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Coordination chemistry in the solid state

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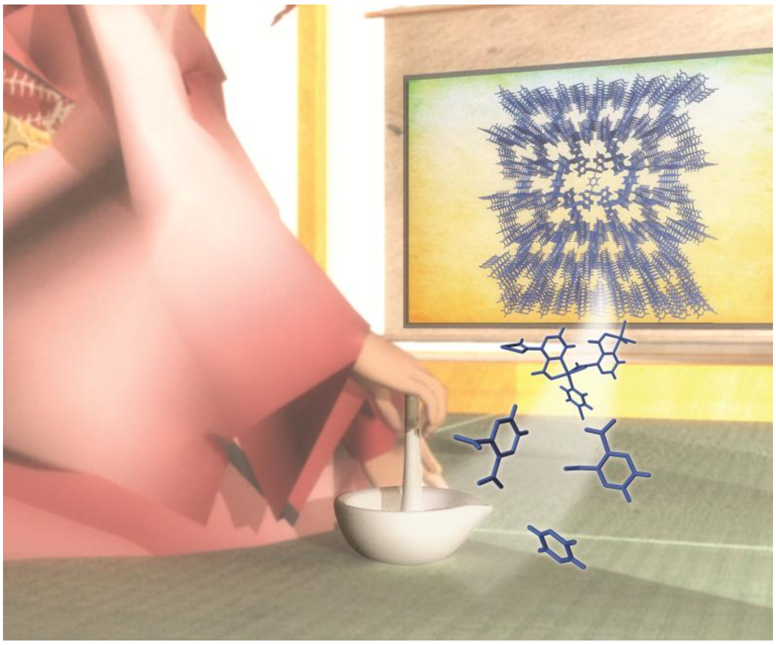

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PAPER

A family of 2D and 3D coordination polymers involving a trigonal tritopic linker†

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Five new coordination polymers, namely, $[Zn_2(H_2O)_2(BBC)](NO_3)(DEF)_6$ (DUT-40), $[Zn_3(H_2O)_3(BBC)_2]$ (DUT-41), $[(C_2H_5)_2NH_2][Zn_2(BBC)(TDC)](DEF)_6(H_2O)_7$ (DUT-42), $[Zn_{10}(BBC)_5(BPDC)_2(H_2O)_{10}](NO_3)(DEF)_{28}(H_2O)_8$ (DUT-43), and $[Co_2(BBC)(NO_3)(DEF)_2(H_2O)](DEF)_6(H_2O)$ (DUT-44), where BBC – 4,4′,4″-(benzene-1,3,5-triyl-tris(benzene-4,1-diyl))tribenzoate, TDC – 2,5-thiophenedicarboxylate, BPDC – 4,4′-biphenyldicarboxylate, DEF – *N*,*N*-diethylformamide, were obtained under solvothermal conditions and structurally characterized. It has been shown that compounds DUT-40, DUT-41 and DUT-44 exhibit 2D layered structures with large hexagonal channels. Utilization of additional angular dicarboxylic TDC linker led to the formation of the DUT-42 compound with the structure consisting of three interpenetrated 3D networks. Using the linear co-linker dicarboxylic BPDC, DUT-43 was obtained which forms a complicated 3D architecture arising from the polycatenation of triple-layered 2D building units and 2D single layer units. The pore accessibility of the synthesized compounds in the liquid phase was proved by the adsorption of dye molecules.

Introduction

Porous coordination polymers (PCPs) also referred to as metal–organic frameworks (MOFs), have stayed on the cutting edge at the focus of research for the last two decades.[1] The wide field of application of such materials ranges from gas storage and gas separation to heterogeneous asymmetric catalysis,[2] and separation of enantiomers.[3] The great success of MOFs in these application fields can be attributed to their outstanding porosity (specific area up to 6240 m^2 g^{-1})[4] and modular building-blocks concept.

On the other hand, the coordination polymers are interesting from the crystal engineering point of view, due to their crystallinity and the tendency to produce supramolecular isomers. Even for a fixed chemical composition, structural diversity of resulting coordination polymers is nearly indefinite.[5] The study of such isomers can be helpful to understand the influence of different synthesis parameters on the resulting structure and to achieve certain control over the composition, structure, net topology and eventually the properties of new compounds. Up to now, such control still remains a challenge in the synthesis of coordination polymers.

The use of tritopic linkers turns out to be very successful in the construction of highly porous MOFs. The most investigated and even commercially available MOF named HKUST-1 ($Cu_3(BTC)_2$) is composed of Cu paddle-wheel clusters and a small aromatic tritopic linker (BTC = benzene-1,3,5-tricarboxylate). The robust and highly porous framework has the **tbo** topology. The use of elongated tritopic BTB linker (BTB = benzene-1,3,5-tribenzoate) in combination with the same secondary building unit (SBU) leads to the three different structures, namely DUT-34[6] (or MOF-143)[7] (**pto** net), MOF-14[8] (interwoven **pto** net), and DUT-33[6] (interwoven **tbo** net). Utilization of Zn_4O^{6+} cluster as SBU and BTB as linker produces MOF-177, which has been the best performance material up to last year, regarding the hydrogen storage capacity. Furthermore, Caskey *et al*. reported three new phases of Zn/BTB adopting polyreticular frameworks, which were obtained using polymer-induced nucleation and different crystallization conditions.[5b]

4,4′,4″-(Benzene-1,3,5-triyl-tris(benzene-4,1-diyl))tribenzoate (BBC) ligand is a further elongated homologue of BTC with a distance between the carboxylic groups of about 2 nm. The presence of 7 aromatic rings in the molecule promotes the formation of numerous weak π⋯π and C–H⋯π interactions in the

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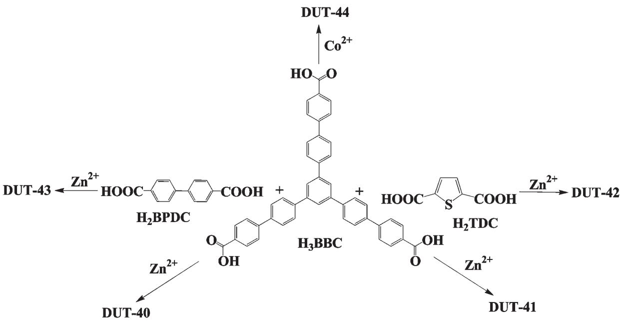
† Electronic supplementary information (ESI) available: Synthesis and characterization of H_3BBC, PXRD patterns and TG curves of DUT-40, DUT-42, DUT-43, and DUT-44, details of dye adsorption experiments, further crystallographic data, selected geometrical parameters for investigated compounds. CCDC reference numbers 850713–850717. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/c2dt12072k



Scheme 1 Overview of the resulted MOFs.

resulted structures, which may cause interpenetration and polycatenation.

Zhou *et al*. used the BBC ligand in combination with zinc.[9] The synthesis in the presence of two different bases has resulted in the formation of two porous MOFs: $Zn_4(OH)_2(H_2O)_2(py)_2(BBC)_2$ (py = pyridine) and $Zn_8(OH)_4(BBC)_4$ with novel SBUs. Recently, Furukawa *et al.* reported a new highly porous material MOF-200 constructed from the BBC linker and Zn_4O^{6+} cluster as SBU.[4] Shortly after, the same group reported on MOF-399 – ($Cu_3(BBC)_2$) material based on Cu paddle-wheels, which is isoreticular to $Cu_3(BTC)_2$. The substitution of BTC by BBC leads to the enlargement of the cubic unit cell edge from 26.34 Å in $Cu_3(BTC)_2$ to 68.31 Å in MOF-399.[7]

In the present work, we report the synthesis and characterization of five new 2D and 3D coordination polymers, based on the BBC linker (Scheme 1). The synthesis conditions as well as bitopic co-linkers (H_2TDC, H_2BPDC) or crystallization agents have a crucial influence on the structure and topology of the resulting compounds.

Results and discussion

Crystallographic results

Crystal structure of $[Zn_2(H_2O)_2(BBC)](NO_3)(DEF)_6$ (1, DUT-40‡). The H_3BBC was synthesized (for more details see ESI†) and used for the reaction with $Zn(NO_3)_2{\cdot}4H_2O$ in DEF at 373 K. This led to the formation of 2D coordination polymer DUT-40, which crystallizes in the monoclinic space group *C*2/*c* (No. 15). The asymmetric unit contains one half of the formula unit, which is generated by the crystallographic two-fold axis. The SBU unit consists of two symmetrically equivalent Zn atoms forming $Zn_2(COO)_3$ paddle-wheels with coordinated water molecules in axial positions (Fig. 1a). It should be mentioned, that only few structures with $Zn_2(COO)_3$ SBU unit are available in the Cambridge Structural Database.[10] The distance between Zn atoms is 3.32(7) Å. The Zn–O distances have expected values in the range of 1.93(1)–2.16(4) Å. The $Zn_2(COO)_3$ paddle-wheels are interconnected *via* BBC linker molecules (Fig. 1a). All carboxylate groups of the linker adopt a μ-carboxylato-κ*O*:κ*O*′ coordination mode leading to the formation of layers parallel to (20-1) plane. The layers are interconnected by several weak π⋯π interactions (see ESI†). As expected from the trigonal geometry of both the SBU unit and the linker, the crystal structure of **1** contains hexagonal channels along the *c* direction with approximate dimensions of 18 × 26 Å (Fig. 1b), measured from atom to atom centre. After the lattice solvent molecules were excluded from the structural model the solvent-accessible voids were assessed by PLATON to be 67.8%.

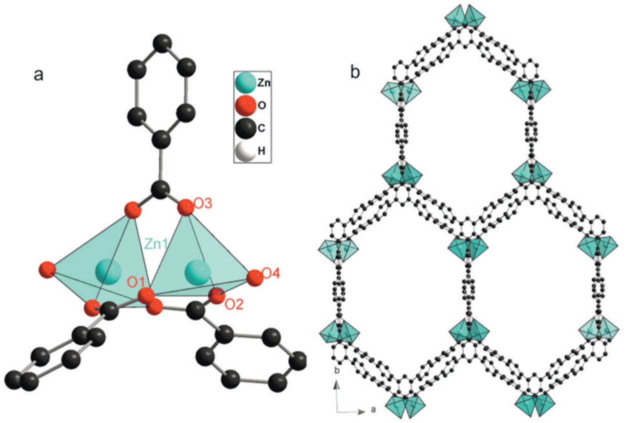


Fig. 1 SBU unit of DUT-40 (a) and the crystal structure along the *c* axis (b).

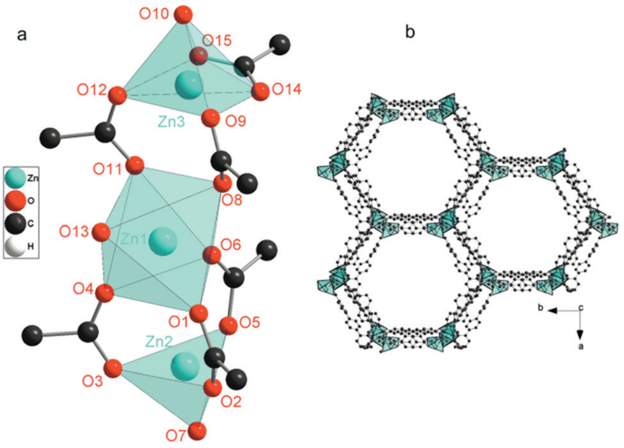


Fig. 2 SBU unit of DUT-41 with numbering scheme (a), and the crystal structure along the *c* axis (b).

Crystal structure of $Zn_3(H_2O)_3(BBC)_2$ (2, DUT-41). Heating $Zn(NO_3)_2{\cdot}4H_2O$, H_3BBC, and 2,6-bipyridylnaphthalene at 80 °C for 24 h in DMF as solvent led to the formation of a mixture of different products. The crystals of one of them were studied by single crystal X-ray diffraction. The compound named DUT-41 crystallizes in the monoclinic space group *Cc* (No. 9). The compound contains a three-nuclear zinc cluster (Fig. 2a), where Zn atoms exhibit different coordination geometry and are interconnected by 5 carboxylate groups in μ-carboxylato-κ*O*:κ*O*′ coordination mode. The Zn1 has a nearly regular octahedral ZnO_6 coordination geometry with neighbouring O–Zn–O angles range 80.93(12)–97.26(9)°. The Zn2 adopts strongly distorted tetrahedral geometry with a wide O–Zn–O angle range 94.27(11)–126.54(11)° and is connected to Zn1 *via* three μ-carboxylic groups.

The Zn1–Zn2 and Zn1–Zn3 distances within the cluster are sufficiently longer in comparison to **1** (3.843(1) Å and 4.267(1) Å, respectively) and the Zn2–Zn1–Zn3 angle is 152.0°.

Every Zn atom in the cluster is additionally coordinated by one solvent molecule. Two BBC molecules, which lie in the parallel planes, connect the above-mentioned SBU units into a 2D network. The crystal structure of **2** consists of the layers and exhibits nearly regular hexagonal channels along [001] direction with approximate diameter of 25 Å (Fig. 2b). The layers are held together by numerous weak π⋯π interactions (see ESI†). After the lattice solvent molecules were excluded from the structural model the solvent-accessible voids were assessed by PLATON to be 67.5%.

Crystal structure of $[(C_2H_5)_2NH_2][Zn_2(BBC)(TDC)](DEF)_6(H_2O)_7$ (3, DUT-42). Recently, the highly porous 3D coordination polymer, namely UMCM-3, was obtained by Koh *et al.*[11] by combining angular 2,5-thiophenedicarboxylate (TDC) linker, BTB and Zn_4O cluster. Under similar reaction conditions and using H_3BBC instead of H_3BTB, we obtained the yellow hexagonally shaped crystals of DUT-42. Single crystal diffraction data revealed the hexagonal crystal system and chiral space group $P6_522$ (No. 179). The paddle-wheel SBU units are connected by three μ-carboxylate groups of the BBC linker to form a layer. The layers are interconnected into the 3D network by TDC linkers, their carboxylic groups coordinate in a monodentate fashion (Fig. 3a). This leads to non-equivalent C–O bond lengths in the carboxylic group (see ESI†) as well as to the disorder of non-coordinated carboxylate oxygen atoms.

Assuming that the linker molecules are fully deprotonated, a negatively charged framework is formed. Unfortunately, it was impossible to locate the counterions from the difference Fourier map, obviously due to the strong disorder. However, the elemental, as well as thermal gravimetric analyses of supercritically dried sample give evidence of the presence of diethylammonium cation, which can be formed under the synthetic conditions. TG analysis indicates 6.83% weight loss in the range 25–250 °C (boiling point of diethylamine 55.5 °C) (see ESI†). Additionally, the nitrogen content of 1.22%, found from the elemental analysis, corresponds to the framework composition $[(C_2H_5)_2NH_2][Zn_2(BBC)(TDC)]$. A similar observation was made by Hou *et al.* for the MCF-26 (MCF – metal–carboxylate framework) compound,[12] which is isoreticular to DUT-42.

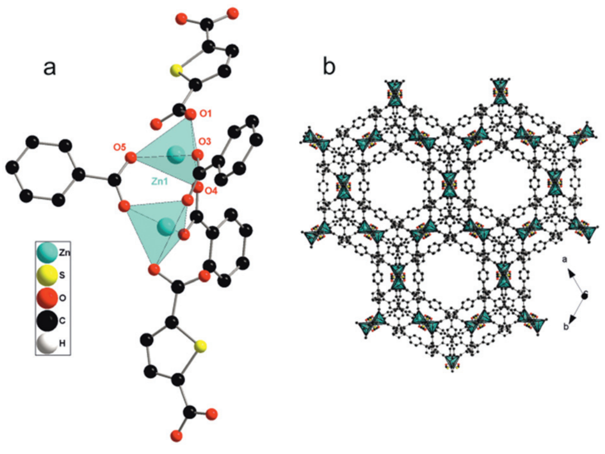


Fig. 3 SBU unit of DUT-42 (a), and view on the crystal structure along *c* axis (b).

The paddle-wheel geometry in DUT-42 is mostly similar to that in DUT-40 (Fig. 3), but the Zn–O bond lengths lie in the narrower range 1.937(1)–1.977(1) Å. Numerous weak π⋯π interactions between the frameworks stabilize the crystal structure (see ESI†). Despite of interpenetration, the structure has hexagonal channels along the *c* direction. After exclusion of lattice solvent molecules and cations from the structural model the solvent-accessible voids were assessed by PLATON to be 60.9%.

Crystal structure of $[Zn_{10}(BBC)_5(BPDC)_2(H_2O)_{10}](NO_3)(DEF)_{28}(H_2O)_8$ (4, DUT-43). Maintaining the same synthetic conditions as for compound **1** and using additional 4,4′-biphenyldicarboxylic acid (H_2BPDC), DUT-43 could be obtained. The main differences between TDC and BPDC as bridging units are the distances between carboxylate groups as well as the angles between them. Thus, the distance between two carboxylate carbon atoms in TDC is 5.33 Å and the angle between them is 147.5°. In the case of linear BPDC linker, the distance between carboxylate groups is nearly twice as long as in TDC (10.11 Å).

DUT-43 crystallizes in the monoclinic space group $C2/c$ (No. 15). The crystal structure of DUT-43 is built up by two types of 2D units. The first one is a honeycomb layer containing Zn4/Zn5 trigonal paddle-wheel units (Fig. 4a) interconnected by BBC linkers. The second unit consists of three honeycomb layers connected together by BPDC molecules (Fig. 4d). The Zn1 atom of Zn1/Zn3 containing paddle-wheel is bound by the BPDC linker to the Zn2 atom from the neighbouring layer (Fig. 4c, 4d).

The resulted 3D architecture of DUT-43 (Fig. 4e) is formed by the polycatenation of triple layers and interpenetration of single and triple layers at the same time (Fig. 8).

Three pairs of zinc atoms (Zn1/Zn3, Zn2/Zn2$^{\#1}$ ($^{\#1}2-x$, y, $2.5-z$), and Zn4/Zn5) are interconnected into trigonal paddle-wheels similar to that in compounds **1** and **3**: two Zn atoms in the SBU are interconnected by three μ-coordinated carboxylic groups from the BBC linkers.

The coordination sphere of Zn4 is completed by one solvent molecule (H_2O) to form a distorted trigonal pyramid, and the coordination sphere of Zn5 is completed by three solvent molecules giving rise to distorted octahedra (Fig. 4a). The coordination environment of Zn3 is completed by one water molecule (Fig. 4c). After the lattice solvent molecules were excluded from the structural model the solvent-accessible voids were assessed by PLATON to be 62.9%.

Crystal structure of $[Co_2(BBC)(NO_3)(DEF)_2(H_2O)](DEF)_6(H_2O)$ (5, DUT-44). Heating $Co(NO_3)_2\cdot 6H_2O$ and H_3BBC at 120 °C for 12 h in DEF leads to the formation of crystalline product **5**. The structure was solved in the monoclinic space group $C2/c$ (No. 15). The SBU unit of DUT-44 consists of two cobalt atoms, which are coordinated each by six oxygen atoms (Fig. 5a). The Co1–O bond lengths and O–Co1–O angles lie within wide ranges of 1.988(2)–2.296(3) Å, and 57.87(13)–105.06(10)°, respectively. This is caused by the coordination of NO_3^- anion and one of the carboxylate groups in a bidentate manner to Co1 (Fig. 5a). In contrast to Co1, Co2 has nearly regular octahedral coordination environment having Co2–O bond lengths and O–Co2–O angles in the range of 2.047(2)–

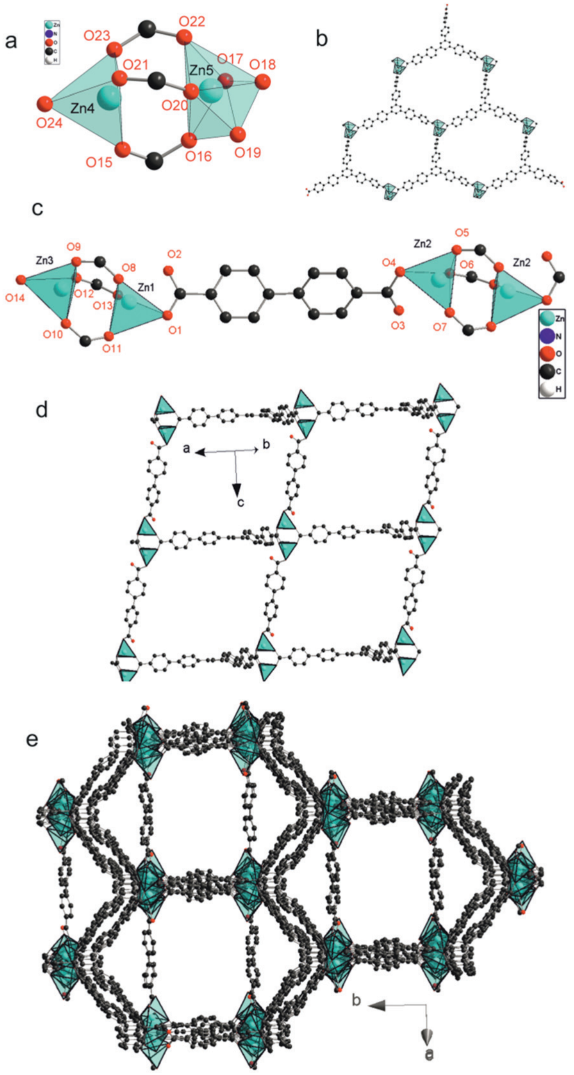


Fig. 4 Crystal structure of DUT-43: (a) SBU of the single-layer; (b) single-layer; (c) SBUs of triple-layer connected by BPDC; (d) triple-layer; (e) view along *c* direction.

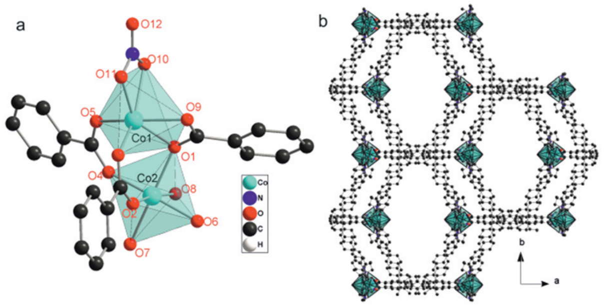


Fig. 5 SBU unit of DUT-44 (a) and view on the crystal structure along the *c* axis (b).

2.122(2) Å and 85.78(15)–94.46(11)°, respectively. The two Co atoms are interconnected by two μ-carboxylate groups and one oxygen atom from the third carboxylate group. In the case of Co2, the coordination environment is completed by 3 DEF molecules. The structure consists of 2D layers lying in the *ab* plane (Fig. 5b). The layers are interconnected by weak C–H···O, C–H···π and numerous π···π interactions (Table S7, ESI†). After exclusion of lattice solvent molecules from the structural model, the solvent-accessible voids were assessed by PLATON to be 54.9%.

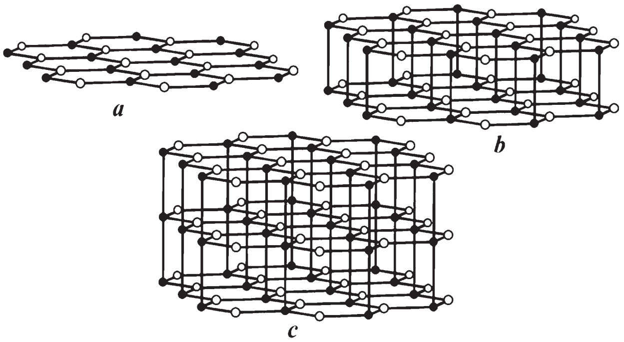


Fig. 6 Underlying nets of layered coordination polymers DUT-40 and DUT-44 (a); DUT-41 (b); and DUT-43 (c). Black circles represent the centroids of Zn-clusters and open circles correspond to BBC.

Topological analysis

The topology of all coordination polymers presented in this paper is either identical to or can be easily derived from that of a honeycomb net (6^3). In the DUT-40 and DUT-44 structures the trivalent nodes of the underlying net correspond (alternately) to the paddle-wheel units and BBC linkers (black and white circles, respectively, in Fig. 6a). Although the two structures belong to the same *C*2/*c* space group, they are different with respect to the stacking of the honeycomb layers: in the structure DUT-40 the stacking direction is $[10\bar{1}]$ and there are six layers per translation period while in DUT-44 the layers are packed in a more *usual* fashion, namely, along [001] with four layers per translation period.

Double honeycomb (3,4)-connected layers (Fig. 6b) characterize the topology of the DUT-41 structure. Double layers are formed since trinuclear Zn-clusters are interconnected by two linkers lying in the parallel planes (Fig. 3a). The stacking direction is [001] with only two double layers per translation period.

The hexagonal structure of DUT-42 consists of three interpenetrated frameworks with the topology of the (3,5)-connected **gra** net. Here, the BBC ligands again give rise to the trivalent nodes of the underlying net. Binuclear Zn-units correspond to the 5-connected nodes since they are bound to three BBC ligands and additionally – by TDC – to the two symmetrically equivalent Zn-units (Fig. 7). The crystal structure of DUT-42 consists of three-fold interpenetrated 3D networks related by 3_2 screw axis (rare interpenetration class IIa).[13]

The structure of the compound DUT-43 represents the most complicated example (Fig. 4a) since it comprises four honeycomb layers (identical to those in DUT-40) and furthermore four triple honeycomb (3,4,5)-connected layers (Fig. 6c) per translation period along [001]. Nevertheless, the sequences of symmetry operations generating the 4-layered stacking (*ABCD*) along [001] are different for single and

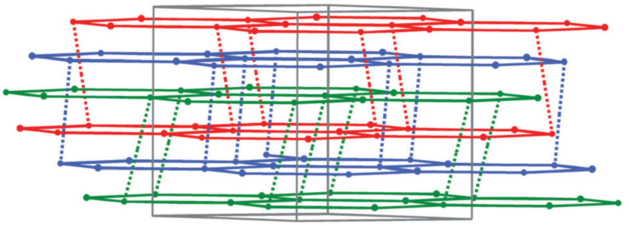


Fig. 7 Three-fold interpenetrating nets (**gra** type) in the structure **3** (schematic view). TDC cross-linkers correspond to the dotted lines.

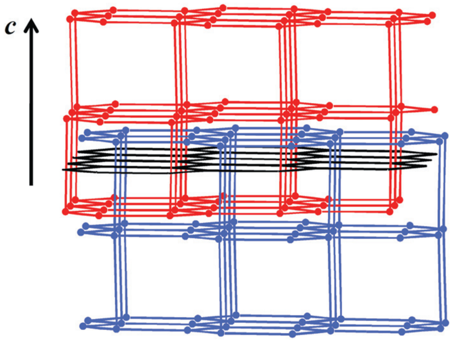


Fig. 8 Schematic view of polycatenation and interpenetration in the structure of DUT-43: catenated triple honeycomb layers (red and blue) and a single honeycomb layer (black) penetrating them.

triple layers $A \xrightarrow{C_2(y)} B \xrightarrow{\bar{1}} C \xrightarrow{C_2(y)} D$ and $A \xrightarrow{c(xz)} B \xrightarrow{\bar{1}} C \xrightarrow{c(xz)} D$, respectively. The triple layers are formed owing to the BPDC ligands which connect binuclear Zn-units (within a given layer) to the two additional ones in the neighbouring (up and down) layers. Finally, triple layers are catenated with each other and also penetrated by a set of single honeycomb layers (Fig. 8). Thus, in this structure we have a rare example of simultaneous occurrence of both *polycatenation*[14] (between triple layers) and *interpenetration* (between triple and single honeycomb layers, respectively).

Physisorption experiments

To estimate the porosity of investigated compounds the nitrogen adsorption experiments were performed at 77 K. Thermogravimetric analyses of the compounds showed that up to 47.3% (for **1**), 49.2% (for **2**), 40.1% (for **3**), and 49.7% (for **4**) of the total mass is lost in the temperature range 298–573 K, but no pronounced steps are present (Fig. S1, S3–S5, ESI†). The conventional thermal activation in vacuum at 423 K leads to the materials which show no significant nitrogen adsorption. After activation with supercritical CO_2, the samples lose the pristine structure (Fig. S1, S2, S4, S5, ESI†), but they are able to adsorb nitrogen at 77 K and the specific surface area could be estimated from the isotherms (Fig. 9). The multipoint BET surface areas are 34 $m^2 g^{-1}$ for DUT-40, 397 $m^2 g^{-1}$ for DUT-43, and 479 $m^2 g^{-1}$ for DUT-44. The DUT-42 shows no nitrogen uptake.

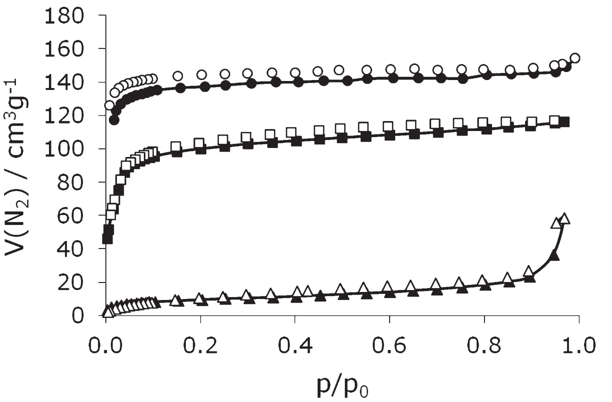


Fig. 9 The nitrogen adsorption (solid symbols) and desorption (open symbols) isotherms at 77 K on DUT-40 (triangles), DUT-43 (squares), and DUT-44 (circles).

Measured surface areas are much lower than expected from the calculation. The geometrically calculated surface area[15] is 2606 $m^2 g^{-1}$ for DUT-40, 2505 $m^2 g^{-1}$ for DUT-41, 2037 $m^2 g^{-1}$ for DUT-42, 1932 $m^2 g^{-1}$ for DUT-43, 1939 $m^2 g^{-1}$ for DUT-44.

This is remarkable, that the original structures of DUT-40, DUT-42 and DUT-43 can be restored by soaking in DMF, or by the adsorption of DMF from vapour. In the case of DUT-44 the structural changes caused by activation are irreversible, and the resolvation does not lead to the recovery of the as-made structure (Fig. S5, ESI†).

For some applications (for example, heterogeneous catalysis in the liquid phase), the availability of the solvent free compound is non-essential. More important in this case is that the accessibility of the pore system for the substrate molecules is guaranteed.

The dye molecules are a good model system, because the adsorption can be monitored optically, by the colour change of the crystals. Additionally, some information about the substrate size limitation can be collected, since a vast series of dyes with different sizes and polarity is available. The adsorption of Isatin, Brilliant green, Nile red, Nile blue, Methylene blue, Fluorescein, Disperse red 1, Disperse red 13, Food red No. 2, and Brilliant yellow (Table S1, ESI†) carried out in DMF or DEF as solvent confirm the accessibility of the pores for most of the investigated dyes. It was found, that in the case of DUT-40 all tested dyes can penetrate the framework. The DUT-42 can adsorb Brilliant green, Nile blue, Nile red, Methylene blue, Disperse red 1, Disperse red 13 and Brilliant yellow. Furthermore, DUT-43 is able to adsorb Fluorescein and Isatin in addition to the dyes which could be adsorbed on DUT-42. It should be mentioned, that the estimation of the adsorption ability of Co based DUT-44 was difficult, because of its own intensive purple colour of the crystals. In this case, the adsorption of Brilliant green, Nile red, Nile blue, and Methylene blue (Fig. 10) could be postulated definitely.

Conclusions

Five new coordination polymers, namely DUT-40 – DUT-44, based on the trigonal linker BBC were obtained under different synthesis conditions. DUT-40, DUT-41 and DUT-44 possess 2D-layered crystal structures topologically related to that of the

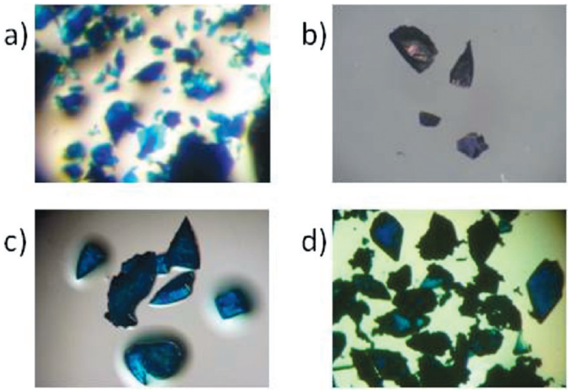


Fig. 10 Adsorption of methylene blue on (a) DUT-40, (b) DUT-42, (c) DUT-43 and (d) DUT-44.

honeycomb net (6^3). Using the H_2TDC as additional bifunctional co-linker led to the formation of DUT-42 with triply interpenetrated 3D architecture. DUT-43, obtained by co-polymerization of H_3BBC, H_2BPDC and Zn^{2+}, shows an exceptional 3D structure, formed by polycatenation of triple layers and interpenetration between triple and single layers at the same time.

During solvent removal, the transformation of the structures takes place and the resulting porous solids have specific surface areas up to 480 $m^2\ g^{-1}$. The original crystal structures of DUT-40, DUT-42 and DUT-43 can be restored by exposing the activated materials to DMF. All investigated compounds have pores accessible for large dye molecules, which was confirmed by liquid phase adsorption experiments.

Experimental

General remarks

Zinc nitrate tetrahydrate (≥98.5%, Merck), cobalt nitrate hexahydrate (99%, Chempur), H_2TDC (≥98%, TCI) and H_2BPDC (97%, Aldrich) were used as received. *N*,*N*′-Diethylformamide (DEF) was dried over phosphorous pentoxide and stored under argon atmosphere. The H_3BBC was synthesized according to published procedure (see ESI† for more details).[16]

Synthesis of $[Zn_2(H_2O)_2(C_{45}H_{27}O_6)](NO_3)(DEF)_6$ (1, DUT-40)

H_3BBC (48.6 mg, 0.07 mmol) and $Zn(NO_3)_2\cdot 4H_2O$ (85.0 mg, 0.33 mmol) were dissolved in 10.5 mL DEF and two drops of acetic acid were added. The solution was heated in a Pyrex tube for 48 h at 373 K. The resulting light yellow crystals were collected by filtration under argon atmosphere, washed with DMF and dried under reduced pressure at room temperature (yield: 84.8 mg, 87% based on H_3BBC).

Elemental analysis: calc.: % C 60.08, % H 6.52, % N 6.54; found: % C 60.43, % H 6.90, % N 6.08. IR: ν/cm^{-1} = 3040 (w), 2938 (w), 2864 (w), 1651 (s), 1602 (s), 1564 (m), 1548 (w), 1528 (w), 1495 (m), 1383 (vs), 1252 (m), 1180 (w), 1090 (s), 1060 (w), 1005 (m), 829 (m), 785 (s), 735 (w), 706 (w), 688 (w).

Synthesis of $[Zn_3(H_2O)_3(C_{45}H_{27}O_6)_2]$ (2, DUT-41)

$Zn(NO_3)_2\cdot 4H_2O$ (26.15 mg, 0.100 mmol), H_3BBC (20 mg, 0.030 mmol) and 2,6-bipyridylnaphthalene (10 mg, 0.035 mmol) were dissolved in 2 mL DMF. The solution was sonicated for 2 min and heated in a Pyrex tube for 24 h at 353 K. Small single crystals of **2** and other amorphous by-products were obtained.

Yield could not be determined and elemental analysis could not be performed due to the product impurity.

Synthesis of $[(C_2H_5)_2NH_2][Zn_2(C_{45}H_{27}O_6)(C_6H_2O_4S)](DEF)_6(H_2O)_7$ (3, DUT-42)

$Zn(NO_3)_2\cdot 4H_2O$ (156.0 mg, 0.6 mmol), H_3BBC (45.0 mg, 0.067 mmol) and H_2TDC (51.6 mg, 0.3 mmol) were dissolved in 2 mL DEF and heated in a Pyrex tube for 96 h at 353 K. The resulting yellow hexagonal sticks were separated by decanting the mother liquor. The crystals were washed with fresh DMF three times and dried in argon flow at room temperature (yield: 89 mg, 77.6% based on H_3BBC).

Elemental analysis of as-synthesized material: calc.: % C 57.66, % H 6.84, % N 5.54% S 1.81; found: % C 57.42, % H 6.64, % N 5.41, % S 1.42. Elemental analysis of supercritically dried material: calc.: % C 63.65, % H 3.95, % N 1.35% S 3.09; found: % C 61.72, % H 4.21, % N 1.22, % S 3.08. IR of "as-synthesized" phase: ν/cm^{-1} = 2984 (w), 2947 (w), 2897 (w), 1632 (s), 1607 (s), 1526 (m), 1402 (vs), 1387 (s), 1263 (m), 1215 (m), 1204 (w), 1111 (m), 1005 (m), 947 (w), 824 (m), 783 (s), 733 (w), 735 (w), 648 (m), 555 (w), 517 (m). IR of CO_2 supercritically dried phase: 2976 (w), 2939 (w), 1683 (m), 1604 (s), 1523 (m), 1386 (s), 1177 (m), 1003 (m), 825 (m), 783 (s), 733 (w), 650 (m), 505 (m).

Synthesis of $[Zn_{10}(C_{45}H_{27}O_6)_5(C_{14}H_8O_4)_2(H_2O)_{10}](NO_3)(DEF)_{28}(H_2O)_8$ (4, DUT–43)

$Zn(NO_3)_2\cdot 4H_2O$ (283.0 mg, 1.08 mmol), H_3BBC (162.1 mg, 0.23 mmol), and H_2BPDC (65.5 mg, 0.27 mmol) were suspended in 10 mL DEF and heated in a Pyrex tube 72 h at 373 K to give colourless crystals. They were filtered under argon atmosphere, washed with DMF and dried in an argon flow at room temperature (yield: 181.3 mg, 51.5% based on H_3BBC).

Elemental analysis: calc.: % C 61.53, % H 6.50, % N 5.30; found: % C 61.03, % H 5.94, % N 5.77. IR: ν/cm^{-1} = 3067 (w), 3035 (w), 2933 (w), 2860 (w), 1668 (s), 1605 (s), 1568 (m), 1548 (m), 1527 (w), 1494 (m), 1384 (vs), 1253 (m), 1178 (w), 1088 (s), 1063 (w), 1005 (m), 828 (m), 784 (s), 771 (m), 734 (m), 707 (m), 688 (m).

Synthesis of $[Co_2(C_{45}H_{27}O_6)(NO_3)(DEF)_2(H_2O)](DEF)_6(H_2O)$ (5, DUT-44)

$Co(NO_3)_2\cdot 6H_2O$ (157.5 mg, 0.54 mmol) and H_3BBC (81.0 mg, 0.12 mmol) were dissolved in 10.5 mL DEF and heated in a Pyrex tube for 12 h at 120 °C. The resulting purple crystals were collected by filtration under argon atmosphere, washed with fresh DEF and dried in an argon flow at room temperature (yield: 99.0 mg, 48.9% based on H_3BBC).

Elemental analysis: calc.: % C 60.45, % H 7.10, % N 7.46; found: % C 60.45, % H 7.09, % N 7.44. IR: ν/cm^{-1} = 3046 (w), 2935 (w), 2861 (w), 1663 (s), 1602 (s), 1568 (m), 1551 (m), 1527 (w), 1496 (m), 1384 (s), 1303 (w), 1255 (m), 1179 (w), 1090 (s), 1060 (w), 1004 (m), 830 (m), 785, 732 (m), 708 (m), 681 (m), 659 (m).

Single crystal X-ray analysis

The single crystals of investigated compounds DUT-40–44 were placed inside the 0.3 mm capillary with small amount of the mother liquor. The datasets were collected at Helmholtz-Zentrum Berlin for Materials and Energy on beamline BESSY-MX BL14.2, equipped with MAR225 CCD area detector and 1-circle goniometer. The monochromated radiation with $\lambda = 0.88561$ Å was used for all experiments. The images were collected using ϕ-scan technique with scan step $\Delta\phi = 1°$. The indexing, integration and scaling were performed using XDS program.[17] Due to low absorption coefficients, absorption corrections were not performed. The structures were solved by direct methods and refined in anisotropic approximation for all non-hydrogen atoms by full matrix least-square on F^2 using SHELX.[18] Hydrogen atoms are placed in calculated positions according to the geometry of parent atoms and refined using "riding model" with Uiso(H) = 1.5Uiso(C) for CH_3 groups and Uiso(H) = 1.2Uiso(C) for all other atoms. Due to the high amount of disordered solvent molecules in all investigated structures, the SQUEEZE routine of PLATON was applied to all datasets to modify reflections intensities and to exclude the electron density of disordered solvent molecules.[19] The full data for crystallographic experiments are given in Table S2, ESI.†. CCDC reference numbers 850713–850717 contain the full information for crystal structures DUT-40–44.† The topology of the networks was analysed using program package TOPOS.[20]

Crystal data for:

DUT-40: $C_{45}H_{27}O_8Zn_2$; monoclinic, *C*2/*c*, *F*w = 826.41, *a* = 19.834(4); *b* = 42.111(8); *c* = 12.913(3) Å, β = 118.69(3)°, *V* = 9461(3), *T* = 296(2) K, *Z* = 4, *D*c = 0.580 g cm^{-3}, μ = 0.952 mm^{-1}, *F* (000) = 1684, θ_{max} = 30.48°, reflections collected 47 983, unique 10 707 [R_{int} = 0.0838), final *R* indices [$I > 2\sigma(I)$] were *R*1 = 0.0703, w*R*2 = 0.1866, *R* indices (all data) *R*1 = 0.1311, w*R*2 = 0.2089, GOF = 0.845.

DUT-41: $C_{90}H_{54}O_{15}Zn_3$; monoclinic, *Cc*, *F*w = 1571.44, *a* = 24.127(5); *b* = 41.811(8); *c* = 20.186(4) Å, β = 115.27(3)°, *V* = 18 414(6), *T* = 296(2) K, *Z* = 4, *D*c = 0.567 g cm^{-3}, μ = 0.747 mm^{-1}, *F* (000) = 3216, θ_{max} = 36.87°, reflections collected 96 110, unique 40 518 [R_{int} = 0.0544), final *R* indices [$I > 2\sigma(I)$] were *R*1 = 0.0567, w*R*2 = 0.1484, *R* indices (all data) *R*1 = 0.0710, w*R*2 = 0.1576, GOF = 0.912.

DUT-42: $C_{51}H_{29}O_{10}SZn_2$; hexagonal, $P6_522$, *F*w = 964.54, *a* = 24.057(3); *c* = 26.996(5) Å, *V* = 13 530(3), *T* = 296(2) K, *Z* = 6, *D*c = 0.710 g cm^{-3}, μ = 1.053 mm^{-1}, *F* (000) = 2946, θ_{max} = 36.97°, reflections collected 155 346, unique 11 149 [R_{int} = 0.0934), final *R* indices [$I > 2\sigma(I)$] were *R*1 = 0.0428, w*R*2 = 0.1086, *R* indices (all data) *R*1 = 0.0524, w*R*2 = 0.1150, GOF = 1.061.

DUT-43: $C_{273}H_{195}N_4O_{52}Zn_{10}$; monoclinic, *C*2/*c*, *F*w = 5017.03, *a* = 23.934(5); *b* = 41.860(8); *c* = 45.532(9) Å, β = 90.12(3)°, *V* = 45 617(16), *T* = 296(2) K, *Z* = 4, *D*c = 0.731 g cm^{-3}, μ = 0.558 mm^{-1}, *F* (000) = 10 308, θ_{max} = 36.97°, reflections collected 132 373, unique 32 809 [R_{int} = 0.0584), final *R* indices [$I > 2\sigma(I)$] were *R*1 = 0.0911, w*R*2 = 0.2671, *R* indices (all data) *R*1 = 0.1066, w*R*2 = 0.2840, GOF = 1.129.

DUT-44: $C_{55}H_{49}Co_2N_3O_{12}$; monoclinic, *C*2/*c*, *F*w = 1061.83, *a* = 39.776(8); *b* = 24.693(5); *c* = 21.823(4) Å, β = 117.94(3)°, *V* = 18 936(6), *T* = 296(2) K, *Z* = 8, *D*c = 0.745 g cm^{-3}, μ = 0.386 mm^{-1}, *F* (000) = 4400, θ_{max} = 30.60°, reflections collected 57 847, unique 13 628 [R_{int} = 0.0344), final *R* indices [$I > 2\sigma(I)$] were *R*1 = 0.0702, w*R*2 = 0.2145, *R* indices (all data) *R*1 = 0.0787, w*R*2 = 0.2242, GOF = 1.086.

Physisorption experiments

Nitrogen physisorption isotherms were measured at 77 K up to 1 bar using a Quadrasorb apparatus (Quantachrome Co.). Prior to all adsorption measurements, the samples were activated using supercritical CO_2.

The BET surface area was also geometrically calculated according to a published procedure.[15]

Liquid phase adsorption experiments: 1 mmol L^{-1} solutions of Isatin, Brilliant green, Nile red, Nile blue, Methylene blue, Fluorescein, Disperse red 1, Disperse red 13, Food red No. 2 and Brilliant yellow in DMF (DUT-40 and 42) or DEF (DUT-43 and 44), were prepared. The crystals of investigated compounds were placed into corresponding dye-containing solution. After three days, the Dye@MOF crystals were investigated under the microscope.

For resolvation experiments from the liquid phase, the crystals of activated compounds were soaked in DMF or DEF for three days. For resolvation experiments from the vapour, the samples were stored in a saturated vapour atmosphere of DMF for 7 days.

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Notes and references

‡ The compositions of DUT-40, DUT-42, DUT-43, and DUT-44 were derived from TG and elemental analysis data. The composition of DUT-41 is based on the single crystallographic X-ray analysis and does not include the solvent guest molecules.

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