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Synthesis and Structure of Zinc(II) and Cobalt(II) Coordination Polymers Involving the Elongated 2',3',5',6' Tetramethylterphenyl-4, 4''-dicarboxylate Ligand

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Keywords: Zn(II) and Co(II) coordination polymers, linear tetramethylterphenyl dicarboxylate; mixed ligands.

Abstract: The elongated linker 2',3',5',6'-tetramethylterphenyl-4,4"-dicarboxylic acid (H₂L) was employed in the synthesis of zinc(II) and cobalt(II) coordination polymers with single or mixed bridging ligands. Seven compounds, that include the solvate H₂L·2DMSO (1·2DMSO), the 1D coordination polymer $[Zn(L)(DMF)_2]_n$ (2), the two 2D coordination polymers $\{[Zn(L)(DEF)]_2 \cdot 2DEF\}_n$ (3) and $\{[Co(L)(DEF)]_2 \cdot 2DEF\}_n$ (4), and the three mixed ligand 3D coordination polymers { $[Zn_2(L)_2(BIBP)] \cdot 2DEF$ }_n (5), { $[Co_2(L)_2(BIBP)] \cdot 2DEF$ }_n (6) and $\{[Zn_3(L)_3(BIPY)_{1.5}] \cdot 4DMF \cdot 1.5H_2O\}_n$ (7), (where DMSO is dimethylsulfoxide, DMF) dimethylformamide, DEF is is diethylformamide, BIBP stands for 4,4'-bis(1imidazolyl)biphenyl, and BIPY for 4,4'-bipyridine) have been synthesized and characterized by IR spectroscopy, thermogravimetry, and single-crystal X-ray diffraction. In 2 the zinc atom adopts a tetrahedral O₄ environment due to the monodentate coordination of two DMF molecules and two deprotonated bridging L²⁻ ligands. The latter connect the zinc atoms in a zigzag-like chain. In the coordination polymers 3 to 7 the secondary building unit (SBU) is the paddle-wheel moiety $\{M_2(O_2C)_4(N/O)_2\}$. The metal atoms are five coordinated with distorted square pyramidal coordination geometry by oxygen atoms from carboxylate groups of four different L²⁻ linkers, and one axial DEF-O atom in 3 and 4, BIBP-imidazolyl-N atom in 5 and 6 or BIPY-N atom in 7. Furthermore, the L²⁻ ligands link the SBUs to a (4,4) 2D sql net. In 5-7 these sql nets are additionally linked by BIBP or BIPY ligands as pillars to provide pillared-layer 3D and three-fold interpenetrated frameworks. Remarkably, the BIBP pillar yields **bsn** (beta-Sn) topology, the BIPY pillar **pcu** (α -Po) topology.

1. Introduction

Metal-organic frameworks (MOFs) are constructed from organic ligands and metal ions or metal clusters [1, 2] and have uniform micropore structures with high surface areas and large pore volumes. An immense research advancement has been made in the utilization of MOFs since the past 10-15 years [3, 4], e.g. in catalysis [5–7], gas storage [8–10] and gas separation [11–13] and recently in cycling heat transformations [14–24]. Numerous overviews or review articles have been published in the last years indicating the increasing interest in MOF chemistry [25–29]. In constructing the open frameworks, organic polycarboxylate linkers, especially rigid linear di- or tri-carboxylic acids, are frequently utilized because they can act as counter anions and allow for a predictable architecture using the concept of isoreticular design [30-33]. In the Cambridge Crystallographic Structure Databank, CCSD [34] six compounds of Ca, Mg, Zn and Zr were established with the linear ligand 2',3',5',6'tetramethylterphenyl-4,4"-dicarboxylic acid (H₂L) (Scheme 1) [35–40]. By solvothermal reaction using H₂L and Zn(NO₃)₂·6H₂O two Zn^{II} complexes were synthesized, in which L²⁻ coordinates in different modes to generate a wavy 2D (4,4) network and in the other a planar 2D (4,4) network [36]. A mixed-ligand strategy was used in the synthesis of the mixed-ligand coordination polymer { $[Zn_2(L)_2(tib)] \cdot DMF \cdot 10H_2O$ }_n (tib = 1, 3, 5-tris(1-imidazolyl)benzene) in which the Zn atoms are connected by carboxylate groups to form paddle-wheel binuclear secondary building units $\{Zn_2(O_2C_{-})_4\}$ within a 2D $\{Zn_2(L)_2\}$ network. The tib ligands also acts as a bidentate bridging ligand and links the $\{Zn_2(L)_2\}$ network into a 3-fold interpenetrating 3D framework [37]. As pillar linker H₂L was used in the coordination copolymerization of the ditopic linker BDC (1,4-benzenedicarboxylate) and the tritopic linker TPA (4,4',4"-tricarboxylate-triphenylamine) to produce a non-interpenetrated pillared-layer structure with the $\{Zn_4O(O_2CR)_6\}$ SBU [38]. From solvothermal reaction of Mg(NO₃)₂ and H_2L a 3D magnesium MOF of formula $[Mg(L)(DMSO)]_n$ with infinite 1D Mg chain SBUs and coordinated DMSO molecules was obtained. These chains are linked via the carboxylate groups of the L^{2-} ligand into a 3D network. The Mg MOF shows good thermal and moisture stability and can selectively adsorb CO₂ over N₂ [39]. From the mixture of the solvents DMF/dioxane/H₂O the calcium(II) framework $\{[Ca(L)(dioxane)] \cdot 2H_2O\}_n$ was synthesized. The central Ca²⁺ ion is eight-coordinated by six carboxylate oxygen atoms from four different L²⁻ molecules and two oxygen atoms from two coordinated dioxane molecules. Both carboxylate groups of a L²⁻ ligand are linked with two Ca²⁺ ions each to form 1D metal chains. Further, each L²⁻ ligand bridges two chains, forming a 3D framework [40].

Herein, we report the synthesis, characterization and crystal structures of seven compounds based on the H₂L ligand that include the solvate (H₂L·2DMSO) (1·2DMSO), the 1D coordination polymer [Zn(L)(DMF)₂]_n (2), the two 2D coordination polymers $\{[Zn(L)(DEF)]_2 \cdot 2DEF\}_n$ (3) and $\{[Co(L)(DEF)]_2 \cdot 2DEF\}_n$ (4), and the three mixed-ligand 3D coordination polymers $\{[Zn_2(L)_2(BIBP)] \cdot 2DEF\}_n$ (5), $\{[Co_2(L)_2(BIBP)] \cdot 2DEF\}_n$ (6) and $\{[Zn_3(L)_3(BIPY)_{1.5}] \cdot 4DMF \cdot 1.5H_2O\}_n$ (7) (where DMSO is dimethylsulfoxide, DMF is dimethylformamide, DEF is diethylformamide, BIBP stands for 4,4'-bis(1imidazolyl)biphenyl, and BIPY denotes 4,4'-bipyridine) (Scheme 1).



Scheme 1. The ligands used in the synthesis of the coordination networks 2-7.

2. Experimental

2.1. Materials and methods

All chemicals used for synthesis were of analytical grade, purchased commercially (mostly from Sigma Aldrich) and used without further purification. The BIBP ligand was prepared according to a reported procedure [41]. To obtain the linker H₂L (1), 1,2,4,5tetramethylbenzene was first brominated in chloroform at 0 °C, to give the brominated compound 1,4-dibromo-2,3,5,6-tetramethylbenzene in about 96% yield. In the next step, a Suzuki reaction 1,4-dibromo-2,3,5,6-tetramethylbenzene between and 4-carboxyphenylboronic acid afforded H₂L in an overall yield of 67% [42]. CHN elemental analysis was performed on a VarioELIII elemental analyzer. FT-IR spectra were recorded using a Bruker Tensor 37 system equipped with an ATR unit (Platinum ATR-QL, Diamond) in the 4000-550 cm⁻¹ region with 2 cm⁻¹ resolution. The intensity of absorption bands is given as strong (s), medium (m), broad (br) and weak (w). ¹H and ¹³C spectra were recorded on Bruker Avance DRX-200 and Bruker Avance DRX-500 instruments respectively. Thermogravimetric analysis (TGA) was performed on a TG 209 F3 Tarsus. Nitrogen sorption experiments were carried out with Quantachrome NOVA 4200 volumetric gas sorption instrument. Prior to N_2 isotherm measurements at 77 K, the samples were outgassed at 180 °C under a vacuum of 10^{-3} mbar for 4 h. For the sorption measurements 20 to 40 mg of freshly synthesized samples were weighed before and after the degassing procedure to confirm the evacuation of the solvent.

2.2. Synthesis

2.2.1. Preparation of $H_2L \cdot H_2O(1 \cdot H_2O)$

To the solution of 1,4-dibromo-2,3,5,6-tetramethylbenzene (584 mg, 2.0 mmol) in toluene (20 mL) in a 250 mL flask were added Na₂CO₃ (20 mL, 2 mol/L) and Pd(PPh₃)₄ (60 mg, 0.038 mmol) in toluene (5 mL). Through this mixture nitrogen was bubbled for 15 min. 4-Carboxyphenylboronic acid (730 mg, 2.2 mmol) dissolved in ethanol (20 mL) was added to the flask with the mixture and nitrogen was continued to be bubbled through the solution for 5 more minutes. The mixture was refluxed during three days at 105 °C. Afterwards, the mixture was evaporated till dryness. The residue was dissolved in water (50 mL) and the pH was adjusted to ~2 with HCl (conc.) The desired product was extracted with ethyl acetate (3x100 mL). The organic layer was dried over Na₂SO₄, and the solvent was removed in vacuum. Recrystallization from tetrahydrofuran/methanol gave the desired product. Yield: 527.2 mg (67%); M.p. - not melting, dec. ~300°C. Elemental analysis calcd (%) for C₂₄H₂₂O₄·H₂O (M.W. 392.44), C 73.45, H 6.16; found C 73.97, H 6.31 %. ¹H NMR (DMSO-d₆): $\delta = 1.88$ (s; 12H, CH₃), 7.29 (d; 4H, aromatic-CH), 8.06 (d; 4H, aromatic-CH), 13.00 (s; 2H, COOH). FTIR (cm⁻¹; ATR): v = 2991(w), 2954(w), 2877(w), 2654(w), 2538(w), 2285(w), 2102(w), 1942(w), 1830(w), 1679(s), 1607(s), 1563(w), 1515(w), 1462(w), 1420(s), 1383(w), 1312(s),1291(s), 1277(s), 1177(m), 1138(w), 1125(w), 1103(w), 1014(w), 994(m), 944(m), 879(m), 838(w), 811(w), 769(s), 740(w), 708(m), 676(w), 666(w). Single crystals of H₂L for structural study were obtained by recrystallization from DMSO as 1.2DMSO.

2.2.2. $[Zn(L)(DMF)_2]_n$ (2).

 $Zn(NO_3)_2 \cdot 6H_2O$ (59.5 mg, 0.2 mmol), H_2L (39.2 mg, 0.1 mmol) and 1,2,4-triazole (5.6 mg, 0.05 mmol) were mixed in dimethylformamide (DMF, 10 mL) and homogenized by stirring for 2 h. The slurry was heated to 120 °C in a Teflon-lined stainless-steel bomb reactor for 48 h to obtain a white microcrystalline precipitate. The product was washed with DMF and ethanol and dried in an oven at 100 °C. Yield: 45 mg (77%). Elemental analysis calcd (%)

for $C_{30}H_{34}N_2O_6Zn$ (M.W. 583.96) C 61.70, H 5.87, N 4.79; found C 61.61, H 5.47, N 4.59. FTIR (cm⁻¹; ATR): v = 3104(w), 2924(w), 1664(m), 1596(s), 1550(m),1515(s), 1403(s), 1391(s), 1375(s), 1304(m), 1275(m), 1215(w), 1197(w), 1176(m), 1151(m), 1091(m), 1071(m), 1040(w), 1021(w), 1004(m), 989(w), 877(m), 857(m), 775(s), 757(w), 714(m), 679(w).

2.2.3. $\{[Zn(L)(DEF)]_2 \cdot 2DEF\}_n$ (3).

A mixture of Zn(NO₃)₂·6H₂O (59.5 mg, 0.2 mmol) and H₂L (39.2 mg, 0.10 mmol) was dissolved in diethylformamide (DEF, 10 mL) in a 100 mL glass flask. The flask was placed in a 90 °C oil bath and heated for 96 h. Colorless crystals were collected and washed with DEF. Yield: 93 mg (73%); Elemental analysis calcd (%) for C₆₈H₈₄N₄O₁₂Zn₂ (M.W.1280.13) C 63.80, H 6.61, N 4.38; found C 63.75, H 6.55, N 4.31. FTIR (cm⁻¹; ATR): v = 3677(w), 3144(w), 2989(s), 2973(s), 2902(s), 1653(s), 1596(s), 1548(m), 1439(m), 1407(s), 1394(s), 1384(s), 1277(w), 1253(m), 1232(w), 1174(w), 1100(m), 1075(s), 1066(s), 1058(s), 1019(m), 989(w), 880(w), 858(w), 779(s), 753(w), 714(m), 676(w).

2.2.4. { $[Co(L)(DEF)]_2 \cdot 2DEF$ }_n (4).

A mixture of Co(NO₃)₂·6H₂O (58.2 mg, 0.2 mmol) and H₂L (39.2 mg, 0.1 mmol) was dissolved in DEF (10 mL) in a 100 mL glass flask. The flask was placed in a 90 °C oil bath and heated for 96 h. Pink crystals were collected and washed with DEF. Yield: 92 mg (73%); Elemental analysis calcd (%) for C₆₈H₈₄N₄O₁₂Co₂ (M.W.1267.25) C 64.45, H 6.68, N 4.42; found C 64,38, H 6.61, N 4.38. FTIR (cm⁻¹; ATR): v = 3677(w), 3231(w), 2989(s), 2973(s), 2902(s), 1636(m), 1583(s), 1529(m), 1450(m), 1405(s), 1394(s), 1383(s), 1251(m), 1242(w), 1232(w), 1174(w), 1075(s), 1066(s), 1057(s), 1028(m), 943(w), 892(w), 879(w), 794(w), 777(s), 743(w), 711(w). This compound showed a BET surface area 28 m²/g.

Single crystal synthesis of 3 and 4 for structure determination. A mixture of $M(NO_3)_2$ ·6H₂O (29.8 mg, 0.10 mmol) (M = Zn or Co) and H₂L (19.6 mg, 0.05mmol) was dissolved in DEF (2.0 mL) in a 4 mL vial. The vial was tightly capped with a Teflon-lined cap, placed in a 90 °C oven and heated for 96 h.

2.2.5. { $[Zn_2(L)_2(BIBP)] \cdot 2DEF$ }_n (5).

A mixture of BIBP (14.3 mg, 0,05 mmol) and H₂L (19.6 mg, 0,05 mmol) was dissolved in 3 mL or DEF at moderate heating in a 12 mL screw-capped glass test tube. To this ligand solution was added $Zn(NO_3)_2$ ·6H₂O (29.9 mg, 0.1 mmol) dissolved in 2 mL of

DEF. The mixture was heated at 120 °C for 24 h, then cooled to room temperature at the rate of 5 °C/h. Colorless crystals were collected and washed three times with 3 mL of DMF and three times with 3 mL of ethanol. The crystalline product was dried in air at room temperature. Yield: 31.3 mg (92%). Elemental analysis calcd (%) for $C_{76}H_{76}N_6O_{10}Zn_2$ (M.W.1364.23): C 66.91, H 5.62, N, 6.16; found C 66.50, H 5.76, N, 5.78. FTIR (cm⁻¹; ATR): v = 3135(w), 2976(w), 2338(w), 1670(m), 1609(s), 1554(m) 1519(s), 1435(m), 1399(s), 1363(s), 1311(m), 1260(m), 1172(w), 1129(m), 1094(m), 1064(s), 1018(w), 1007(w), 992(w), 964(m), 945(w), 901(w), 880(w), 845(m), 821(m), 795(w), 780(s), 753(w), 713(m), 675(w).

2.2.6. { $[Co_2(L)_2(BIBP)] \cdot 2DEF$ }_n (6).

A mixture of BIBP (14.3 mg, 0.05 mmol) and H₂L (19.6 mg, 0.05 mmol) was dissolved in 3 mL of DEF with moderate heating in a 12 mL screw-capped glass test tube. To this ligand solution was added Co(NO₃)₂·6H₂O (29.1 mg, 0.1 mmol) in 2 mL of DEF. The mixture was heated at 120 °C for 24 h then cooled to room temperature at the rate of 5 °C/h. Pink crystals were collected and washed three times with 3 mL of DMF and three times with 3 mL of ethanol. The crystalline product was dried in air at room temperature. Yield: 32. 1 mg (95%). Elemental analysis calcd (%) for C₇₆H₇₆N₆O₁₀Co₂ (M.W. 1351.32): C 67.55, H 5.67, N 6.22; found C 67.38, H 5.61, N 6.17. *FTIR* (cm⁻¹; ATR): v = 3132(w), 2971(w), 1666(m), 1607(s), 1549(m), 1516(s), 1434(sh), 1402(s), 1309(m), 1290(w), 1279(w), 1257(m), 1217(w), 1177(w), 1130(w), 1105(m), 1063(m), 1021(w), 1005(w), 991(w), 964(w), 944(w), 878(w), 856(m), 844(m), 821(m), 776(s), 750(m), 712(w), 688(w), 673(w).

2.2.7. { $[Zn_3(L)_3(BIPY)_{1.5}]$ ·4DMF 1.5H₂O}_n (7).

Zn(NO₃)₂·6H₂O (59.5 mg, 0.2 mmol), H₂L·(39.2 mg, 0.1 mmol) and 4,4-BIPY (5.6 mg, 0.05 mmol) were mixed in DMF (10 mL) and homogenized by stirring for 2 h. The slurry was heated to 120 °C in a Teflon-lined stainless-steel bomb reactor for 48 h to obtain a white microcrystalline precipitate. The product was washed with DMF and ethanol and dried in an oven at 100 °C. Yield: 90 mg (71%). Elemental analysis calcd (%) for C₆₇H₇₁N₅O₁₂Zn₂ (M.W. = 1269.03) C 63.41, H 5.64, N 5.52; found C 63.34, H 5.57, N 5.49. FTIR (cm⁻¹; ATR): v = 2988(w), 1674(w), 1609(s), 1587(s), 1536(s), 1493(w), 1403(s), 1277(w), 1255(w), 1225(m), 1175(w),1131(w), 1096(w), 1075(m), 1049(w), 1019(w), 990(w), 877(w), 854(m), 818(m), 796(w), 777(s), 755(w), 727(w), 714(m), 675(w).

2.3. X-ray crystallography

Experimental data for 1·2DMSO, 2, 3', 4 and 7 were collected on a Bruker APEX DUO with APEX II CCD area detector, equipped with microfocus sealed tube, Mo-K α ($\lambda = 0.71073$ Å) or Cu-K α ($\lambda = 1.54178$ Å) radiation and multilayer mirror monochromator and for 3, 5 and 6 on an Xcalibur E CCD diffractometer (graphite monochromator) using MoK $_{\alpha}$ radiation, ω -and ϕ -scan. Data collection on the Bruker APEX DUO diffractometer has been carried using Apex2 [43], cell refinement and data reduction with SAINT [44], experimental absorption correction with SADABS [45], and on the Xcalibur with CrysAlis [46].

For compound 7 the data set was initially tried to refine with the solvent molecules of crystallization, revealing the presence of about four DMF and 1.5 water molecules per $\{Zn_3(L)_3(BIPY)_{1.5}\}$ formula unit. As refinement for the crystal solvent was unsatisfactory, and also in view of the low data set quality which is common for MOF structures, the SQUEEZE option as implemented in PLATON [47] was used. A total of 1111 electrons were found (and squeezed) in the solvent accessible volume of 4521 Å³ (within the unit-cell volume of 10372 Å³) with a void probe radius of 1.2 Å.

Final unit cell dimensions for 1 - 7 were obtained and refined on the entire data set. All calculations necessary to solve the structures and to refine the proposed model were carried out with the SHELX program [48]. Non-hydrogen atoms were treated anisotropically (full-matrix least squares method on F^2). Carbon bonded H atoms were placed in calculated positions and were treated using riding model approximations with Uiso(H) = 1.2Ueq(C), while the oxygen bonded H-atoms were found from differential Fourier maps at an intermediate stage of the refinement, and their positions were constrained using the AFIX 83 instruction in SHELX. These hydrogen atoms were refined with the isotropic displacement parameter Uiso(H) = 1.5Ueq(O).

The X-ray data and the details of the refinement for 1 - 7 are summarized in Table S1, the selected bond lengths (Å) and angles (deg) in coordination metal environment in 2 - 7 are given in Table S2 and S3, and hydrogen-bonding geometry in 1 - 7 in Table S5 in the Supplementary material.

3. Results and discussion

3.1. Synthesis

From the reaction of H₂L (1) and zinc(II) or cobalt(II) nitrate under solvothermal conditions (T = 90 °C, t = 96 h, DEF as solvent) the 2D coordination polymers of composition $\{[Zn(L)(DEF)]_2 \cdot 2DEF\}_n$ (3) and $\{[Co(L)(DEF)]_2 \cdot 2DEF\}_n$ (4) were synthesized. In the presence of a weak base such as 1,2,4-triazole under the same solvothermal conditions (T = 90 °C, t = 96 h), but using DMF as solvent a 1D-coordination polymer with composition $[Zn(L)(DMF)_2]_n$ (2) was obtained. The 1,2,4-triazole did not participate in the formation of coordination polymer. The interaction of H₂L with Zn and Co nitrate salts in the presence of BIBP under solvothermal conditions (T = 120 °C, t = 24 h, DEF as solvent) led to formation of 3D coordination polymers with composition $\{[Cn_2(L)_2(BIBP)] \cdot 2DEF\}_n$ (6). By using BIPY under solvothermal conditions (T = 120 °C, t = 48 h, DMF as solvent) the 3D coordination polymer $\{[Zn_3(L)_3(BIPY)_{1.5}] \cdot 4DMF \cdot 1.5H_2O\}_n$ (7) was formed.

3.2 IR-spectra.

The FTIR spectra of the materials are very similar and are given in Figures S1–S7, Supplementary material. The spectra show moderate intense bands between 3300 cm⁻¹ and 2902 cm⁻¹ that may be assigned to asymmetric and symmetric C–H stretching of the aromatic aryl rings. Broad bands between 3600 and 3200 cm⁻¹ correspond to asymmetric and symmetric O–H stretching vibrations of water molecules. The strong absorption peaks at 1679–1583 cm⁻¹ can be associated with asymmetric COO⁻ vibration, and peaks at 1312–1391 cm⁻¹ with symmetric COO⁻ vibration of the carboxylate groups [49]. The strong bands between 1609 cm⁻¹ and 1540 cm⁻¹ may be assigned to C=C stretching of the aromatic aryl rings. The absorption bands in the IR spectra of **4** and **5** at 1064 and 964 cm⁻¹ indicate the presence of N-substituted imidazole rings. Because the stretching vibrations of the carboxylate groups and the characteristic stretching vibrations of the imidazole rings and phenyl rings both appear at 1550–1700 cm⁻¹ and overlap partially, the absorption bands in this region are comparatively broad. A single absorption band at 845 cm⁻¹ might be attributed to the bending vibration of a para-substituted benzene ring [49].

3.3 Thermogravimetric analysis

In order to assess the thermal stability of the coordination architecture of compounds 1–7, thermogravimetric analyses (TGA) were carried out on the crystalline materials in air at a heating rate of 5 °C/min in the temperature range of 30–1000 °C (Figures S8-S14, Supplementary material). From its synthesis the ligand was obtained with one molecule of

solvent water as $H_2L \cdot H_2O$ (1·H₂O). During the thermogravimetric analysis $H_2L \cdot H_2O$ loses this one molecule of water at ~100 °C (found 4.5 wt.%, calc. 4.6 wt.%) and is then stable up to 350 °C, after which a rapid decomposition occurs. Compound 2 is stable up to 160 °C, and after losing of two DMF molecules (found 25 wt.%, calc. 25.0 wt.%) at 160-200 °C it remains stable up to 340 °C, after which the coordination polymer decomposes. For complexes 3 and 4, the initial weight loss of ~16 wt.% before 320 °C is due to the release of two coordinated DEF molecules (calc. 15.8 wt.% and 16.0 wt.%, respectively). The second weight loss occurs in the temperature range of 320-450 °C, and is ascribed to the release of the L²⁻ ligand from the framework. The TGA investigations of the isostructural compounds 5 and 6 indicate a gradual weight loss of ~15 wt.% in the temperature range of 100-300 °C, which is due to the release of the two non-coordinated DEF molecules (calc. 14.8 wt.% and 15.0 wt.%, respectively). The second weight loss of ~70 wt.% occurs in the temperature range of 350-500 °C, and is attributed to the release of the BIBP co-ligand and the L ligand from the framework. Compound 7 is stable up to 100 °C after which it loses 18.3 wt.% of solvent (calc. 18.7 wt.%) up to 180 °C, and reaches a plateau until 380 °C, where the structure collapses. The solvent-depleted coordination polymers 2-7 are mostly stable until at least 300 °C, except for 4 which start to decompose around 250 °C.

3.4 Gas sorption studies

Compounds 3-7 contain non-coordinated solvent of crystallization. This solvent was tried to remove by activating 20-40 mg of sample through heating at 180 °C under vacuum of 10^{-3} mbar for 4 h. Figure S15-S19 in the Supplementary Material present the N₂ sorption curves for the activated compounds. The Brunauer-Emmett-Teller (BET) surface areas (S_{BET}) of the activated 2D networks were calculated for **3** as S_{BET} = 145 m²/g and for **4** with S_{BET} = 28 m²/g. For the pillar-layer frameworks **5** and **6** with BIBP as coligand the surface areas are 83 and 19 m²/g, respectively. In the 3D framework 7 the surface area was 66 m²/g. Overall, these surface area of a fine powder. From the TGA studies, heat-vacuum activation under the used conditions should have been successful to sufficiently remove even low volatile DEF and DMF solvent of crystallization. Evidently, the solvent-depleted networks are not stable and collapse.

3.5 Structural characterization

Compound $[Zn(L)(DMF)_2]_n$ (2) crystallizes in monoclinic space group C2/c (Table S1, Supplementary material). The asymmetric unit comprises one half of a zinc atom located on the twofold rotation axis, one half of the L²⁻ ligand which resides on an inversion center and one DMF molecule. The zinc atom adopts a tetrahedral O₄ surrounding due to coordination of two DMF molecules and two fully deprotonated monodentate L²⁻ ligands (Fig. 1). The interatomic distances Zn1-O1 and Zn1-O3 are 1.935(1) and 1.979(2) Å, respectively, O-Zn-O angles cover the range 100.30(8) - 119.08(7)° (Table S2, Supplementary material). The orientation of the DMF molecules is stabilized by intramolecular C-H···O2 3.122 Å (H···O 2.36Å, ∠CHO 139°) interactions (Table S5, Supplementary material). The dicarboxylate ligand bridges the zinc atoms and both form a zigzag-like chain along the (-101) crystallographic direction with coplanar arrangement of metal atoms and carboxyphenyl moieties (Fig. 1). The Zn…Zn separation through the L²-ligand along the chain equals 19.5 Å and the Zn…Zn angle is 116.1°. The carboxyphenyl fragments of the ligand are coplanar and form a dihedral angle of 72.8° with the central tetramethylphenyl moiety. In the crystal the parallel chains are united in supramolecular layers parallel to the (101) crystallographic plane by inter-chain C-H···O2 (x, y+1, z) interactions with parameters H···O 2.50, C···O 3.200 Å, ∠CHO 137°, shown in Fig. 2a. Between these parallel layers only van der Waals interactions are observed (Fig. 2b).



Fig. 1. View of the 1D coordination polymer in **2** with partial atomic numbering scheme (50% thermal ellipsoids).



Fig. 2. Fragment of the crystal packing of **2** to illustrate (a) the formation of the supramolecular layer parallel to the (101) plane and (b) the parallel arrangement of layers; hydrogen atoms in (b) were omitted for clarity.

The two isostructural compounds **3** and **4** with composition $\{[Zn(L)(DEF)]_2 \cdot 2DEF\}_n$ and $\{[Co(L)(DEF)]_2 \cdot 2DEF\}_n$, crystallize in the monoclinic space group C2/c (Table S1, Supplementary material). The asymmetric part of unit cell of these compounds contains one Zn or Co atom, two-halves of the L²⁻ ligands, one of which resides on an inversion center and another one on a two-fold axis, together with one coordinated and one crystal solvent DEF molecule (Fig. 3a). The carboxyphenyl fragments and central tetramethylphenyl moiety of the L²⁻ ligands form dihedral angles close to perpendicular (82.2–89.0°). The structure of **3** has been described earlier [38], but we have repeated the structural study of this compound at two temperatures: 293 (**3**) and 95 K (**3**°).

The secondary building unit of the metal and ligand donor atoms is the dinuclear paddle-wheel unit. Thus, metal atoms are five coordinated with slightly distorted square pyramidal coordination geometry by four oxygen atoms from carboxylate groups of four L²⁻ in the base of pyramid and one oxygen from DEF in axial position. The Addison parameter τ [50] equals 0.008, 0.003 and 0.008 in **3**, **3'** and **4**, respectively ($\tau = 1$ for an ideal trigonal bipyramid and $\tau = 0$ for an ideal square pyramid). The Zn–O distances fall in narrow range of 1.979(3) – 2.062(3) Å at 293 K (for **3**) and of 1.980(3) – 2.061(3) Å at 95 K (for **3'**). The Co–O distances are in the range of 1.999(6) – 2.085(6) Å (for **4**, Table S2, Supplementary material). The linker L²⁻ acts as ($\kappa 1-\kappa 1$)-($\kappa 1-\kappa 1$)- μ_4 bridge to connect four metal atoms. Together, the ligands link the dinuclear paddle-wheel units to form a (4,4) 2D square lattice (**sql**) (Fig. 3b). The **sql** layers are parallel to the (-102) crystallographic plane, separated by the terminal DEF axial ligands and DEF crystal-solvent guest molecules, and stack in

ABABAB... fashion along the crystallographic *c* axis (Fig. 3c). The metal…metal separation in the dinuclear moiety equals 2.949(1)/2.950(1) Å in **3** and **3'** at room and low temperature, respectively, and 2.828(3) Å in **4** (Table S2, Supplementary material). The distances between the centroids of the paddle-wheel units in the square lattice across the L ligands are 19.4 and 19.5 Å, 19.5 and 19.5 Å, and 19.4 and 19.5 Å, and the distances between mean planes of the layers equal 4.6, 4.4 and 4.5 Å in **3**, **3'** and **4**, respectively. The comparison of room and low temperature data shows that the metrics of the **sql** net is slightly dependent on temperature, while the distance between the mean planes of the grids vary by about 2%, which is in a good agreement with the difference in the unit cell parameter *c*. Only weak C–H…O interactions have been found in the structures of **3** and **4** between the grids and between the grids and solvent DEF molecule (Table S5, Supplementary material). Without the solvent molecules open channels would be formed between the grids (Fig. 3d) which are at least partially retained upon activation as seen from the N₂ sorption measurements which gave a BET surface area of 145 m²/g for **3**.



Fig. 3. (a) $[M_2(L)_4(DEF)_2]$ dinuclear unit in 4 (isostructural to 3 with M = Zn) with partial atomic numbering scheme (50% thermal ellipsoids). (b) Fragment of a 2D sql coordination polymer. (c, d) Stack of parallel layers with (c) and without (d) the DEF crystal solvent shown in space filling mode.

The total solvent accessible void volume for **3**, **3'** and **4** was calculated by PLATON [47] upon removal of the solvent DEF molecules and equals 28, 27 and 27 % of the total unit cell volume, respectively.

In **3** and **4** the paddle-wheel dinuclear units serve as four-connected square nodes with terminal axial ligands and the carboxylate C atoms serve as sole points of extension, resulting in the 2D grid-like **sql** structure. These 2D nets may be used to generate 3D porous MOFs via "pillaring" of these layered structures by bridging the axial metal sites of the paddle-wheel moieties [51]. The terminal ligands at the SBU can be replaced by a ditopic ligand, typically a nitrogen donor, and the paddle-wheel binuclear units then serve as six-connected octahedral 6-c nodes resulting in 3D mixed-ligand MOFs [52].

We used this strategy to transform the 2D coordination polymers **3** and **4** into 3D MOFs by addition of BIBP or BIPY as N,N-exo-bidentate rigid ligands into the reaction mixture. The latter replace the terminal axial DEF ligands and result in the 3D and three-fold interpenetrated frameworks { $[Zn_2(L)_2(BIBP)] \cdot 2DEF$ }_n (**5**), { $[Co_2(L)_2(BIBP)] \cdot 2DEF$ }_n (**6**) and { $[Zn_2(L)_2(BIPY)] \cdot 4DMF \cdot 1.5H_2O$ }_n (**7**). Remarkably, the BIBP pillar yields **bsn** (beta-Sn) topology, the BIPY pillar **pcu** (primitive cubic, α -Po) topology.

The two isostructural and isomorphic compounds 5 and 6 crystallize in the monoclinic space group C2/c and have nearly identical unit-cell parameters, (Table S1, Supplementary material). The asymmetric part of the unit cell comprises one Zn or Co atom, two-halves of the L²⁻ ligands, one-half of the BIBP ligand and one DEF solvent molecule (Fig. 4a). Similar to 3 and 4 one of the L²⁻ ligands resides on an inversion center and another one on the twofold axis and both form a square lattice, sql network for the $\{M(L)_2\}_n$ substructure (Fig. 5b). Compared with 3 and 4, the structures of 5 and 6 demonstrate some difference in the formation of the paddle-wheel dinuclear unit. Two symmetry independent L²⁻ ligands reveal different coordination modes $(\kappa 1 - \kappa 1) - (\kappa 1 - \kappa 1) - \mu_4$ and $(\kappa 2 - \kappa 1) - (\kappa 2 - \kappa 1) - \mu_4$. For the first coordination mode the Zn-O and Co-O distances equal 2.016(2) and 2.023(3) Å, while for second one they are in the range 2.085(2) - 2.492(3) and 2.087(3) - 2.299(3) Å (Table S3 in Supp. Inf.), respectively. It should be mentioned unusual (κ^2 - κ^1) bridging function of carboxylic group in paddle-wheel unit for second coordination mode which is more pronounced in 5 and 6: one of the oxygen atoms of carboxylic group serves as a bridge between two metal atoms with Zn–O distances 2.085(2) and 2.492(2) Å, and Co–O 2.087(3) and 2.298(3) Å. The survey of CSD did not reveal so short second metal – oxygen atoms contacts in paddle-wheel (Zn₂/Co₂) units. The shortest second metal-oxygen atoms contacts

observed before are 2.648 Å [53] and 2.780 Å [54] for Co₂ and 2.805 Å [55] for Zn₂ units, respectively. The couples of the ligands with the identical coordination mode in **5** and **6** are *trans*-situated with respect to the couple of two-fold related metal atoms and unite them in distorted paddle-wheel dinuclear SBUs with molecular symmetry essentially different from C_4 (Fig. 5c). The metal atoms are five coordinated with square pyramidal coordination geometry, $\tau = 0.019$ and 0.012 [50].

The interatomic distances Zn…Zn/Co…Co in the dinuclear SBU core equal to 3.0134(6) and 2.931(1) Å, being longer than in 3, 3' and 4. The distances between the centroids of the dinuclear moieties in the square lattice across the dicarboxylic ligands equal 19.1 and 19.5 Å, and 19.1 and 19.5 Å, for 5 and 6, respectively. The slightly larger difference between each of the two values when compared with 3, 3' and 4 is related with the diverse coordination modes for the two unique ligands in 5 and 6. The ditopic BIBP ligands coordinate at the axial position of the square-pyramidally coordinated metal atoms (Zn-N 2.008(2), Co-N is 2.045(4) Å, Table S3 in Supplementary material). This completes their distorted octahedral NO₅ surrounding, and unite the square $\{Zn_2(L)_2\}$ grids to provide a pillared-layer 3D framework with **bsn** topology (Fig. 5b) [52]. The distance between the mean planes of the layers separated by the BIBP ligands as pillars equals to 14.2 and 14.1 Å for 5 and 6, respectively. The crystal structures of 5 and 6 displays a 3-fold parallel interpenetration of the networks (Fig. 5d). Despite the interpenetration, the resulting structure still possesses potential porosity in the form of isolated and solvent-filled cavities. These cavities are filled with DEF crystal solvent molecules (Fig. 5e). Upon omitting these DEF molecules, the total solvent accessible volume for 5 and 6 was calculated by PLATON to 2025.5 and 2021.7 Å³ [47] or 29% of the total unit cell volume.





Fig. 5. (a) View of the $[Zn_2(L)_4(BIBP)_2]$ dinuclear units in 5 (isostructural with 6) with atomic numbering scheme (50% thermal ellipsoids). (b) Section of a single 3D framework with **bsn** (beta-Sn) topology. (c) SBU in the structures of 5. Green double arrow shows the position of two-fold axis. (d) Fragment of the crystal packing to illustrate the three-fold interpenetration of the 3D networks in 5, by depicting only the connectivity of the Zn_2 centroids, with (e) showing also the solvent DEF molecules in space filling mode.

Compound 7 with the formula $\{[Zn_3(L)_3(BIPY)_{1.5}] \cdot 4DMF \cdot 1.5H_2O\}_n$ crystallized in the monoclinic non-centrosymmetric space group C2 (Table S1 in Supp. Inf.). The asymmetric unit contains three Zn atoms, three L²⁻ and one and a half BIPY ligands, together with about 4 DMF and 1.5 water molecules as solvates. For the final structure solution the the SQUEEZE option as implemented in PLATON [49] was used. The L²⁻ ligands in the structure of 7 act as $(\kappa 1 - \kappa 1) - (\kappa 1 - \kappa 1) - \mu_4$ bridges and form two symmetry-independent dinuclear paddlewheel units $[Zn_2(O_2C)_4(N_{BIPY})_2]$. One of them resides around the two-fold axis (Fig. 6a) and another one in a general position (Fig. 6b). Each SBU gives rise to its own, independent 3D framework. The zinc atoms are five coordinated with a distorted square-pyramidal NO₄ surrounding. The Zn. Zn distances in the two different paddle-wheel units almost coincide with 2.890(2) and 2.893(1) Å. The Zn–O distances are in the range 2.002(8)–2.093(8) Å, and Zn-N 2.2011(6)-2.033(6) Å. Metal atoms are five coordinated with square pyramidal coordination geometry (the parameter of distortion τ equals 0.045, 0, and 0.028 for Zn(1), Zn(2) and Zn(3), respectively). Linked through the dicarboxylate ligands the paddle-wheel units form sql grids parallel to the (ab) crystallographic plane. Similar to the structures of 5 and 6, these grids are connected by the BIPY ligands to result in 3D frameworks albeit now with pcu (α -Po) topology (Fig. 6c). The crystal structure comprises three such frameworks with parallel interpenetration (Fig. 6d). Two symmetry-independent frameworks are based on the two symmetry-independent SBUs, the third one is generated by symmetry from the SBU with Zn2 and Zn3 (Fig. 6b). The distances between the centroids of the dinuclear moieties in

the square grid and the distances between the mean planes of the square grids separated by BIPY ligands as pillars adopt the same value in the symmetry independent 3D frameworks with 19.4 and 13.9 Å, respectively, irrespective of the conformational difference in the bridging ligands.



Fig. 6. View of the symmetry independent $[Zn_2(L)_4(BIPY)_2]$ dinuclear paddle-wheel units in 7 with partial atomic numbering scheme (50% thermal ellipsoids). (a) Paddle-wheel units on two-fold axis and (b) in general position. (c) 3D framework with **pcu** (primitive cubic, α -Po) topology and (d) three-fold interpenetration of frameworks in crystal of 7, blue and red coloured frameworks are symmetry related and the green one is symmetry independent in the crystal structure. The crystal solvent molecules were omitted for clarity.

In the three crystallographically independent L^{2–} ligands in 7 the three phenyl rings are not coplanar. The peripheral phenyl rings form mutual dihedral angles of 16.2, 9.2 and 32.7°, between each other. Further, the peripheral and the central phenyl rings are again closer to

perpendicular to each other, with dihedral angles of 75.9 and 88.3°, 83.7 and 75.8, and 71.2 and 76.1. In the BIPY ligands the pyridine rings form dihedral angles 39.0 and 37.9°.

Also, the three-fold interpenetrated framework in 7 results in a potentially porous structure. The pore volume in 7 is filled by ordered and disordered solvent DMF and water molecules. Based on the solvent-depleted structure, the total solvent accessible volume in 7 was calculated by PLATON [47] to 4081.7 Å³ or 39% of the total unit cell volume.

4. Conclusions

We have synthesized six new coordination polymers based on a tetramethylterphenyldicarboxylic acid. Compound $[Zn(L)(DMF)_2]_n$ (2) is a 1D polymer in which the deprotonated ditopic tetramethyl-terphenyldicarboxylate ligand acts as a bridge to connect two zinc atoms. Compounds $\{[M(L)(DEF)]_2 \cdot 2DEF\}_n$ (M = Zn, 3 and M = Co, 4) are isostructural, and the tetradentate terphenyldicarboxylate ligand coordinates to four metal atoms to form paddlewheel SBUs which are interconnected in 2D sql coordination polymers. In the isostructural compounds $\{[M_2(L)_2(BIBP)]: 2DEF\}_n$ (M = Zn, 5 and M = Co, 6) the sql coordination grids are pillared by BIBP ligands into 3D and three-fold interpenetrated frameworks of bsn topology. When the BIPY ligand serves as pillar a 3D and three-fold interpenetrated framework of pcu $(\alpha - Po)$ topology has been found in structure of $\{[Zn_3(L)_3(BIPY)_{1.5}] \cdot 4DMF \cdot 1.5H_2O\}_n$ (7). The present results suggest that the assembly of the ditopic tetramethyl-terphenyldicarboxylate ligand with other metals will attract even more attention to us. In order to synthesize porous coordination polymers we plan to apply shorter nitrogen-containing neutral ligands, which will act as pillars such as 1,4diazabicyclo[2.2.2]octane or pyrazine to avoid the interpenetration and increase the stability of the framework upon activation, that is in the absence of solvent of crystallization.

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Appendix A. Supplementary material

Crystallographic data for compounds **1** - **7** have been deposited with the Cambridge Crystallographic Data Center, CCDC 1939645 (**1**), 1939640 (**2**), 1939639 (**3**), 1939646 (**3'**), 1939641 (**4**), 1939642 (**5**), 1939643 (**6**), 1939644 (**7**). Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data (IR-spectra, TGA curves, sorption isotherms and crystallographic details of compounds **1**-**7**) can be found, in the online version, at http://

References

- [1] H.-C. Zhou, J.R. Long, O.M. Yaghi, Chem. Rev. 112 (2012) 673.
- [2] V. Guillerm, D. Kim, J.F. Eubank, R. Luebke, X. Liu, K. Adil, M.S. Lah, M. Eddaoudi, Chem. Soc. Rev. 43 (2014) 6141.
- [3] J.R. Long, O.M. Yaghi, Chem. Soc. Rev. 38 (2009) 1213.
- [4] S. Kitagawa, S. Natarajan, Eur. J. Inorg. Chem. (2010) 3685.
- [5] M. Yoon, R. Srirambalaji, K. Kim, Chem. Rev. 112 (2012) 1196.
- [6] D. Farrusseng, S. Aguado, C. Pinel, Angew. Chem. Int. Ed. 48 (2009) 7502.
- [7] J. Lee, O. K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, Chem. Soc. Rev. 38 (2009) 1450.
- [8] R.B. Getman, Y.-S. Bae, C.E. Wilmer, R.Q. Snurr, Chem. Rev. 112 (2012) 703.
- [9] Z. Chen, S. Xiang, H. D. Arman, P. Li, S. Tidrow, D. Zhao, B. Chen, Eur. J. Inorg. Chem. (2010) 3745.
- [10] F. Ma, S. Liu, D. Liang, G. Ren, C. Zhang, F. Wei, Z. Su, Eur. J. Inorg. Chem. 24 (2010) 3756.
- [11] Z. Zhang, Y. Zhao, Q. Gong, Z. Li, J. Li, Chem. Commun. 49 (2013) 653.
- [12] J.-R. Li, Y. Ma, M.C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P.B. Balbuena, H.-C. Zhou, Coord. Chem. Rev. 255 (2011)1791.
- [13] J.-R. Li, J. Sculley, H.-C. Zhou, Chem. Rev. 112 (2012) 869.
- [14] S.K. Henninger, F. Jeremias, H. Kummer, C. Janiak, Eur. J. Inorg. Chem. (2012) 2625.
- [15] C. Janiak, S.K. Henninger, Chimia 67 (2013) 419.
- [16] P. Küsgens, M. Rose, I. Senkovska, H. Fröde, A. Henschel, S. Siegle, S. Kaskel, Micropor. Mesopor. Mater. 120 (2009) 325.
- [17] J. Ehrenmann, S.K. Henninger, C. Janiak, Eur. J. Inorg. Chem. (2011) 471.
- [18] S.K. Henninger, H.A. Habib, C. Janiak, J. Am. Chem. Soc. 131 (2009) 2776.

- [19] G. Akiyama, R. Matsuda, S. Kitagawa, Chem. Lett. 39 (2010) 360.
- [20] G. Akiyama, R. Matsuda, H. Sato, A. Hori, M. Takata, Micropor. Mesopor. Mater. 157 (2012) 89.
- [21] C. Janiak, S.K. Henninger, Nachr. Chemie 61 (2013) 520.
- [22] F. Jeremias, V. Lozan, S.K. Henninger, C. Janiak, Dalton Trans. 42 (2013) 15967.
- [23] F. Jeremias, D. Fröhlich, C. Janiak, S.K. Henninger, New J. Chem. 38 (2014) 1846.
- [24] F. Jeremias, D. Fröhlich, C. Janiak, S.K. Henninger, RSC Adv. 4 (2014) 24073.
- [25] C. Janiak, Dalton Trans. (2003) 2781.
- [26] C. Janiak, J.K. Vieth, New J. Chem. 34 (2010) 2366.
- [27] G. Férey, Chem. Soc. Rev. 37 (2008) 191.
- [28] N. Stock, S. Biswas, Chem. Rev. 112 (2012) 933.
- [29] (a) S. Kitagawa, R. Kitaura S. Noro, Angew. Chem. Int. Ed. 43 (2004) 2334; (b) S. Kitagawa, R. Kitaura S. Noro, Angew. Chem. 116 (2004) 2388.
- [30] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi, Science. 295 (2002) 469.
- [31] D.J. Tranchemontagne, Z. Ni, M. O'Keeffe, O.M. Yaghi, Angew. Chem. Int. Ed. 47 (2008) 5136.
- [32] (a) O. Delgado Friedrichs, M. O'Keeffe, O.M. Yaghi, Acta Crystallogr. A59 (2003) 22;
 (b) M. O'Keeffe, M.A. Peskov, S.J. Ramsden, O.M. Yaghi, Acc. Chem. Res. 41 (2008) 1782.
- [33] M. O'Keeffe, O.M. Yaghi, Chem. Rev. 112 (2012) 675.
- [34] F.H. Allen, O. Kennard, Cambridge Crystallographic Data Base. Chem. Design Automat. News. 8 (1993) 31.
- [35] H.-L. Jiang, D. Feng, T.-F. Liu, J.-R. Li, H.-C. Zhou, J. Am. Chem. Soc. 134 (2012) 14690.
- [36] X.-L. Zhao, P. Wang, P.-P. Cui, K.Chen, W.-Y. Sun, J. Coord. Chem. 67 (2014) 3854.
- [37] Y. Deng, P. Wang, Y. Zhao, Y.-S. Kang, W.-Y. Sun, Micropor. Mesopor, Mater. 227 (2016) 39.
- [38] A. Dutta, A.G. Wong-Foya, A.J. Matzger, Chem. Sci. 5 (2014) 3729.
- [39] Y. Liu, Y. Chen, T. Liu, A.A. Yakovenko, A.M. Raiff, H. Zhou, CrystEngComm 15 (2013) 9688.
- [40] Y. Wang, W. Fan, X. Wang, D. Liu, Z. Huang, F. Dai, J. Gao, Polyhedron 155 (2018)261.
- [41] J. Fan, B.E. Hanson, Chem. Commun. (2005) 2327.

- [42] J.K. Kallitsisa, M. Rehahn, G. Wegner, Makromol. Chem. 193 (1992) I021.
- [43] Apex2, Data Collection Program for the CCD Area-Detector System; SAINT, Data Reduction and Frame Integration Program for the CCD Area-Detector System. Bruker Analytical X-ray Systems, Madison, Wisconsin, USA, 1997-2006.
- [44] SAINT, data reduction and frame integration program for the CCD area-detector system; Bruker Analytical X-ray Systems: Madison, WI, 2006.
- [45] G. Sheldrick, Program SADABS: Area-detector absorption correction, University of Göttingen, Germany, 1996.
- [46] CrysAlis RED. O.D.L. Version 1.171.34.76.2003.
- [47] a) A.L. Spek, Acta Crystallogr. D65 (2009) 148; (b) A.L. Spek. J. Appl. Crystallogr. 36 (2003) 7; (c) A. L. Speck, PLATON A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2008; Windows implementation: L.J. Farrugia, University of Glasgow, Scotland, Version 40608 (2008).
- [48] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112.
- [49] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A: Theory and Applications in Inorganic Chemistry; Part B: Application in Coordination, Organometallic, and Bioinorganic Chemistry, fifth ed., Wiley, New York, 1997.
- [50] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
- [51] (a) S. Millan, B. Gil-Hernández, E. Milles, S. Gökpinar, G. Makhloufi, A. Schmitz, C. Schlüsener, C. Janiak, Dalton Trans. 48 (2019) 8057. (b) S. Glomb, D. Woschko, G. Makhloufi, C. Janiak, ACS Appl. Mater. Interfaces. 9 (2017) 37419.
- [52] J.F. Eubank, L. Wojtas, M.R. Hight, T. Bousquet, V.C. Kravtsov, M. Eddaoudi, J. Am. Chem. Soc. 133 (2011) 17532.
- [53] E.V. Pakhmutova, A.E. Malkov, T.B. Mikhailova, A.A. Sidorov, I.G. Fomina, G.G. Aleksandrov, V.M. Novotortsev, V.N. Ikorskii, I.L. Eremenko, Izv. Akad. Nauk SSSR, Ser. Khim.(Russ.), Russ. Chem. Bull. 52 (2003) 2117.
- [54] R.J. Pakula, J.F. Berry, Dalton Trans. 47 (2018) 13887.

[55] J. Cui, W. Zhang, Synth. React. Inorg., Met.-Org., Nano-Met. Chem. 44 (2014) 1154.

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

The elongated linker 2',3',5',6'-tetramethylterphenyl-4,4"-dicarboxylic acid (H₂L) was employed in the synthesis of zinc(II) and cobalt(II) coordination polymers with single or mixed bridging ligands. Seven compounds, that include the solvate H₂L·2DMSO (1·2DMSO), the 1D coordination polymer $[Zn(L)(DMF)_2]_n$ (2), the two 2D coordination polymers $\{[Zn(L)(DEF)]_2 \cdot 2DEF\}_n$ (3) and $\{[Co(L)(DEF)]_2 \cdot 2DEF\}_n$ (4), and the three mixed ligand 3D coordination polymers $\{[Zn_2(L)_2(BIBP)] \cdot 2DEF\}_n$ (5), $\{[Co_2(L)_2(BIBP)] \cdot 2DEF\}_n$ (6) and $\{[Zn_3(L)_3(BIPY)_{1.5}] \cdot 4DMF \cdot 1.5H_2O\}_n$ (7), (where DMSO is dimethylsulfoxide, DMF is dimethylformamide, DEF is diethylformamide, BIBP stands for 4,4'-bis(1imidazolyl)biphenyl, and BIPY for 4,4'-bipyridine) have been synthesized and characterized by IR spectroscopy, thermogravimetry, and single-crystal X-ray diffraction. In 2 the zinc atom adopts a tetrahedral O₄ environment due to the monodentate coordination of two DMF molecules and two deprotonated bridging L²⁻ ligands. The latter connect the zinc atoms in a zigzag-like chain. In the coordination polymers 3 to 7 the secondary building unit (SBU) is the paddle-wheel moiety $\{M_2(O_2C)_4(N/O)_2\}$. The metal atoms are five coordinated with

distorted square pyramidal coordination geometry by oxygen atoms from carboxylate groups of four different L²⁻ linkers, and one axial DEF-O atom in **3** and **4**, BIBP-imidazolyl-N atom in **5** and **6** or BIPY-N atom in **7**. Furthermore, the L²⁻ ligands link the SBUs to a (4,4) 2D **sql** net. In **5-7** these **sql** nets are additionally linked by BIBP or BIPY ligands as pillars to provide pillared-layer 3D and three-fold interpenetrated frameworks. Remarkably, the BIBP pillar yields **bsn** (beta-Sn) topology, the BIPY pillar **pcu** (α -Po) topology.