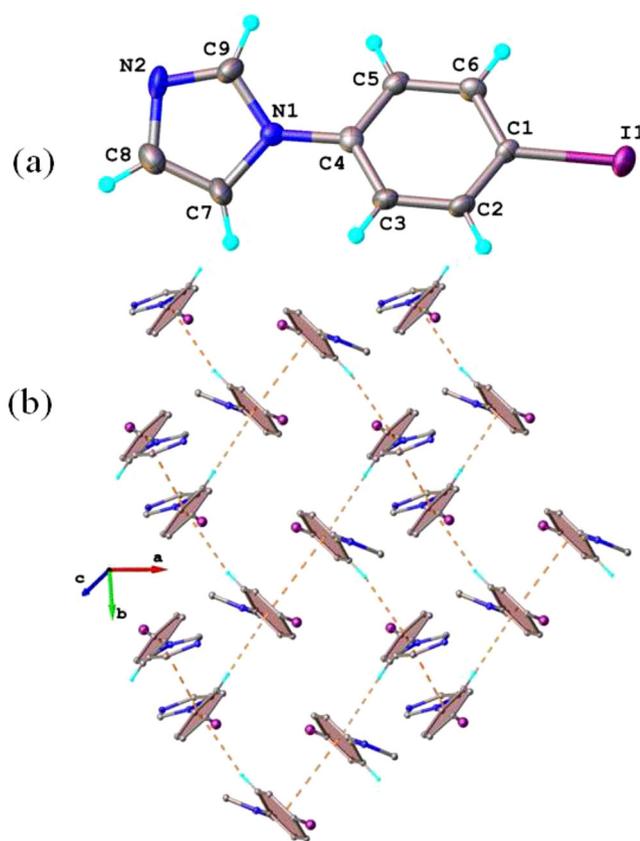
**Table 1**  
Crystal data and details of data collection.

Compound	1	2	HL1	[Zn(L1) <sub>2</sub> ]	[Zn <sub>2</sub> (L2) <sub>2</sub> (Ac) <sub>2</sub> ]
Empirical formula	C <sub>9</sub> H <sub>7</sub> IN <sub>2</sub>	C <sub>13</sub> H <sub>9</sub> IN <sub>2</sub>	C <sub>16</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>32</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> Zn	C <sub>44</sub> H <sub>32</sub> N <sub>4</sub> O <sub>8</sub> Zn <sub>2</sub>
<i>F</i> <sub>w</sub>	270.07	320.12	264.28	591.91	875.48
space group	<i>Pbca</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>Aea2</i>	<i>P2<sub>1</sub></i>
<i>a</i> [Å]	10.1493(7)	6.4196(4)	3.8466(7)	15.9969(18)	10.7083(4)
<i>b</i> [Å]	8.2568(7)	10.8844(7)	27.589(5)	21.6823(19)	13.3839(6)
<i>c</i> [Å]	21.3201(13)	16.7899(10)	11.6689(18)	7.5937(9)	13.3399(5)
$\alpha$ [°]	90.0	90.0	90.0	90.0	90.0
$\beta$ [°]	90.0	92.937(5)	97.948(16)	90.0	97.819(4)
$\gamma$ [°]	90.0	90.0	90.0	90.0	90.0
<i>V</i> [Å <sup>3</sup> ]	1786.6(2)	1171.63(12)	1226.5(4)	2633.9(5)	1894.08(13)
<i>Z</i>	8	4	4	4	2
$\rho_{\text{calcd}}$ [g cm <sup>-3</sup> ]	2.008	1.815	1.431	1.493	1.535
Crystal size [mm]	0.40 × 0.25 × 0.15	0.45 × 0.12 × 0.08	0.30 × 0.10 × 0.07	0.40 × 0.20 × 0.10	0.30 × 0.25 × 0.20
<i>T</i> [K]	200	293	200	200	200
$\mu$ [mm <sup>-1</sup> ]	3.527	2.705	0.096	0.983	1.329
2 $\theta$ range	5.54–50.04	4.46–50.06	2.96–50.06	3.76–65.28	3.84–50.06
Reflections collected	4310	5155	3698	5019	14,908
Independent reflections	1572	2061	3703	2094	6698
	[ <i>R</i> <sub>int</sub> = 0.0403]	[ <i>R</i> <sub>int</sub> = 0.0323]	[ <i>R</i> <sub>int</sub> = 0.045]	[ <i>R</i> <sub>int</sub> = 0.0447]	[ <i>R</i> <sub>int</sub> = 0.0360]
Data/restraints/ parameters	1572/0/109	2061/0/145	3703/0/183	2094/1/186	6698/14/529
<i>R</i> <sub>1</sub> <sup>[a]</sup>	0.0472	0.0236	0.0560	0.0844	0.0349
<i>wR</i> <sub>2</sub> <sup>[b]</sup>	0.1289	0.0720	0.0986	0.0525	0.0718
GOF <sup>[c]</sup>	1.079	1.054	0.932	0.1154	1.023
Largest diff. peak/hole/e Å <sup>-3</sup>	1.23/–1.78	0.59/–0.61	0.21/–0.21	0.47/–0.55	0.39/–0.20
Flack parameter	–	–	–	0.02(3)	–0.012(8)

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

$$^c \text{GOF} = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{(n - p)} \right\}^{1/2}, \text{ where } n \text{ is the number of reflections and } p \text{ is the total number of parameters refined.}$$



**Fig. 1.** DSC curves for 1-(4-Iodo-phenyl)-1H-imidazole – 1.

and 1-(4-iodophenyl)-1H-benzo[d]imidazole (**2**) by adopting the conditions reported by Cristau et al., that is Cu<sub>2</sub>O, salicyladoxime and Cs<sub>2</sub>CO<sub>3</sub> in dry MeCN (Scheme 1) [67]. Slight variations in the imidazole to 1,4-diiodobenzene ratio and reaction conditions used (base, solvent) did not lead to the formation of the bis-coupled product and had no significant effect on the yield of the reaction (Supp. Inf. Table S1). The best conditions for the *N*-arylation appeared to be the use of a slight excess of 1,4-diiodobenzene, a reaction time of 24 h and a temperature of 82 °C.

Then the iodophenyl-imidazole derivatives were reacted with 4-carboxyphenylboronic acid, in order to obtain the imidazole-biphenyl-carboxylic acid target ligands (Scheme 1, reaction 2). Thus, 4'-(1H-imidazol-1-yl)biphenyl-4-carboxylic acid (**HL1**), recently synthesized by Gharat et al. through a different route [71], was obtained in 83% yield in the presence of tetrakis(triphenylphosphine)palladium(0) (5 mol%) by using a ternary mixture of solvents (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>/Et<sub>2</sub>O/H<sub>2</sub>O), Na<sub>2</sub>CO<sub>3</sub> as a base and a reaction time of 24 h (Scheme 1, reaction 2, conditions A). Alternatively, a yield of 85% was obtained by generating the palladium(0) species *in situ* from Pd(OAc)<sub>2</sub> and PPh<sub>3</sub>, in a mixture of *n*-C<sub>3</sub>H<sub>7</sub>OH/H<sub>2</sub>O, as previously reported [72–73]. However, this required a higher palladium loading (10 mol%) (Scheme 1, reaction 2, conditions B). 4'-(1H-benzo[d]imidazol-1-yl)biphenyl-4-carboxylic acid (**HL2**), reported by us for the first time, was obtained in 62% yield in the presence of tetrakis(triphenylphosphine)palladium(0) and a 72% yield when the catalytic system used was Pd(OAc)<sub>2</sub>/PPh<sub>3</sub>.

### 3.2. Synthesis of coordination polymers [Zn(L1)<sub>2</sub>] and [Zn<sub>2</sub>(L2)<sub>2</sub>(Ac)<sub>2</sub>]

The synthesis of the zinc compounds with the ligands **HL1** and **HL2** was successful by reacting a solution of linker and zinc nitrate hexahydrate in 1:2 ratios (L:M) in DMF under solvothermal conditions (120 °C). In the case of **HL2** acetic acid was added in addition as

modulating agent to give suitable single crystals of the Zn-coordinated polymer  $[\text{Zn}_2(\text{L2})_2(\text{Ac})_2]$ .

### 3.3. Characterization

In the  $^1\text{H}$  NMR spectra of the iodophenyl-imidazoles **1** and **2** the aromatic protons of the phenyl groups appear as two doublets in the region 7–8 ppm (Supp. Inf. Figs. S1–S8). Additional information for the signals assignment of the 1*H*-imidazole/1*H*-benzimidazole ring was obtained through 2D NMR homo- and hetero-nuclear correlations. For example, for **1** the signals of the imidazole ring appear as three singlets at 8.26, 7.75 and 7.10 ppm, the first being assigned to the proton of the *N*-C-N group. Characteristic to *para*-substituted phenyl groups, in the  $^{13}\text{C}$  NMR spectra, two signals of the CH groups appear in the region 120 to 145 ppm. The chemical shift value for the aromatic quaternary carbon of the C–I bond, at about 94 ppm is noticed for both precursors. For the imidazole-biphenyl-carboxylic acid ligands **HL1** and **HL2**, the aromatic protons from the 4,4'-substituted biphenyl group appear as four doublets with the “roof effect”, in the region 7.8–8.1 ppm. A new signal, characteristic to the carboxylate group, can be noticed as a broad signal at around 13.0 ppm in the  $^1\text{H}$  NMR spectra of the two ligands. In the  $^{13}\text{C}$  NMR spectra of **HL1** and **HL2**, four signals belonging to the 4,4' substituted biphenyl-group appear in the region 124–135 ppm.

The IR spectra of the iodophenyl-imidazoles **1** and **2** display characteristic absorption bands for imidazolyl and phenyl units (Supp. Inf. Figs. S9–S12). The spectra show moderate intense bands between  $3145\text{ cm}^{-1}$  and  $2921\text{ cm}^{-1}$  that may be assigned to asymmetric and symmetric C–H stretching of the aromatic aryl and imidazole rings. Strong absorption peaks, located in the range of  $1610\text{--}1460\text{ cm}^{-1}$ , indicate the aromatic stretch  $\nu(\text{C}=\text{C})$ , while the peaks at  $1229$  and  $1246\text{ cm}^{-1}$  correspond to the  $\nu(\text{N}-\text{H})$  stretch. The peaks found at  $800\text{--}830\text{ cm}^{-1}$  can be attributed to the  $\nu(\text{C}-\text{C})$  *para*-substituted aromatic ring. In the IR spectra of the imidazole-biphenyl-carboxylic acid ligands **HL1** and **HL2**, the characteristic absorption bands for carboxylate, imidazolyl and phenyl units are displayed. The strong peaks at  $1685$  and  $1690\text{ cm}^{-1}$  are characteristic for the identification of the  $\nu(\text{C}=\text{O})$  stretching vibration of the carboxylate group. The strong absorption peaks of the zinc compounds  $[\text{Zn}(\text{L1})_2]$  and  $[\text{Zn}_2(\text{L2})_2(\text{Ac})_2]$  at  $1620\text{ cm}^{-1}$ – $1596\text{ cm}^{-1}$  can be associated with asymmetric  $\text{COO}^-$  stretch and peaks at  $1404\text{ cm}^{-1}$  and  $1352\text{ cm}^{-1}$  – with symmetric  $\text{COO}^-$  stretch of the carboxylate groups [74].

As far as MS analysis is concerned, for the studied organic compounds, the most intense ions are in good agreement with the calculated monoisotopic mass ( $m/z$ ) for the species  $[\text{M}+\text{H}]^+$  (Supp. Inf. Figs. S13–S16 and Table S2).

The thermal behavior of all compounds was investigated by DSC and TG measurements (Supp. Inf. Figs. S17–S26). The decomposition curves of the iodophenyl-imidazoles **1** and **2** showed a continuous mass loss between 180 and  $320\text{ }^\circ\text{C}$ . The melting points are  $142$  (for **1**) and  $125\text{ }^\circ\text{C}$  (for **2**). The cooling curves showed an exothermic process at approximately  $103$  (for **1**) and  $79\text{ }^\circ\text{C}$  (for **2**), due to the crystallization effect. The nature of the peaks, sharp and very well defined, indicates a high purity of the compounds. Above  $300\text{ }^\circ\text{C}$  the mass loss was more than 90%. The DSC curves of **1** are shown in Fig. 1.

The thermal behaviour of the imidazol-biphenyl-carboxylic acid ligands **HL1** and **HL2** along with their zinc compounds  $[\text{Zn}(\text{L1})_2]$  and  $[\text{Zn}_2(\text{L2})_2(\text{Ac})_2]$  are presented in Supp. Inf. The decomposition curves of **HL1** and **HL2** showed a continuous mass loss between 280 and  $500\text{ }^\circ\text{C}$ , as a result of ligand degradation. For the coordination polymers  $[\text{Zn}(\text{L1})_2]$  and  $[\text{Zn}_2(\text{L2})_2(\text{Ac})_2]$ , the process of the decomposition occurs in one stage and their thermal stability are between  $380$  and  $410\text{ }^\circ\text{C}$ , as shown in Supp. Inf. Figs. S25–26. The thermal behavior of the imidazol-biphenyl-carboxylic acid ligands **HL1** and **HL2** along with their zinc compounds  $[\text{Zn}(\text{L1})_2]$  and  $[\text{Zn}_2(\text{L2})_2(\text{Ac})_2]$  are presented in Supp. Inf. The decomposition curves of **HL1** and **HL2** showed a

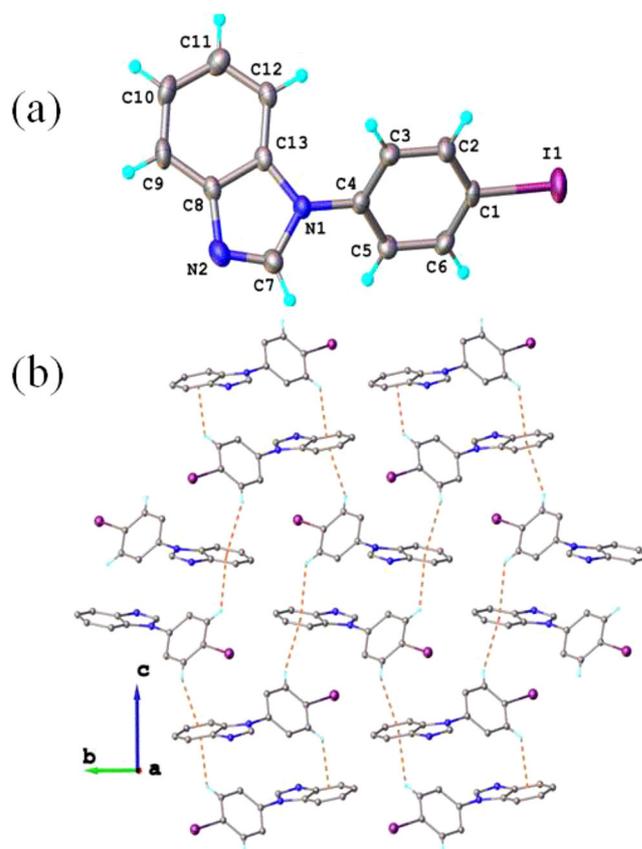


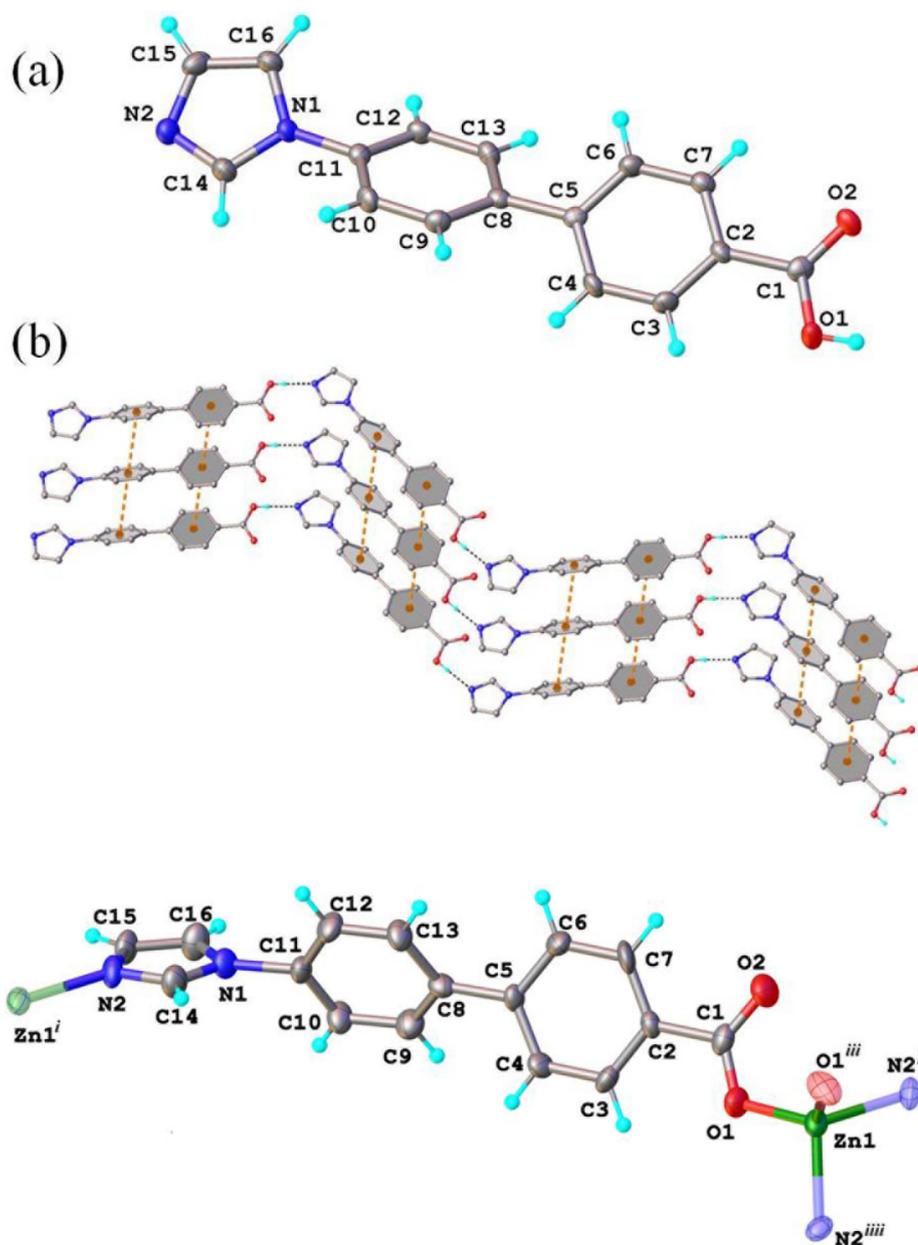
Fig. 2. (a) X-ray molecular structure of **1** with atom labelling scheme and thermal ellipsoids at 50% probability level. (b) 3D supramolecular network in the crystal packing of **1** viewed along *a* axis. Mean planes formed by phenyl rings are shown in brown. Short C–H... $\pi$  (2.964(5) Å) and centroid-to-centroid (3.862(5) Å) intermolecular contacts are drawn as dashed orange, while N...I contacts are shown as dashed black lines. Only the H-atoms involved in intermolecular interactions are shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

continuous mass loss between 280 and  $500\text{ }^\circ\text{C}$ , as a result of ligand degradation. For the coordination polymers  $[\text{Zn}(\text{L1})_2]$  and  $[\text{Zn}_2(\text{L2})_2(\text{Ac})_2]$ , the process of the decomposition occurs in one stage and their thermal stability are between  $380$  and  $410\text{ }^\circ\text{C}$ , as shown in Supp. Inf. Figs. S25–26.

### 3.4. Single crystal X-ray structure determinations

The molecular structures of the iodophenyl-imidazole derivatives **1** and **2** shown in Figs. 2a and 3a, respectively. Bond distances and angles are summarized in Supp. Inf. Table S3. The main crystal structure motif in **1** can be characterized as a parallel packing of two-dimensional supramolecular layers consolidated by  $\pi$ -stacking and C–H... $\pi$  interactions, which take place between the phenyl parts of adjacent molecules. In addition, 2D layers are combined to form a three-dimensional supramolecular architecture due to weak intermolecular nitrogen-halogen bonds at  $\text{N}\cdots\text{I}(x, 1.5 - y, z - 0.5)$  of  $3.126(7)\text{ }^\circ\text{Å}$  (Fig. 2b).

Compared with **1**, the crystal packing of **2** show only the presence of C–H... $\pi$  interactions, which determines the formation of two-dimensional wave-like supramolecular layers extended in the 011 plane. A view of the 2D network is shown in Fig. 3b. We note that the packing of **2** lacks the N...I interactions which are seen in **1**, presumably due to the more important role of the C–H... $\pi$  interactions due to the anellated benzene ring in the 1*H*-benzo[*d*]imidazole part of the ligand. The parallel packing of discrete 2D layers in the crystal, where the interlayer contacts are equal or exceed the sums of van der Waals radii are



**Fig. 3.** (a) X-ray molecular structure of **2** with atom labelling scheme and thermal ellipsoids at 50% probability level. (b) Section of the crystal packing along the *c* axis in **2**. Short C-H... $\pi$  (2.7450(2) and 2.8525(2) Å) intermolecular contacts are drawn as dashed orange lines. Only the H-atoms involved in intermolecular interactions are shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Fig. 4.** (a) Molecular structure for **HL1** with atom labelling scheme and thermal ellipsoids at 50% probability level. (b) Structure of two-dimensional supramolecular network in the crystal of **HL1**. H-atoms not-involved in hydrogen bonding are omitted. Centroid-to-centroid distances are drawn in dashed-orange line. H-bond parameters: O1-H...N2 [O1-H 0.82 Å, H...N2 1.81 Å, O1...N2(1 - *x*, 0.5 + *y*, 0.5 - *z*) 2.632 Å,  $\angle$ OHN 179°]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

illustrated in Fig. S27.

The molecular structure for **HL1** is shown in Fig. 4a, with the geometric parameters listed in Supp. Inf. Table S3. Compound **HL1** exhibits a 1D supramolecular chain structure constructed by *head-to-tail* hydrogen-bonding of the carboxyl group towards the imidazole nitrogen atom (Fig. 4b).

In the crystal, the infinite hydrogen-bonded chains are further interconnected into a two-dimensional wave-like supramolecular network through an extended system of  $\pi$ -stacking interactions, which is evidenced by centroid-to-centroid distances of 3.847 Å for all pairs of phenyl rings, as shown in Fig. 4b.

The results of the X-ray diffraction study for compound  $[\text{Zn}(\text{L1})_2]$  are shown in Fig. 5, the bond distances and angles are summarized in Supp. Inf. Table S3. The asymmetric unit comprises one Zn(II) ion in a special position on a twofold axis and one 4'-(1*H*-imidazol-1-yl)biphenyl-4-carboxylate anion as bridging ligand (**L1**<sup>-</sup>). The zinc atom is tetra-coordinated with a slightly distorted tetrahedral environment provided by two nitrogen atoms (Zn1-N2 2.024(4) Å) and two oxygen atoms (Zn1-O1 = 1.947(3) Å) from four bridging **L1** ligands. The long

Zn1...O2 contact of 2.983(4) Å clearly indicates that the second oxygen of the carboxylate group is not coordinated to any Zn atom.

The zinc-ligand coordination in  $[\text{Zn}(\text{L1})_2]$  forms a 2D coordination network (**sql**) parallel to the 100 crystallographic plane, as shown in Fig. 6a. The shortest separation between two Zn atoms within the 2D network is 17.525(4) Å. The bidentate organic spacers are puckered or lying out of the plane formed by Zn atoms so that the thickness of 2D coordination network is about 5.33 Å (Fig. 6b).

Further analysis of the crystal structure of  $[\text{Zn}(\text{L1})_2]$  revealed the interpenetration [75–77] of three symmetry-related 2D frameworks due to the large openings. The window size in the **sql** network is large enough to allow for a 2D + 2D + 2D interpenetration of the **L1** linkers from a symmetry-related parallel net giving rise to a triple 2D layer propagated in the same 100 orientation, as shown in Fig. 6b, c.

Compound  $[\text{Zn}_2(\text{L2})_2(\text{Ac})_2]$  crystallizes in the monoclinic, non-centrosymmetric space group  $P2_1$ . The asymmetric unit includes two Zn (II) ions, two 4'-(1*H*-benzo[*d*]imidazol-1-yl)biphenyl-4-carboxylate linkers and two acetate anions. The secondary building unit (SBU) is formed by two Zn atoms bridged by two acetate anions in different

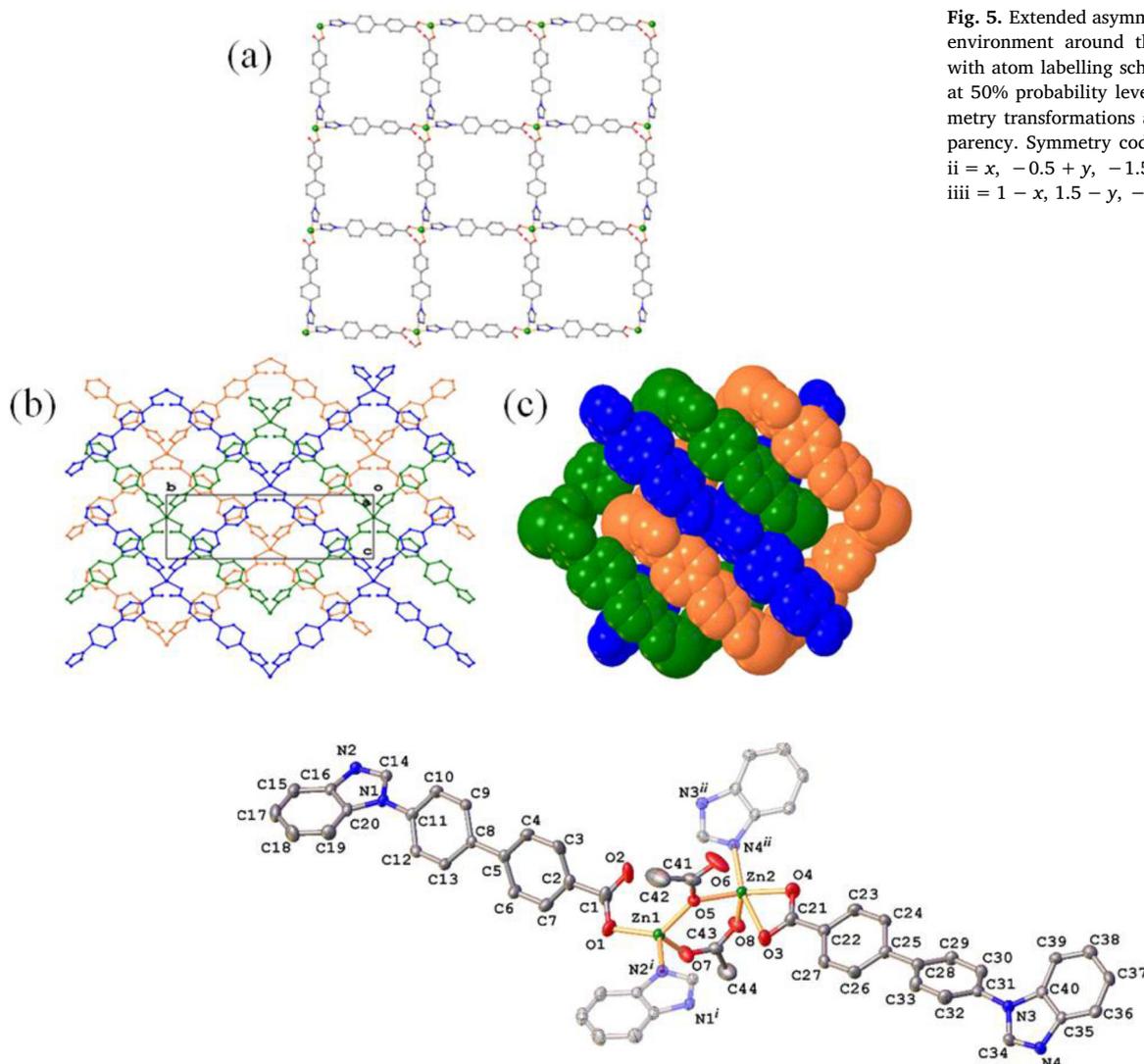


Fig. 5. Extended asymmetric unit and coordination environment around the Zn atom in  $[\text{Zn}(\text{L}1)_2]$  with atom labelling scheme and thermal ellipsoids at 50% probability level. Atoms obtained by symmetry transformations are shown with 50% transparency. Symmetry codes: i =  $x, 0.5 + y, 1.5 + z$ ; ii =  $x, -0.5 + y, -1.5 + z$  iii =  $1 - x, 1 - y, z$ ; iiiii =  $1 - x, 1.5 - y, -1.5 + z$ .

Fig. 6. (a) 2D metal–ligand polymer viewed along the  $a$  axis. Hydrogen atoms are omitted; (b) three interpenetrating metal–ligand networks in the crystal structure of  $[\text{Zn}(\text{L}1)_2]$  viewed along the  $a$  axis; (c) A section of three interpenetrating coordination polymers shown in space filling mode.

coordination modes. One acetate is bridging as a  $\mu_2\text{-}\kappa\text{O}:\kappa\text{O}'$  bidentate ligand, that is, with both oxygen atoms, while the other acetate exhibits a  $\mu_2\text{-}\kappa\text{O}:\kappa\text{O}$  mode where only one oxygen atom bridges between the Zn atoms. The separation between the two Zn atoms is of 3.524(3) Å. The coordination mode of the two carboxylate groups from the independent **L2** ligands is also different: The carboxyl group with O1 and O2 is coordinated as monodentate  $\kappa\text{O}$ : and the carboxyl group with O3 and O4 acts as bidentate chelating ligand ( $\kappa^2\text{O}, \text{O}'$ ). The two Zn atoms, each also coordinated by an imidazole nitrogen atom, differ in their coordination mode. Zn1 is fourfold coordinated by three oxygen and one nitrogen atom. Zn2 is fivefold coordinated by four oxygen atoms and one nitrogen atom. From the Addison  $\tau$  parameter (difference between the two largest angles divided by 60°) the Zn2 coordination has  $\tau = 0.42$ , which puts the coordination slightly more towards square pyramidal (ideal  $\tau = 0.0$ ) than trigonal-bipyramidal (ideal  $\tau = 1.0$ ). It is noted, that the two carboxylic oxygen atoms O2 and (acetate) O6 are not involved into coordination to the metal, as shown in Fig. 7.

The two crystallographically different **L2** linkers are bridging between the same two  $\{\text{Zn}_2(\text{Ac})_2\}$  SBUs. This gives rise to one-dimensional coordination polymeric  $2_1$ -helical double strands which built up the crystal structure of  $[\text{Zn}_2(\text{L}2)_2(\text{Ac})_2]$  (Fig. 8). Adjacent 1D double strands are packed in parallel to 101 direction.

There are known a series of coordination polymer compounds based

on 4-(benzimidazole-1-yl)benzoic and 4-(imidazole-1-yl)benzoic acids, that are structurally close related to imidazole-biphenyl-carboxylate linker used in present work. Although, the dimension of these ligands differ by a phenyl ring, due to the presence of the same functional groups they exhibit similar coordination functions. Mostly, these ligands act as bi-nodal linkers being coordinated towards two different metal atoms through monodentate, [78–81] bidentate (or bidentate-bridging), [78–83] tridentate-bridging [79–80] carboxylate group and through the nitrogen atom of the imidazole ring.

The crystal structure refinement data for the absolute structures, and determined Flack parameters of  $-0.02(3)$  and  $-0.012(8)$  for  $[\text{Zn}(\text{L}1)_2]$  and  $[\text{Zn}_2(\text{L}2)_2(\text{Ac})_2]$ , respectively, (Table 1) indicate that the individual investigated crystals are enantiopure (homochiral). A Flack parameter close to zero confirms the correct absolute structure and excludes the presence of complexes with opposite metal chirality within the investigated crystal in significant amounts [84–86]. For example in  $[\text{Zn}_2(\text{L}2)_2(\text{Ac})_2]$  the fourfold distorted-tetrahedrally coordinated Zn1 atom is origin of the non-centrosimmetry, as it is surrounded by four different ligand donor atoms. In the absence of an inversion center or mirror plane only Zn1 atoms of the same absolute configuration are then assembled into homochiral crystals in a phenomenon which is termed spontaneous resolution [2,87,88]. Bridging ligands in coordination network can transfer induce the crystallization of metal

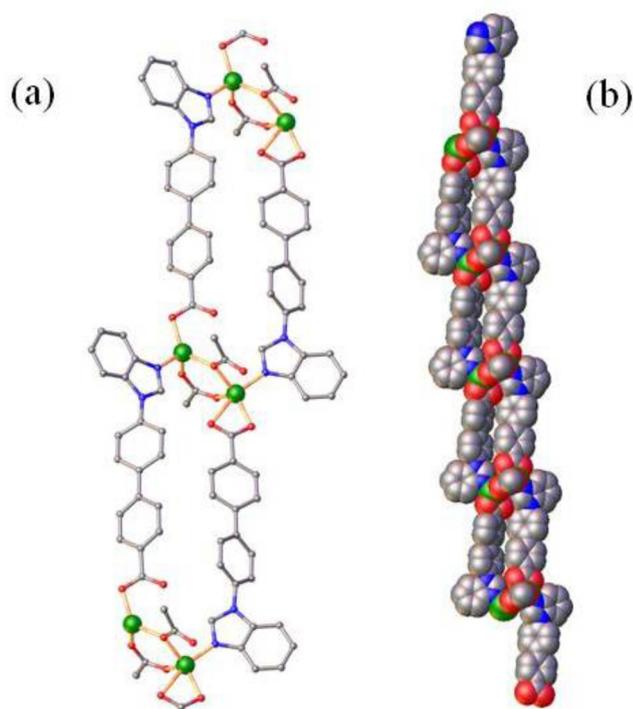


Fig. 7. Asymmetric part in the crystal structure  $[\text{Zn}_2(\text{L}2)_2(\text{Ac})_2]$  with atom labelling scheme and thermal ellipsoids at 50% probability level. H-atoms are not shown. Atoms obtained by symmetry transformations are shown with 50% transparency. Symmetry codes:  $i = -1 + x, y, -1 + z$ ;  $ii = 1 + x, y, 1 + z$ .

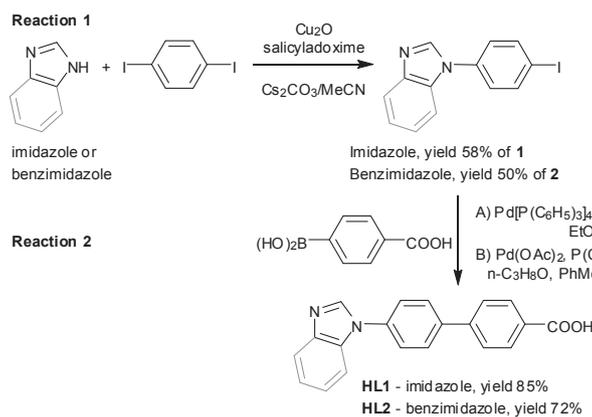


Fig. 8. (a) 1D coordination polymeric double strand in the crystal structure of  $[\text{Zn}_2(\text{L}2)_2(\text{Ac})_2]$ ; (b) Space filling representation. H-atoms are omitted.

centers with the same absolute configuration within a single (homochiral, enantiopure) crystal [89–91]. The crystal ensembles in  $[\text{Zn}(\text{L}1)_2]$  and  $[\text{Zn}_2(\text{L}2)_2(\text{Ac})_2]$  are most likely racemic conglomerates, that is, Zn atoms with the opposite absolute configuration will assemble each in its own crystal, which is then homochiral or enantiopure.

#### 4. Conclusion

In summary, two Zn(II) coordination polymers on the base of new ligand, were synthesized and their crystal structure, as well as those of two organic precursors, were recorded. Compound **HL1** exhibits a 1-D supramolecular chain structure constructed by *head-to-tail* linking of the non-deprotonated molecules through hydrogen bonding formed by carboxylate groups as donors towards imidazole nitrogen as acceptors of protons. The crystal structure of compound  $[\text{Zn}(\text{L}1)_2]$  showed that

the metal is *tetra*-coordinated by two nitrogen atoms from two bridging ligands and oxygen atoms of carboxylate groups to formed a 2D network.

The carboxylic group of 4'-(1H-benzo[d]imidazol-1-yl) biphenyl-4-carboxylic ligands, in the  $[\text{Zn}_2(\text{L}2)_2(\text{Ac})_2]$  compound, shows both mono- as well as bidentate coordination mode to the metal atoms. Also, two zinc atoms are bridged by two acetate anions, with formation a binuclear polymeric compound.

#### Acknowledgements

The financial support of European Social Fund for Regional Development, Competitiveness Operational Programme Axis 1 – Project “Novel Porous Coordination Polymers with Organic Ligands of Variable Length for Gas Storage”, POCPOLIG (ID P\_37\_707, Contract 67/08.09.2016, cod MySMIS: 104810) is gratefully acknowledged.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2018.05.024>.

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