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Electronic Supplementary Information

for

A view on systematic truncation of tetrahedral ligands for coordination polymers

by

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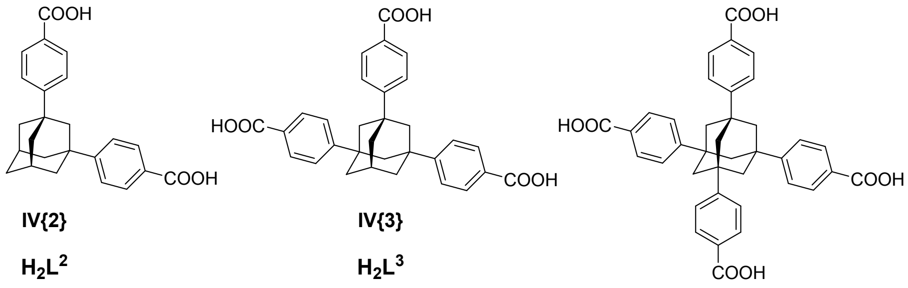
Synthesis

Synthesis of the ligands

Chemicals and materials

1,3-diphenyladamantane, 1,5,7-triphenyladamantane and 1,3,5,7-tetraphenyladamantane were prepared according to the literature procedure [1].(Bis(trifluoroacetoxy)iodo)benzene (PIFA) was prepared from (diacetoxy)iodobenzene) [2] according to a lit. method [3], via exchange with trifluoroacetic acid. Tert-butyl bromide (tBuBr) for the synthesis of phenyladamantanes was freshly prepared from tert-butyl alcohol and hydrobromic acid in presence of sulfuric acid [4, p. 221] and stored for limited time over calcium chloride containing a small amount of calcium oxide. N,N-dimethylformamide (DMF) for the cyanodeiodination (Rosenmund-von Braun reaction) was dried over CaH_2 and distilled shortly before use. Chloroform for iodination with PIFA was freshly distilled from over diphosphorus (V) pentoxide.

Other organic compounds as acetic acid, acetonitrile, benzene, chloroform, 1,2-diethylamine, N,N-dimethylformamide (DMF), dioxane, isopropyl alcohol (iPrOH), methanol (MeOH), tert-buthyl alcohol, toluene, as well as inorganic compounds as aluminium chloride, calcium chloride, calcium oxide, conc. hydrochloric acid, copper cyanide, hydrobromic acid (conc.), hydrochloric acid (conc.), iodic acid (HIO_3), iodine, phosphorus pentoxide, potassium hydroxide, sodium sulfate (anhydr.), sodium sulfite, sulfuric acid (conc.) were of reagent grade and used without additional purification. Distilled water was used, if other is not specified.



IV{2}

H_2L^2

IV{3}

H_2L^3

IV{4}

H_2L^4

Fig. S1. Two notations used for the ligands in this work.

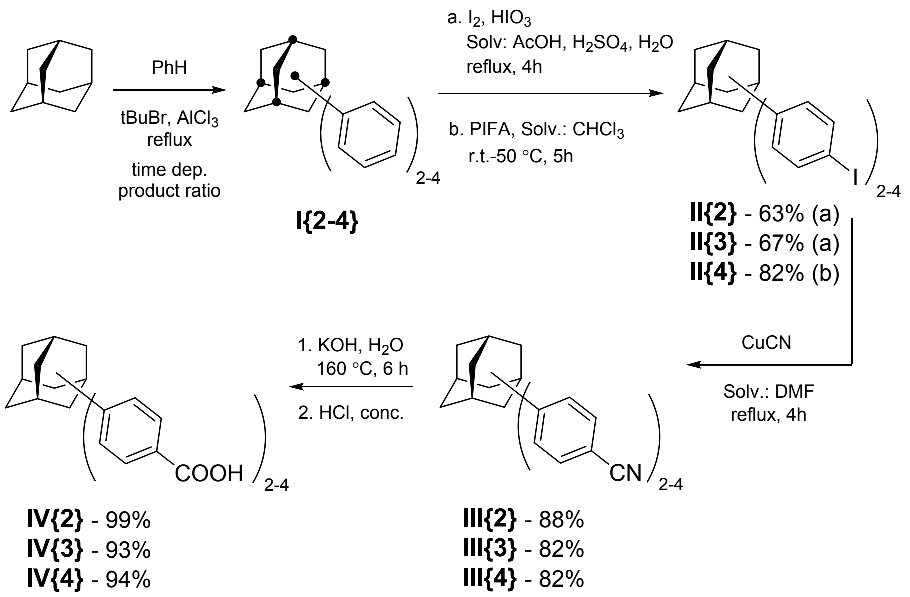


Fig. S2. Synthetic scheme, with concise details given regarding the reagents and conditions used, showing the transformations leading to the used ligands: H_2L^2, **IV{2}**; H_3L^3, **IV{3}**; H_4L^4, **IV{4}**.

The *N*{*M*} compound codes consist of a 'stem' Roman number *N*, reflecting the nature of the functional group, and an Arabic number *M* reflecting the number of the functional groups residing at the 'bridge-head' 1,3,5,7-locants of adamantane.

Syntheses of 1,3-di-(4-iodophenyl)adamantane, **II{2}**; 1,3,5-tri(4-iodophenyl)adamantane, **II{3}**

A 1 L flask equipped by an efficient magnetic stirrer was charged by 25 g (87 mmol) of **I{2}**, 18 g of iodine (143 mmol) and 7.8 g of iodic acid (44 mmol). 500 ml of acetic acid, 50 ml of water and 7.5 ml of conc. sulfuric acid were added. The mixture was mildly refluxed using an air condenser, and the subliming iodine was scratched down time to time, back to the reaction mixture. The reaction progress was monitored by fading of the iodine colour; in 4 h the reaction practically finished as the red colour of the liquid did not fade further. The reaction mixture was poured in 1 L of water and decolourized via drop-by-drop addition of saturated by Na_2SO_3 under stirring. The formed precipitate was filtered off, dried and purified by means of subsequent dissolution in 150 ml of hot dioxane, treatment of the solution with active coal, filtration and dilution by 100 ml of iPrOH. The mixture was cooled (+4 ˚C) and the formed precipitate filtered out and dried in air at 80 ˚C, yielding 29.5 g of the pure product in a form of a white solid (63%).

The same approach, by using 15 g (41 mmol) of **I{3}**, 18 g of iodine (143 mmol), 6.6 iodic acid (38 mmol in 250 ml of acetic acid, 25 ml of water and 4 ml of conc. sulfuric acid and the work-up procedure described above yielded 20.6 g **II{3}** (67%) in a form of white solid.

The isolated yields are significantly lower than the actual ones, due to relatively low efficiency of recrystallizations in these cases. Chromatographic separation is estimated to give yields of 80%+.

Synthesis 1,3,5,7-tetra(4-iodophenyl)adamantane, **II{4}**

The synthetic method is based on a lit. source, [5] with the main exception being that $CHCl_3$ was used instead of CCl_4.[1]

A 2 L flask, equipped with an efficient stirrer was charged by a 50 g (113 mmol) of 1,3,5,7-tetraphenyladamantane, 57.9 (228 mmol, 2 eq) of iodine and 1 L of $CHCl_3$ freshly distilled from over P_2O_5[1]. The flask was placed in a water bath at 25 ˚C and (107.9 g, 2.2 eq) of (bis(trifluoroacetoxy)iodo)benzene (PIFA) was added at once under stirring.[2] The flask was stoppered[3] and the mixing was continued for 3 h.[4] Finally the temperature of the bath was raised to 50 ˚C and the stirring was continued for another 2 h.

After cooling, to the near colourless reaction mixture a saturated solution of 10 g of Na_2SO_3 in water was added, and the contents of the flask was stirred for 1h. Saturated $NaHCO_3$ solution was added under stirring until neutral pH of the water layer. The precipitate was filtered off and washed by 2×100 ml of H_2O, yielding the first, minor crop of the product. The biphastic filtrate was separated, the aqueous layer extracted by 3×100 ml of $CHCl_3$ and the combined organic extracts were, after drying over Na_2SO_4, evaporated under reduced pressure, yielding an oily precipitate. The latter was washed by 3×100 ml of hexanes to remove the phenyl iodide, constituting primarily the oily part of the residues, leaving the major crop of the crude product.[5]

The combined crops were dissolved in ~1 L of hot DMF, leaving app. 10 g of the unreacted starting material, which was filtered out. The volume of the solution was reduced to 80 ml under reduced pressure and the pure product was collected by filtration, followed by washing with small amounts of DMF. The filtrate yielded an additional amount (app. 10 g) of a moderately pure product after addition of 250 ml of boiling methanol and slow cooling down of the formed mixture.[6]

Combined yield of the white shiny microcrystalline solid after drying at 140 ˚C in vacuum was 82.3 g (77%).

II{2}: ^1H NMR, δ_H (400 MHz, $CDCl_3$) (d, *J* = 8.4 Hz, 4H), 7.11 (d, *J* = 8.4 Hz, 4H), 2.29 (s, 2H), 1.92 (s, 2H), 1.88 (s, 8H), 1.75 (s, 2H).

II{3}: ^1H NMR, δ_H (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.5 Hz, 6H), 7.13 (d, *J* = 8.5 Hz, 6H), 1.98 (s, 6H), 1.94 (s, 1H), 1.92 (pseudo-d, i.e. degenerate dd , *J* = 2.7 Hz, 6H).

II{4}: ^1H NMR, δ_H (400 MHz, $CDCl_3$) 7.65 (8 H, d, *J* 8.1), 7.16 (8 H, d, *J* 8.1), 2.04 (12 H, s).

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[1] The general method of iodination, used for the preparation of **II{2}** and **II{3}** did not work for this case. The yield was very small, <10%, and the starting material was recovered mostly. The most probable reason is the very low solubility of the starting 1,3,5,7-tetraphenyladamantane, **I{4}** in practically any solvent, but particularly is the used, quite polar mixture of acetic acid, water and sulfuric acid. The use of PIFA in a solvent of low polarity is, in comparison, a very smooth and efficient method.

[1] According to our experience, it is important that $CHCl_3$ should not contain EtOH, a typical stabilizer. Hence, distillation from over phosphorus pentoxide, preceded by a few hours of refluxing, is recommended.

[2] The attempt to use (diacetoxyiodo)benzene instead of PIFA was not successful.

[3] The stopper was fixed by a rubber band. The thermal effect of the reaction is small and the water bath stabilizes the temperature additionally.

[4] By that time the reaction was finished, as indicated by the fading of the deep red colour. Some amount of the product precipitated in a form of a fine white residue.

[5] The hexane washings were placed in a fridge and an appreciable amount of the product was crystallized out during one week of staying. The total yield reported includes this small additional crop.

[6] The last crop was not mixed with others, which were much purer.

Syntheses of 1,3-di-(4-cyanophenyl)adamantane, **III{2}**; 1,3,5-tri(4-cyanophenyl)adamantane, **III{3}** and 1,3,5,7-tetra(4-cyanophenyl)adamantane, **III{4}**

n g (*n* = 25-55) of the respective iodide derivatives, **II{2-4}**, 20% equivalent excess of copper (I) cyanide (i.e. 2.4, 3.6 and 4.8 times of the molar amounts of **II{2}, II{3}, II{4}** respectively) and 10×*n* ml of dry DMF were placed in a 1 L flask equipped with a magnetic stirrer. The mixture was stirred under under mild reflux for 4 h in argon atmosphere.[1] The reaction medium was cooled down and app. 2×*n* ml of H_2O was added.[2]

Work up of **III{2}**). The liquid was evaporated and the solid residue was powdered and thoroughly treated by app. 15×*n* ml of hot $CHCl_3$, thus picking up the crude product and leaving the residue of copper salts. The filtered solution was concentrated to drieness and the residue was recrystallized in 8×*n* of acetonitrile, employing treatment with active carbon, yielding 14.8 g (88%) of the pure white solid product, starting from 27 g of **II{2}**.

Work up of **III{3}**: The liquid was evaporated and the residual solid was continuously extracted by hot toluene.[3] The extracts were evaporated and the product was recrystallized from acetonitrile (~20 ml/g). Combined yield of the white solid product in two crops was 26.8 g (82%) (starting from 52 g of **III{2}**).

Work up of **III{4}**: The volume of the solution was reduced to app. 2×*n* ml using a rotary evaporator and filtered while hot from copper (I) iodide; the separated solid was washed by a few small portions of hot DMF. To the still warm clear solution of the combined filtrate 0.2×*n* ml of 1,2-diethylamine was added,[4] and the formed solution was poured drop by drop in 10×*n* ml of water. The white precipitate with some occluded copper complexes was filtered out from the bluish solution and wased by water. A repeated purification cycle, consisting of dissolution of the crude product in 2×*n* ml of hot DMF and pouring the solution dropwise under stirring in 10×*n* ml of 10% of aqueous HCl followed. The obtained crude product was, after drying, recrystallized from DMF, by dissolving in minimal amount of hot (~ 80-90 ˚C) solvent, followed by addition of an equal amount of iPrOH and cooling down the mixture in a fridge (+4 ˚C). The procedure yielded 22.2 g (82%) of a practically white solid (combined yield, from multiple crops; starting from 47.2 g of **II{4}**).

III{2}: ^{1}H NMR, δ_H (400 MHz, $CDCl_3$) 7.60 (4 H, d, *J* 8.2), 7.46 (4 H, d, *J* 8.2), 2.35 (2 H, s), 1.97 (2 H, s), 1.93 (8 H, s), 1.79 (2 H, s).

III{3}: ^{1}H NMR, δ_H(400 MHz, DMSO-d_6) 7.79 (6 H, d, *J* 8.4), 7.73 (6 H, d, *J* 8.5), 2.06 (6 H, dd, *J* 37.7, 12.0), 1.94 (6 H, s).

III{4}: ^{1}H NMR, δ_H(400 MHz, DMSO-d_6) 8.22 (8 H, d, *J* 8.8), 7.92 (8 H, d, *J* 8.8), 2.23 (12 H, s).

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[1] During refluxing the solution turned light orange to brownish; precipitation of the tan coloured CuI started within a short time and have been continuing for app. 2 h after the beginning of the reaction. The use of protecting atmosphere seems not to be essential, but plausibly improves the purity of the product.

[2] If water is not added, the subsequent contact with air and evaporation at elevated temperatures caused a darkening of the solution to greenish shades, presumably because of formation of Cu(II) species. In one of the preliminary experiments the complete discolouration was proven to be hard.

[3] We used a liquid-liquid extractor, with an aqueous slurry of the crude product placed in the bottom. For small quantities a non-continuous extraction is also possible, but for large quantities it is quite tedious. For 25 g of the product a few litres of hot, near boiling toluene is needed.

[4] 1,2-Ethylenediamine was added in order to prevent the precipitation of the dissolved copper species after the addition of water. Other complexing agents, like EDTA might work much better, but in the latter case an aeration of the solution by air-bubbling is advisable in order to oxidize the residual copper.

Syntheses of 1,3-di(4-carboxyphenyl)adamantane **IV{2}**; 1,3,5-tri(4-carboxyphenyl)adamantane, **IV{3}** and 1,3,5,7-tetra(4-carboxyphenyl)adamantane, **IV{4}**

General procedure: a stirred suspension of 2 g of the respective nitrile, **III{2-4}** in a solution of 3g of potassium hydroxide sealed in a PTFE-lined autoclave was heated in a copper-chip filled heating bath at 170 ˚C during 6 hours (actual temperature within the vessel was app. 150-160 ˚C).[1] The formed light-yellow solution[2] was diluted by app. 50 ml of distilled water and concentrated aqueous HCl was added dropwise until until pH = 1-2. The formed precipitate was aged by boiling of the slurry during 15 minutes and then by allowing it to stay for a few hours a room temperature. The compound was filtered by suction filtration[3] and washed by copious amount of water until neutral pH of the washings.

The yield of the white product, after drying in air at 100 ˚C, was 2.22 g (99%) for **IV{2}**, 2.09 g (93%) for **IV{3}** and 2.15 g (94%) for **IV{4}**.

IV{2}: ^{1}H NMR, δ_H(400 MHz, DMSO-d_6) 12.81 (2 H, s), 7.89 (4 H, d, *J* 8.2), 7.55 (4 H, d, *J* 8.2), 2.27 (2 H, s), 2.00 (2 H, s), 1.92 (8 H, s), 1.76 (2 H, s). FT-IR (ATR), $\tilde{\nu}$, cm^{-1}: 2909(w), 2849(w), 2674(w), 2545(w), 1681(s), 1606(m), 1569(w), 1423(m), 1289(s), 1189(w), 1128(vw, br), 1015(w), 927(w, br), 862(m), 829(w), 806(vw), 770(m), 739(m), 703(m), 662(w).

IV{3}: ^{1}H NMR, δ_H (400 MHz, DMSO-d_6) 12.83 (3 H, s), 7.91 (6 H, d, *J* 8.3), 7.63 (6 H, d, *J* 8.3), 2.08 (1 H, dd, *J* 40.8, 12.0), 1.97 (1 H, s). FT-IR (ATR), $\tilde{\nu}$, cm^{-1}: 2897(w), 2854(w), 2674(w), 2549(w), 1679(vs), 1609(m), 1572(m), 1512(vw), 1422(m), 1292(s), 1192(m), 1129(w), 1016(m), 942(br, w), 854(m), 808(vw), 771(m), 748(s), 703(m), 664(m).

IV{4}: ^{1}H NMR, δ_H (400 MHz, DMSO-d_6) 12.81 (4 H, s), 7.92 (8 H, d, *J* 8.0), 7.72 (8 H, d, *J* 8.2), 2.17 (12 H, s). FT-IR (ATR), $\tilde{\nu}$, cm^{-1}: 2930(w, vbr), 2666(vw), 2540(vw), 1676(vs), 1606(s), 1571(m), 1511(vw), 1413(s), 1353(vw), 1275(s), 1185(m), 1118(w), 1019(w), 848(m), 754(s), 702(m), 663(m).

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[1] The organic nitriles, **III{2-4}**, are quite hydrophobic, and are not moistened well by the concentrated aqueous KOH solution. Hence the used high temperature was necessary in order to complete the reaction within short time (alternatively, a mixture of water and e.g. ethylene glycol could be, almost certainly, used at reflux temperature).

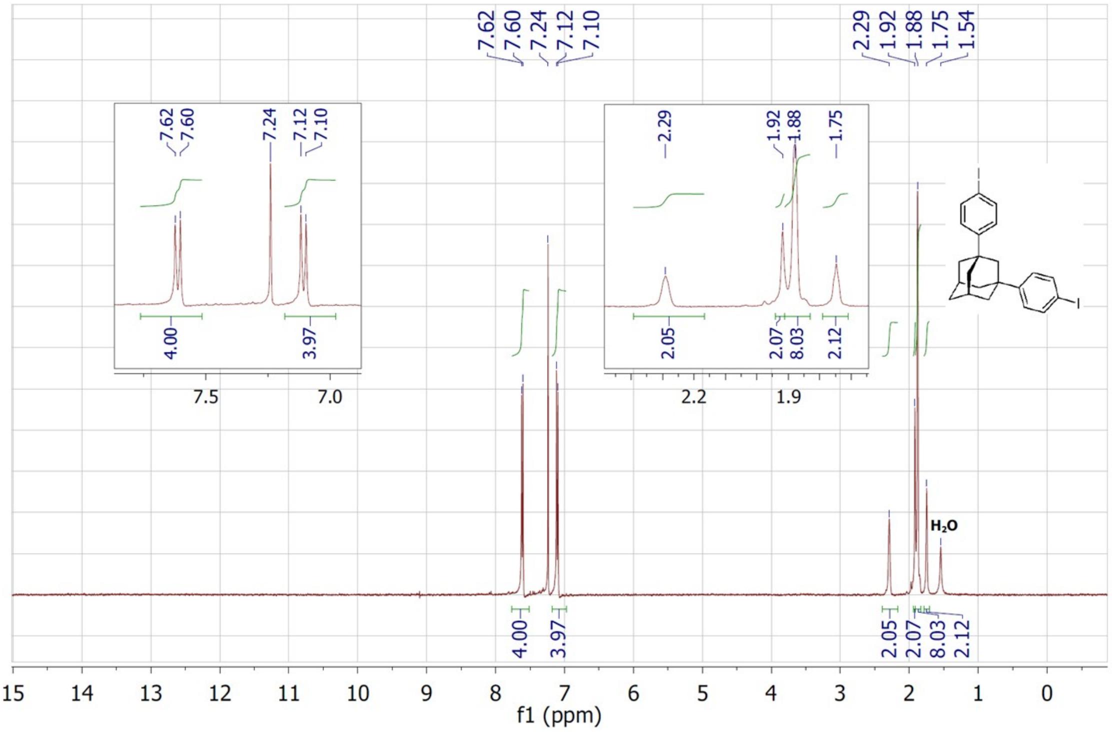
[2] The formed potassium salt of the diacid **IV{2}** has, unlike in other cases, has a relatively lower solubility in water (much better in warm water). The obtained slurry in this case is emptied not in 50 ml, but at least in 100 ml of water, until complete dissolution, with slight heating, if necessary (the possible insoluble rests should be filtered out on this stage).

Sometimes during repeated syntheses a part of the nitrile remained unreacted after the 6 hours of heating due to poor moistening of the hydrophobic precursor by the alkaline solution. In this case the solid residues were scratched down in the autoclave, thoroughly mixed with the solution, and the heating stage was repeated for additional 3 hours.

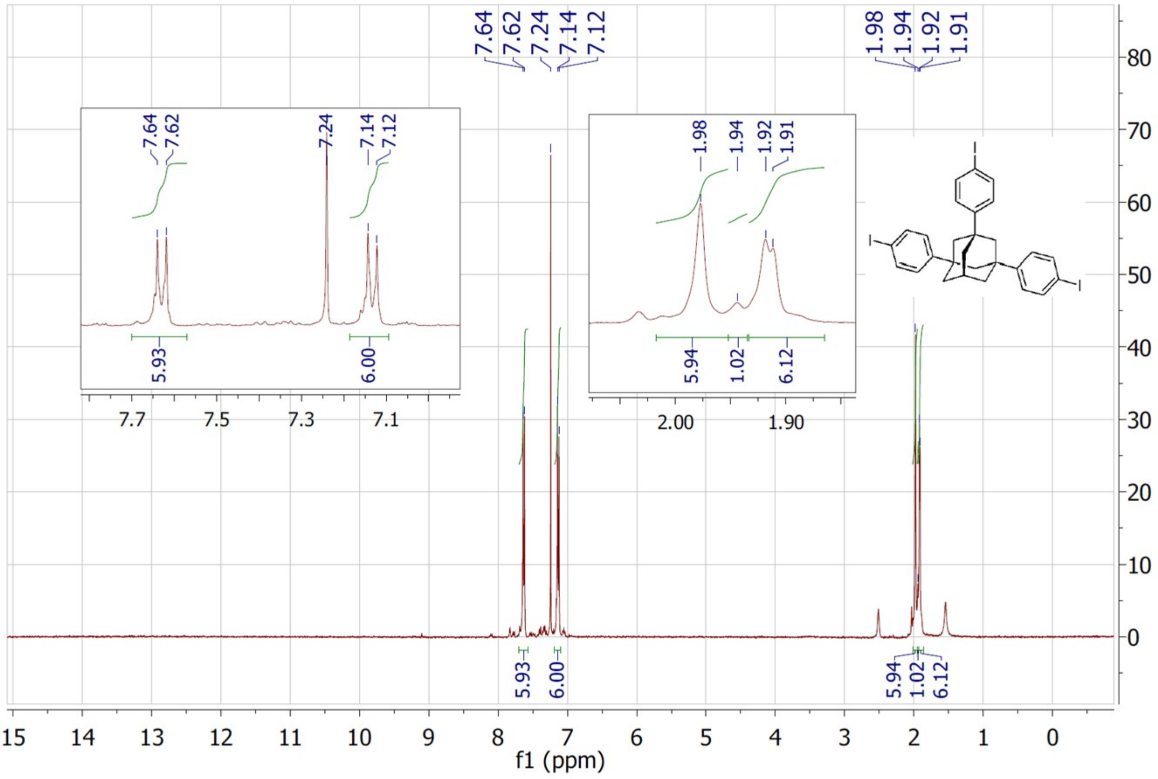
[3] Suction filtration of the gel-like precipitate of product after acidification and the subsequent washing was typically a lengthy an tedious process, especially in the case of **IV{3}**. Centrifugation, if accessible, should be preferred.

NMR spectra

1,3-Di(4-iodophenyl)adamantane (CDCl$_3$)



1,3,5-Tri(4-iodophenyl)adamantane (CDCl$_3$)



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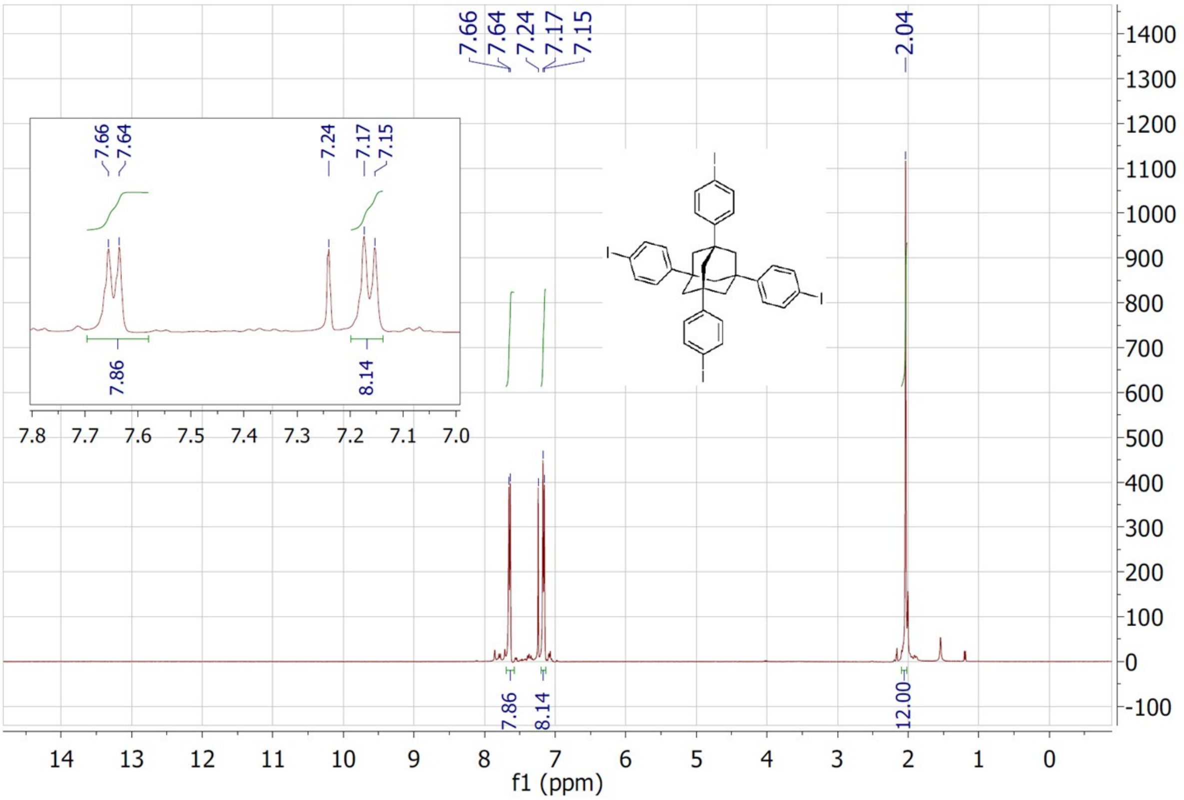

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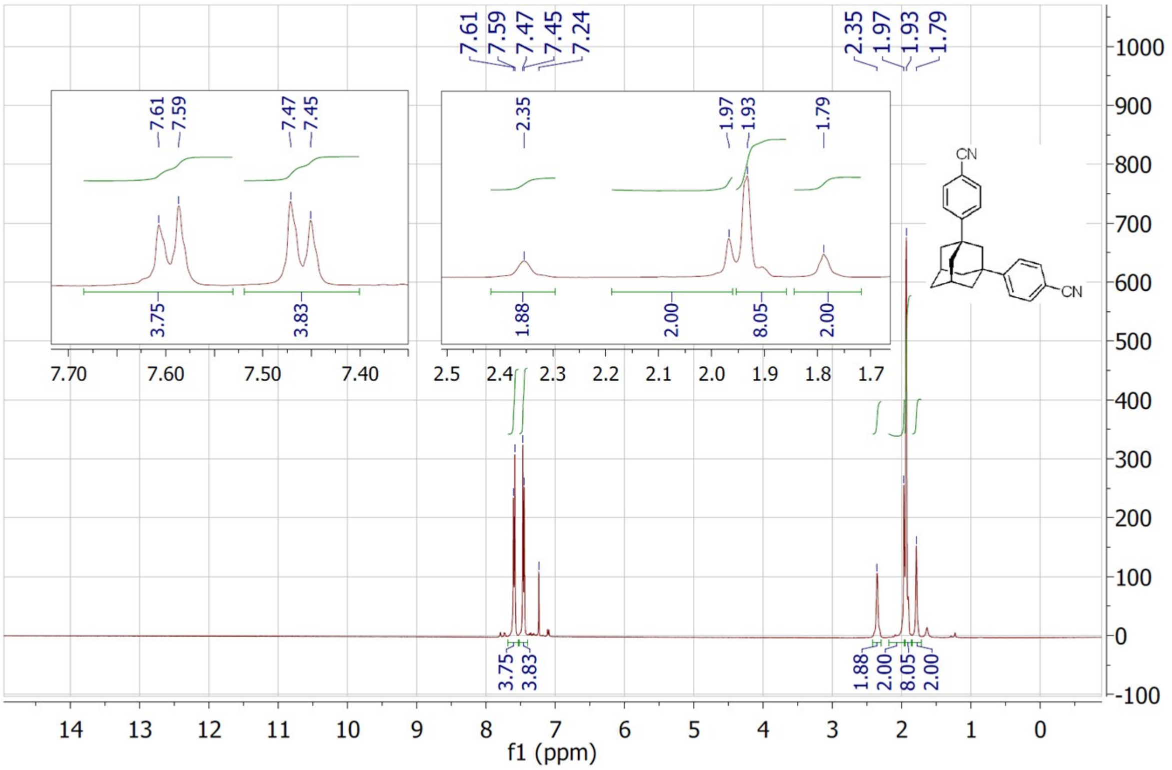

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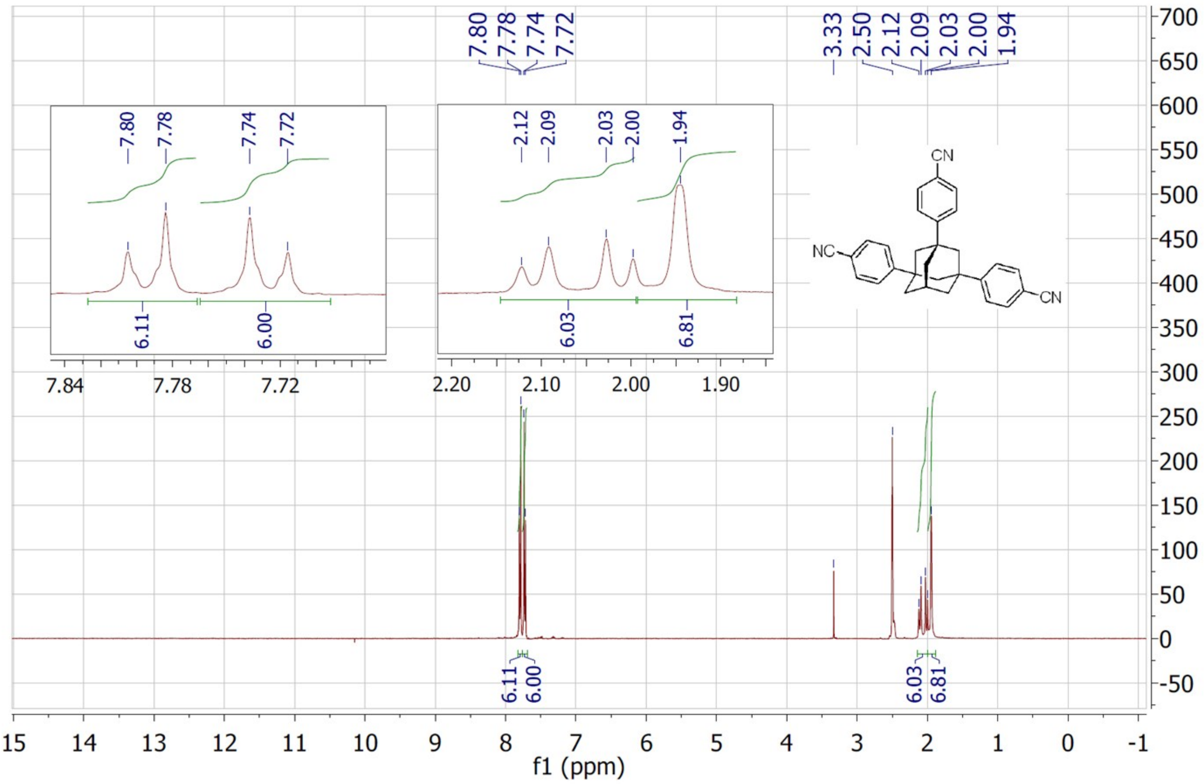
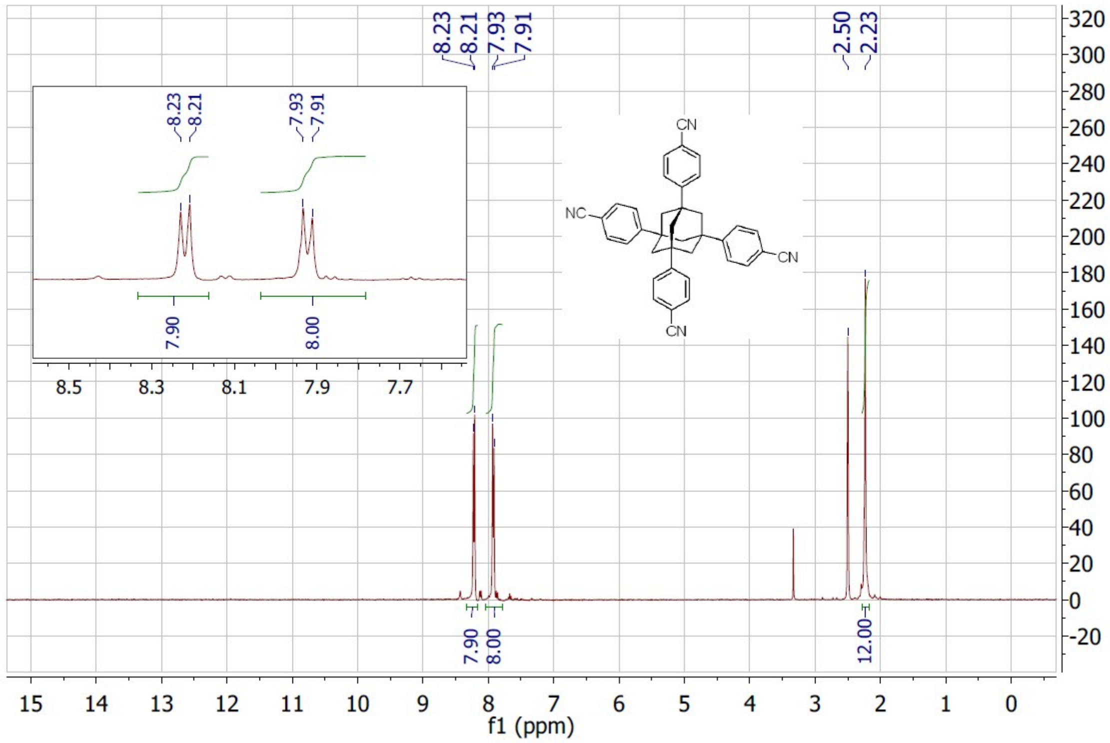
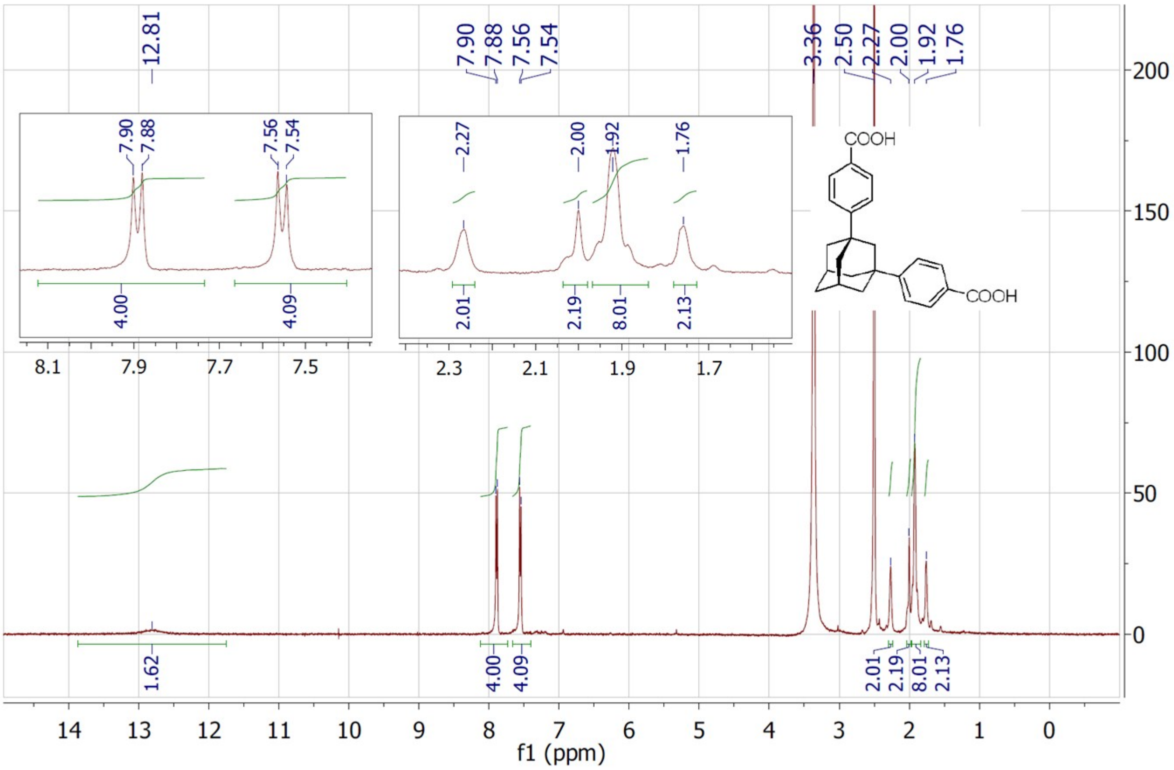


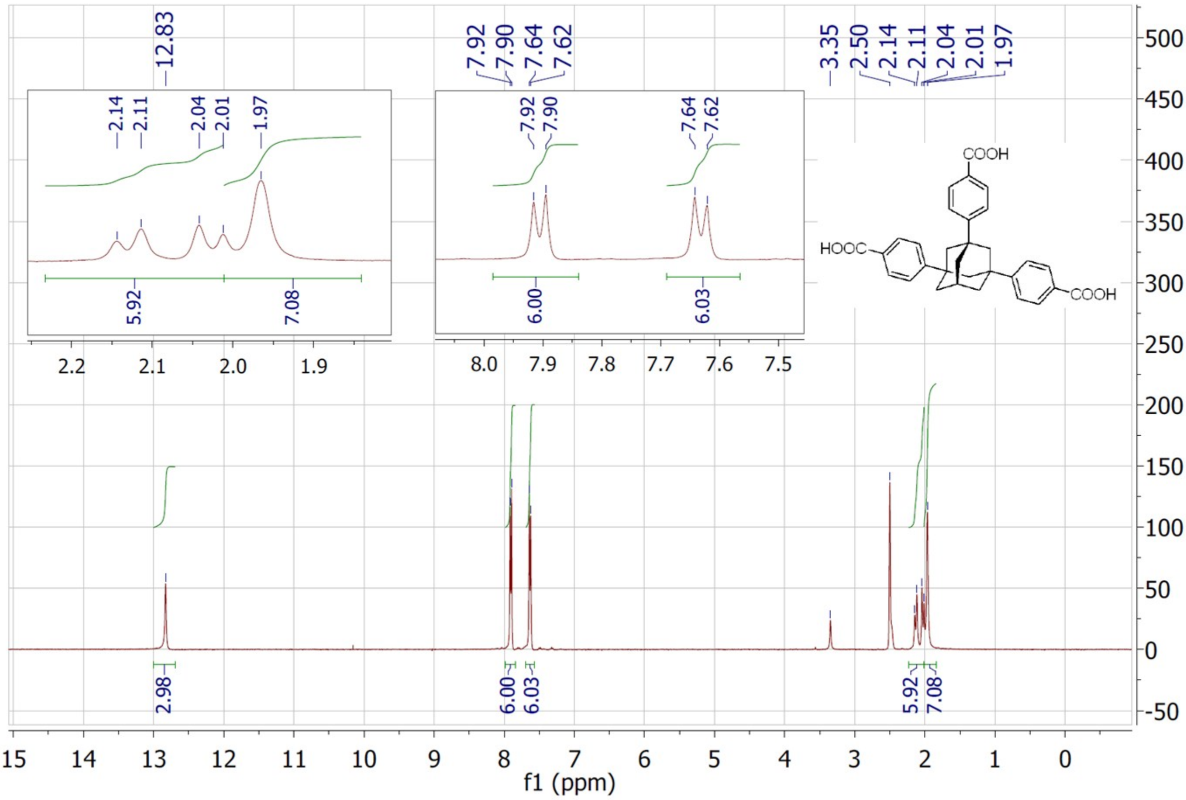
1,3,5,7-Tetra(4-cyanophenyl)adamantane (DMSO-d_6)



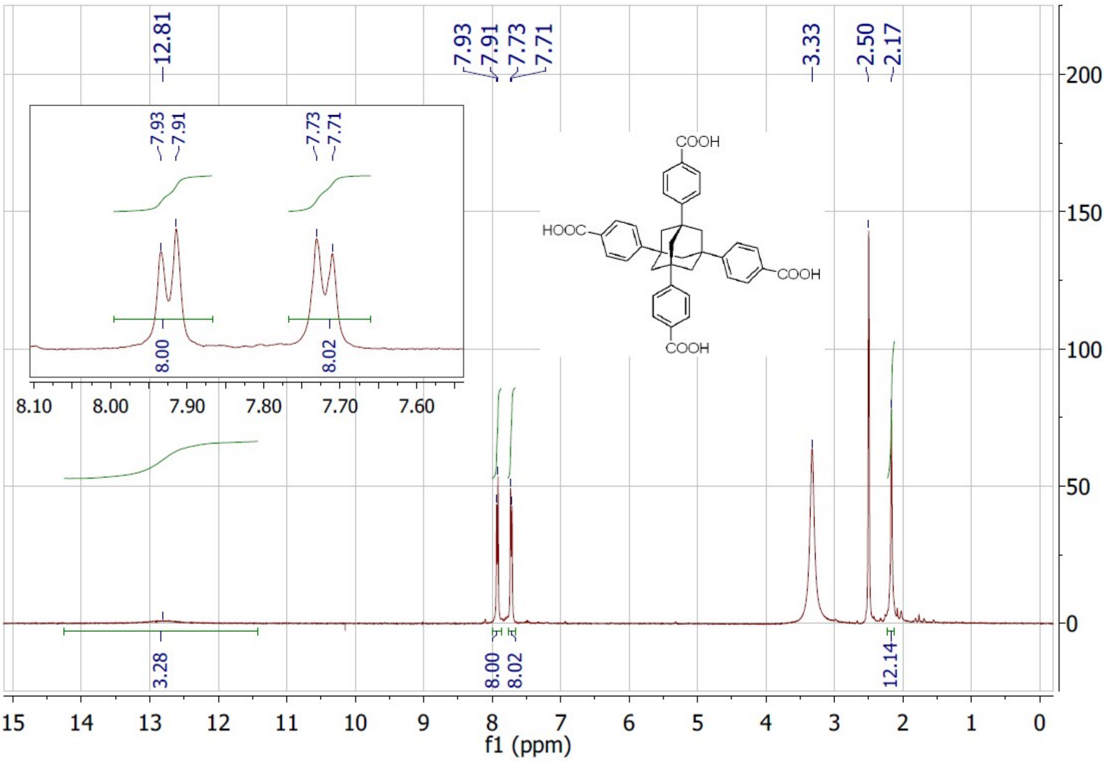
1,3-Di(4-carboxyphenyl)adamantane (DMSO-d_6)



1,3,5-Tri(4-carboxyphenyl)adamantane (DMSO-d_6)



1,3,5,7-tetra(4-carboxyphenyl)adamantane (DMSO-d_6)



Synthesis of the coordination polymers

Chemicals and materials

Manganese (II) chloride tetrahydrate (≥98%, Sigma-Aldrich), cadmium chloride hemi(pentahydrate) (98%, Sigma-Aldrich), cobalt(II) chloride hexahydrate (98%, Sigma-Aldrich), N, N-dimethylformamide (ACS, VWR), ethanol (99.5%, ACS, Merck). All chemicals were used as obtained from commercial sources without further purification.

All synthetic operations were performed in air, without using a protective atmosphere.

The given molecular formulas are ascribed according to a compromise between structural data, TGA data, and elemental analysis (listed in order of decreasing priority for a general case; as except **1**, the structural data gave no precise content of the solvent molecules, the other two methods were only regarded for **2**-**4**).

Synthesis of $[\mathrm{Mn(DMF)(L^2)}]$, 1

A mixture of $MnCl_2{\cdot}4H_2O$ (20 mg, 0.1 mmol) and 1,3-di(4-carboxyphenyl)adamantane, H_2L^2 (19 mg, 0.05 mmol) was dissolved in 1 mL N,N-dimethylformamide (DMF) and sealed in a 3 ml borosilicate glass tube. The tube was placed in an oven and heated at 140 °C for 72 h, then cooled to ambient temperature at a rate of 6 °C h^{-1}.

After cooling, the product were separated, washed by a small amount of DMF and dried in air at r.t. for one day). The ligand-based yield of the almost colourless, very light pink coloured crystals was 23 mg, ~90%.

Elemental analysis, calcd. (%) for $C_{27}H_{29}MnNO_5$: C 64.54, H 5.82, N 2.79; found: C 61.45; H5.57; N 3.02. FT-IR (ATR), $\tilde{\nu}$, cm–1: 3359(m, vbr), 2901(m, br), 2849(w), 1660(m), 1583(s), 1532(s), 1394(vs), 1195(w), 1147(vw), 1105(w), 1015(w), 860(w, br), 777(m), 745(m), 711(m), 663(w, br).

Synthesis of $[\mathrm{Cd(DMF)_{0.5}(H_2O)_{0.5}(L^3)}]\cdot(\mathrm{NH_2Me_2})\cdot 0.5\mathrm{DMF}\cdot 1.5\mathrm{H_2O}$, **2**

A mixture of $CdCl_2{\cdot}2.5H_2O$ (12 mg, 0.05 mmol) and the 1,3,5-tri(4-carboxyphenyl)adamantane, H_3L^3 (12 mg, 0.025 mmol) was dissolved in 1 mL N,N-dimethylformamide (DMF) and sealed in a 3 ml borosilicate glass tube. The tube was placed in an oven and heated at 130 °C for 72 h, then cooled to ambient temperature at a rate of 6 °C h^{-1}.

After cooling, the product was separated, washed by a small amount of DMF and dried in air at r.t. for one day). The ligand-based yield of the colourless crystals was 19 mg, > 90%.

Elemental analysis, calcd. (%) for $C_{36}H_{44}CdN_2O_9$: C 56.81, H 5.83, N 3.68; found: C 56.41, H 5.08, N 2.45. FT-IR (ATR), $\tilde{\nu}$, cm^{-1}: 2922, 2851, 1651, 1585, 1529, 1466, 1394, 1191, 1136, 1107, 1016, 978, 853, 783, 760, 711, 679.

Synthesis of $[\mathrm{Mn(DMF)(L^4)}]\cdot 2(\mathrm{NH_2Me_2})\cdot 3\mathrm{DMF}\cdot 4\mathrm{H_2O}$, **3** and $[\mathrm{Co(DMF)(L^4)}]\cdot 2(\mathrm{NH_2Me_2})\cdot 2\mathrm{DMF}\cdot 5\mathrm{H_2O}$, **4**

A mixture of $MnCl_2{\cdot}4H_2O$ (20 mg, 0.1 mmol) or $CoCl_2{\cdot}6H_2O$ (24 mg, 0.1 mmol) and 1,3,5,7-tetra(4-carboxyphenyl)adamantane, H_4L^4 (31 mg, 0.05 mmol) was dissolved in 2 mL N,N-dimethylformamide (DMF) and sealed in a 6 ml borosilicate glass tube. The tube was heated at 100 °C for 72 h, then cooled to ambient temperature at a rate of 4 °C h^{-1}.

After cooling, the crystals were separated, washed by a small amount of DMF and dried in air at r.t. for one day). The ligand-based yield of the almost colourless, very light-pink coloured crystals of **3**, 44 mg and violet crystals of **4**, 51 mg, was above approx. ~80%.

3: Elemental analysis, calcd. (%) for $C_{51}H_{73}MnN_5O_{15}$: C 58.28, H 7.00, N 6.66; found: C 54.94, H 6.07, N 6.59.[1] FT-IR (ATR), $\tilde{\nu}$, cm^{-1}: 3374 (w, vbr), 2926(w), 2852(w), 1649(s), 1586(s), 1534(s), 1385(vs), 1353(s), 1253(vw), 1189(vw), 1103(m), 1060(m), 1015(m), 860(m), 767(s), 711(m), 676(m).

4: Elemental analysis, calcd. (%) for $C_{48}H_{68}CoN_4O_{15}$: C 57.65, H 6.85, N 5.60; found: C 56.14, H 6.15, N 3.83.[2] FT-IR (ATR), $\tilde{\nu}$, cm^{-1}: 3327(w, vbr), 2928(w), 2852(w), 1649(s), 1606(s), 1554(m), 1403(s), 1349(s), 1253(w), 1189(vw), 1101(m), 1060(vw), 1014(m), 862(m), 796(s), 767(), 712(m), 680(m), 663(m).[3]

Single crystal X-ray diffraction structures

Suitable single crystals placed in viscous oil were carefully selected under a polarizing microscope and mounted in air onto a nylon loop. The diffraction experiments were performed using a Bruker APEX DUO diffractometer equipped with with APEX-II CCD area detector employing Mo-K$_\alpha$ (λ = 0.71073 Å) Adsorption correction was applied by the SADABS program, employing empirical multi-scan technique.[6] The structures were solved by direct methods using SHELXS-97 [7] and refined by full-matrix least-squares fitting on F^2 using SHELXL-2014 [8]. All non-hydrogen atoms, except some parts of the solvent molecules, were refined with anisotropic thermal parameters. In the case of **2** the guest molecules filling the pores were partially modelled (see the special description below), while for **3**, due to low-quality diffraction experiment, it was not possible to locate the guest molecules, including the dimethylammonium cations, and the respective reflections were excluded by SQUEEZE [9] (PLATON [10]). Hydrogen atoms were placed on idealized positions and refined using a riding model with the U_{iso} isotropic thermal displacement parameter set equal to kU_{eq}, where U_{eq} is the equivalent isotropic displacement parameter of the 'parent' heavy atom; *k*=1.2 for carbon parent atoms belonging to aromatic moieties and k=1.5 for others, with C-H distances being 0.93 Å and 0.97 Å respectively). The hydrogen atoms of the solvent molecules were refined completely in **1**, and were not refined for **2** and **3** (in the latter case excluded by SQUEEZE). Crystallographic data are summarized in Table S1. Particular details, including the atom numbering schemes, are given below.

Additional information regarding the refinement of **2**. All non-hydrogen atoms, with two exceptions were refined anisotropically. The exceptions were: (a) the atoms belonging to guest molecules residing in the pores including the components of the disordered dimethylammonium cation (b) the non O-atoms of the coordinated DMF molecule with partial occupancy and disorder.

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[1] In this case the elemental analysis shows significant discrepancy with other methods, suggesting 1-2 additional DMF molecules per formula unit. This is, however, improbable, taking in account the available free volume known from the structural data (see the structural description and TGA data analysis). Such fluctuation is not something impossible, and could, potentially, be attributed to occluded DMF. For a relatively small, 2-3 mg, sample consisting of a small number of relatively large single crystals such occurrence is rather probable.

[2] The N-content is much lower in **4** compared to **3**, which is a possible indication of high variance of the elemental analysis results. The somewhat different composition of solvent of crystallization for isostructural compounds **3**, **4** is not very probable, albeit possible. The assignment of the two different formulas rather reflects the objectively high error of determination of the solvent content by the standard means available for us (one of the two formulas might be true for both of the compounds). No special research aiming more precise determination of the solvent content is planned, as it is out of the aimed research scope of this contribution.

[3] Note the near identity of the IR spectra of **3**, **4**.

The structure could also be solved in lower *P*1 symmetry; in this case the site-sharing of DMF and H_2O molecules (with 'common' O7 atom) seems to be resolved (see below). Still, this subtle difference seems not to be enough to prefer *P*1 over $P\bar{1}$.

The structure contains the next cases of disordered molecules or fragments with partial occupancy:

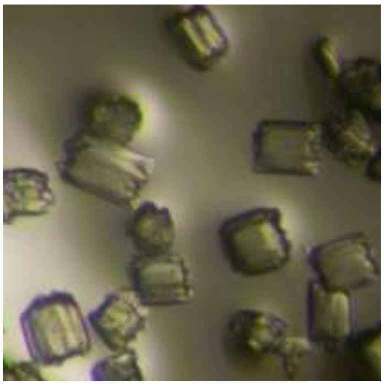
1. Coordinated DMF and H_2O shares a coordination position with 0.5/0.5 occupancy ('shared' O7 atom). The ratio was fixed to be close to the occupancy of the C41 atom (bound to O7 and belonging to DMF molecule) refined freely during an independent test. While DMF is considered to form stronger coordination bonds with cadmium than water, the concurrence of the two in the structure is not impossible and potentially could reflect the requirements for better space filling.

2. The DMF molecule coordinated through the O7 atom features a two-component disorder. The two components were fixed to be equal, in order to avoid instabilities in the refinement. The electronic densities are relatively low and 'smeared' in this region, which means that the use of restraints was practically inevitable in order to reach convergence; for a few atoms the thermal displacement parameters were also fixed.

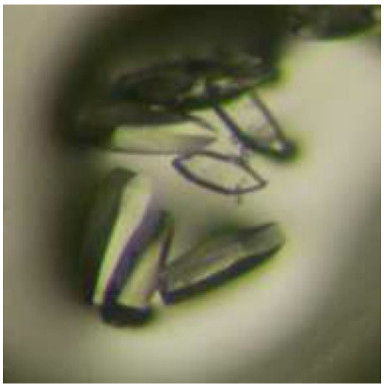
3. An additional DMF molecule fragment, with a consistency demanded occupancy of 0.5, was located near the vicinity of the coordinated DMF molecule (with 0.5 occupancy). The respective electronic density was modelled by C50, C51, C52atoms and interpreted as fragments of a DMF molecule, residing there when the O7 atom is represented by a H_2O molecule (which shares a site with the coordinated DMF molecule, see p. 2).

4. The $[NMe_2H_2]^+$ cations are represented by disordered atom groups of C53 N53 (0.5 occupancy, N53 is delocalized over two positions) and C55 N55 C56 (0.5 occupancy, N55 delocalized over two positions). In the latter case, the disordered anion is positionally coinciding with a partially modelled DMF molecule (0.5 occupancy); the complex disorder was not completely resolved.

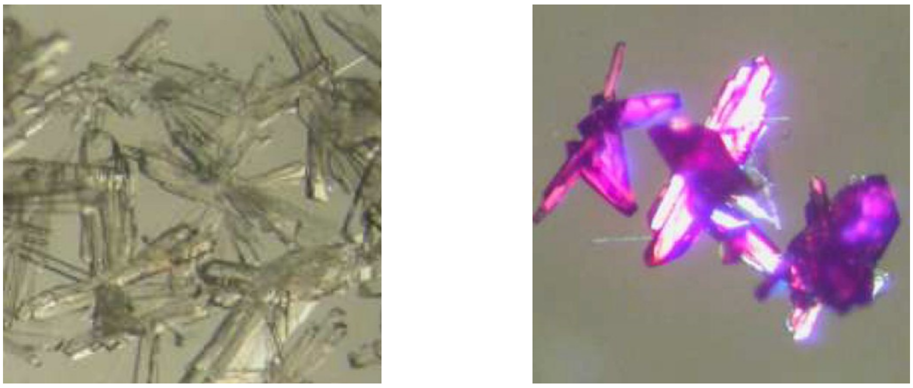
5. Two isolated electronic densities were interpreted as belonging to water molecules: O11 (0.5 occupancy) and O12.



$[Mn(DMF)(L^2)]$, **1**



$[Cd(DMF)_{0.5}(H_2O)_{0.5}(L^3)] \cdot (NH_2Me_2) \cdot$ - $0.5DMF \cdot 1.5H_2O$, **2**



$[Mn(DMF)(L^4)] \cdot 2(NH_2Me_2) \cdot 3DMF \cdot 4H_2O$, **3**

$[Co(DMF)(L^4)] \cdot 2(NH_2Me_2) \cdot 2DMF \cdot 5H_2O$, **4**

Fig. S3. Micrographs of single crystals.

Tab. S1 Crystal data and structure refinement for $[Mn(DMF)(L^2)]$, **1**; $[Cd(DMF)_{0.5}(H_2O)_{0.5}(L^3)] \cdot (NH_2Me_2) \cdot 0.5DMF \cdot 1.5H_2O$, **2** and $[Mn(DMF)(L^4)] \cdot 2(NH_2Me_2) \cdot 3DMF \cdot 4H_2O$, **3**.

	1	**2**	**3** [a]
Empirical formula	$C_{27}H_{29}MnNO_5$	$C_{36}H_{44}CdN_2O_9$	$C_{38}H_{28}MnO_8$ [a]
FW /g mol^{-1}	502.47	761.16	667.54
T /K	296(2)	296(2)	296(2) K
Wavelength / Å	0.71073	0.71073 A	0.71073 A
Crystal system	Monoclinic	Triclinic,	Orthorhombic,
Space group	$P2_1/c$	$P\bar{1}$	*I*mma
a /Å	12.5159(10)	11.0682(4)	17.335(3)
b /Å	19.1864(14)	13.5036(5)	17.748(2)
c /Å	9.9596(8)	14.6691(5)	19.551(3)
α /°	90	70.055(2)	90
β /°	94.649(3)	79.314(2)	90
γ /°	90	87.896(2)	90
V /Å^3	2383.8(3)	2024.37(13)	6014.9(14)
Z	4	2	4
Calc. density / g cm^{-3}	1.400	1.230	0.737 [a]
μ / mm^{-1}	0.592	0.586	0.248 [a]
F(000)	1052	758	1380 [a]
Crystal size / mm^3	0.10 × 0.10 × 0.02	0.10 × 0.10 × 0.10	0.50 × 0.15 × 0.15
θ range /°	1.63 to 27.70	1.605 to 26.571	1.550 to 25.769
Index ranges / *hkl*	[-16;16], [-23;25], [-7-12]	[-13;13], [-16;16], [-18;18]	[-21;20], [-21;21], [-23;22]
Reflections collected	28829	29470	30564 / 2982
Independent reflections	5561 [R_{int} = 0.0605]	8372 [R_{int} = 0.0346]	[R_{int} = 0.1185]
Completeness /%, θ_{max} /°	100.0	99.8	96.5

Max. and min. transmission	None	None	None
Data / restraints / parameters [b]	5561 / 0 / 309	8372 / 9 / 437	2982 / 74 / 142
Goodness-of-fit on F^2 [c]	1.015	1.073	0.944
Final R indices [$I>2\sigma(I)$]; R1, wR2 [d]	0.0409, 0.0877	0.0713, 0.2032	0.0997, 0.2883
R indices (all data); R1, wR2	0.0706, 0.1005	0.0910, 0.2217	0.1334, 0.3047
Largest diff. peak and hole, e·Å-3	0.291 and -0.208	1.658 and -0.959	0.491 and -0.375
Electron count in the voids per cell (by SQUEEZE)[10]	-	-	282

[a] SQUEEZE was applied / given for a structure with applied SQUEEZE procedure

[b] Full-matrix least-squares on F^2

[c] Goodness-of-fit: $[\Sigma[w(F_0^2-F_c^2)^2]/(n-p)]^{1/2}$

[d] $R1 = [\Sigma(\|F_0|-|F_c\|)/\Sigma|F_0|]$; $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$.

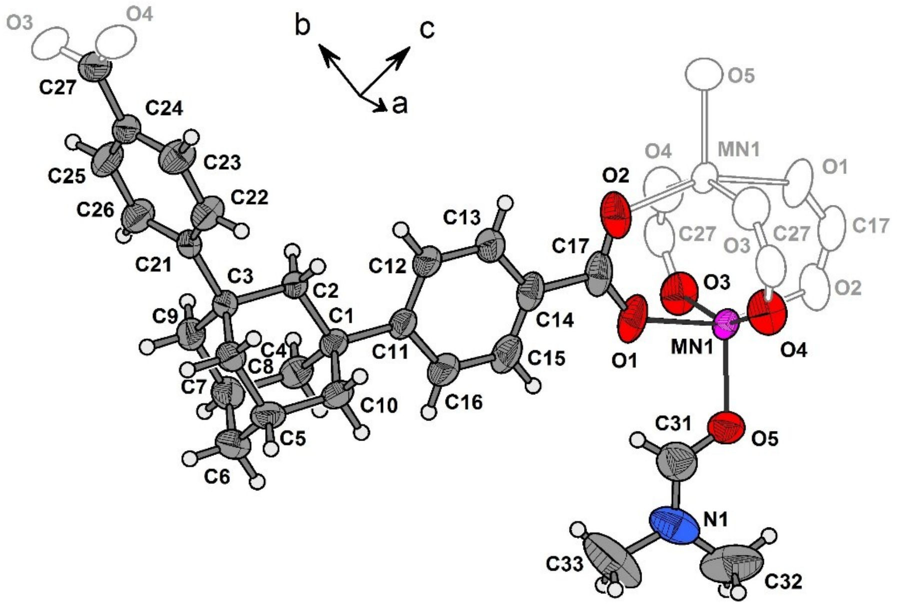


Fig. S4. ORTEP drawing of the asymmetric unit of [Mn(DMF)(L^2)], **1** at 50% probability level with numbering scheme. The bound symmetry equivalents are shown as empty ellipsoids with dark grey outline.

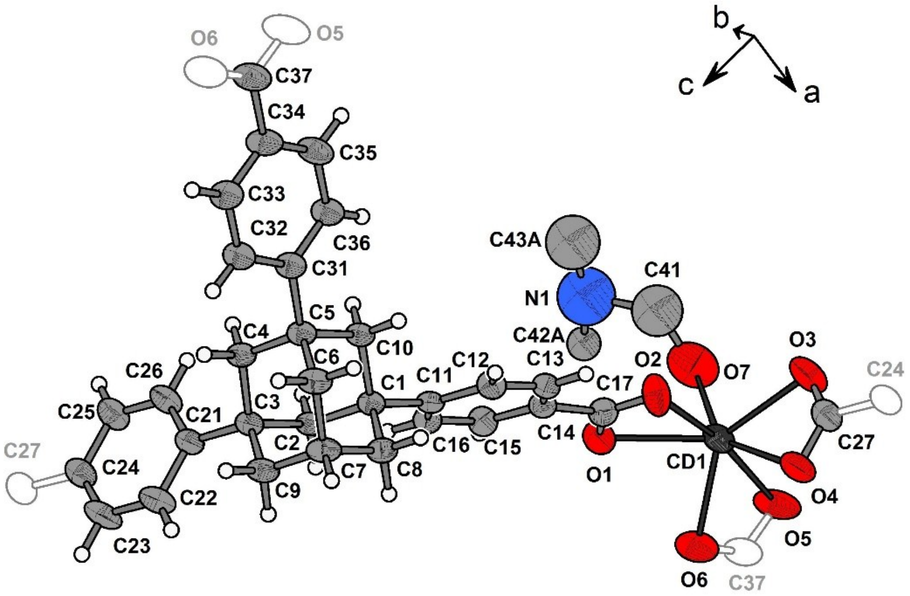


Fig.S5. ORTEP drawing of the asymmetric unit of $[Cd(DMF)_{0.5}(H_2O)_{0.5}(L^3)] \cdot (NH_2Me_2) \cdot 0.5DMF \cdot 1.5H_2O$, **2** at 50% probability level with numbering scheme. The bound symmetry equivalents are shown as empty ellipsoids with dark grey outline.

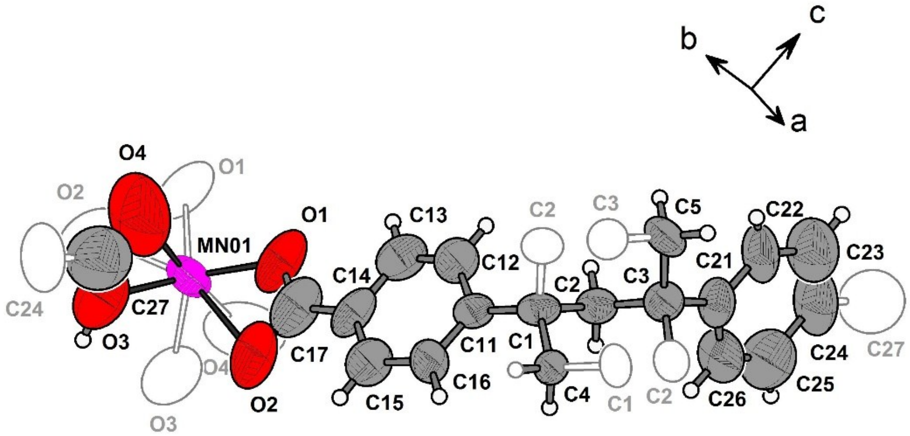


Fig. S6. ORTEP drawing of the asymmetric unit of $[Mn(DMF)(L^4)] \cdot 2(NH_2Me_2) \cdot 3DMF \cdot 4H_2O$, **3** at 50% probability level with numbering scheme. The bound symmetry equivalents are shown as empty ellipsoids with dark grey outline.

Analytics

The information regarding the conditions, analytical instruments and the parameters used are given in the respective sections below, which also contains the collected data. The ^{1}H NMR spectra, collected by a Bruker 400 MHz instrument, are given in the part devoted to the synthesis of the organic compounds. The results of the elemental analyses (CHN), which were carried out on a Perkin Elmer CHN 2400, are given in the description of the synthesis of coordination polymers (p. 14).

PXRD

The diffractograms were obtained using a Bruker D2 Phaser diffractometer equipped by a Lynxeye 1D detector, using a low background silicon sample holder and Cu-Kα radiation source (30 kV, 10 mA; λ = 1.54182 Å, Ni-filtered). The measurements were performed with 0.01 deg s^{-1} scan speed, starting from 2θ = 5˚, which is the lower measurement limit of the instrument in the used mode (the interval of 2θ ~ 5-8˚ is also significantly downscaled). Simulated PXRD patterns were calculated from single-crystal data using the MERCURY 3.0.1 software suite from CCDC with FWHM = 0.1˚. The simulated patterns are slightly scaled at higher angles to fit better the actual intensities of the experimental patterns. For proper estimation of the correspondence it is important to note that non-negligible thickness of the sample together with the relatively small radius of the detection circle of this table-top instrument causes a perceptible shift of the pattern, almost negligible at low angles, but reaching up to 0.2-1˚ at 2θ =30-50˚.

Comparison of experimental and simulated PXRD for all the reported compounds are given below.

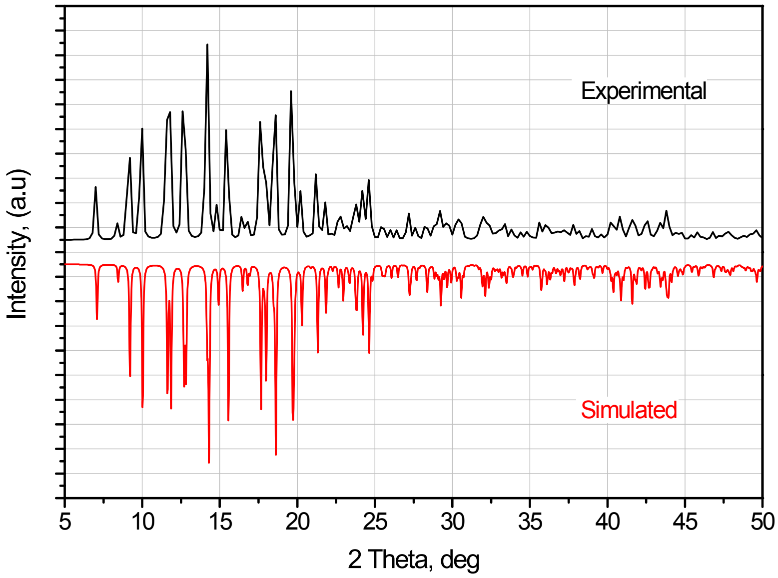


Fig. S7. [Mn(DMF)(L^2)], **1**.

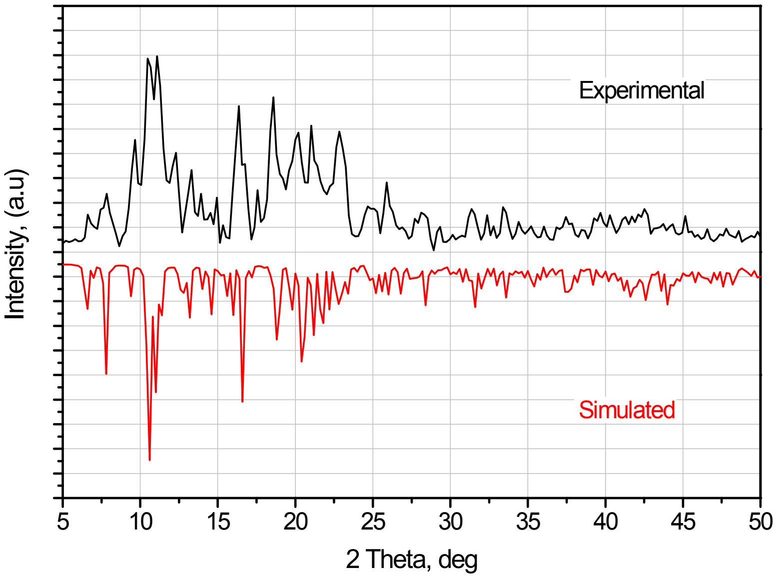


Fig. S8. [Cd(DMF)$_{0.5}$(H$_2$O)$_{0.5}$(L^3)] · (NH$_2$Me$_2$) · 0.5DMF · 1.5H$_2$O, **2**.

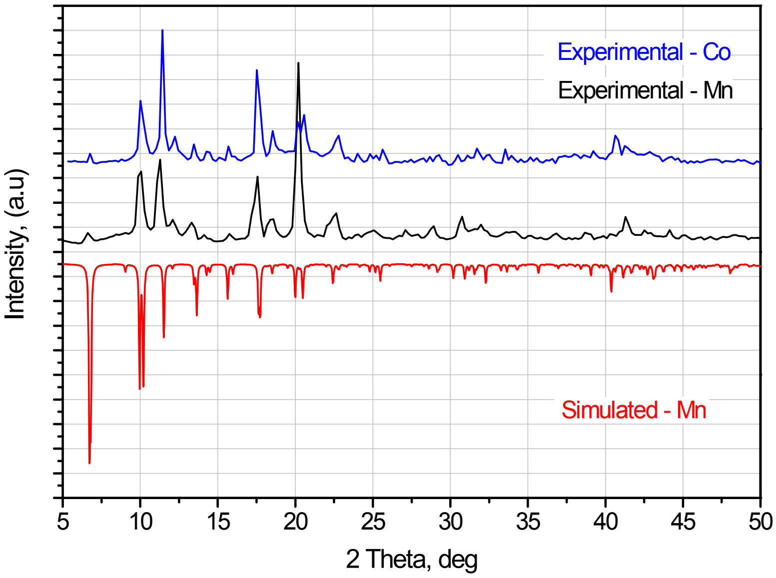


Fig. S9. [Mn(DMF)(L^4)] · 2(NH$_2$Me$_2$) · 3DMF · 4H$_2$O, **3** and [Co(DMF)(L^4)] · 2(NH$_2$Me$_2$) · 2DMF · 5H$_2$O, **4.**

TGA

The thermogravimetric analysis was performed on a Netzsch TG 209 F3 instrument at 5 C° min^{-1} heating rate using aluminium sample holder and nitrogen as carrier gas.

[Mn(DMF)(L^2)], **1**:

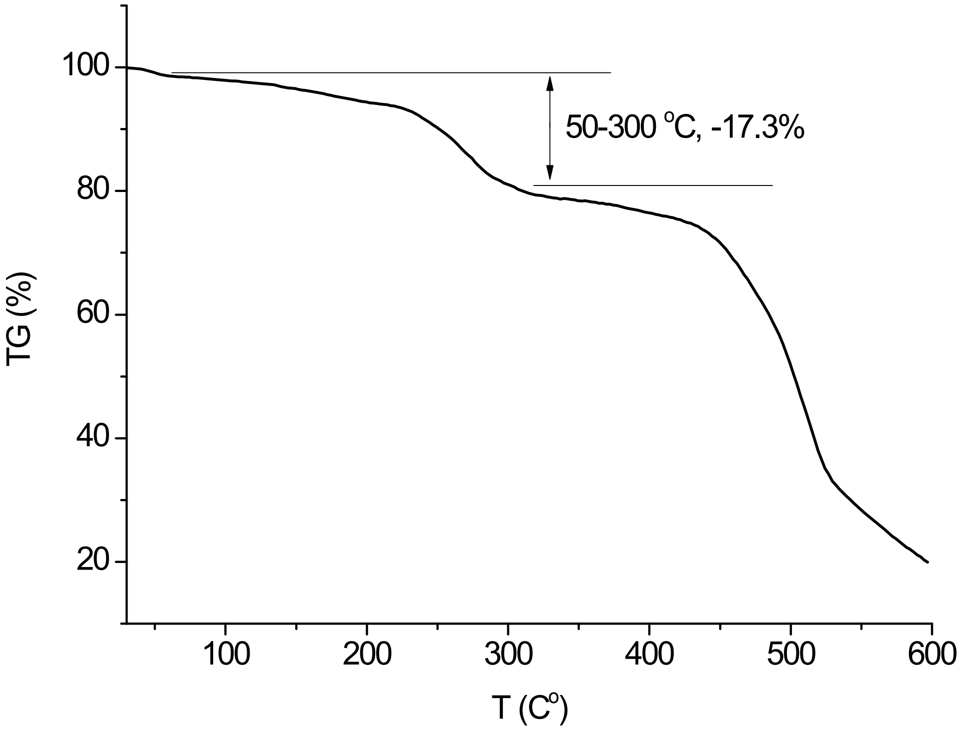


Fig. S10. TGA weight loss curve for [Mn(DMF)(L^2)], **1**.

The weight loss between 50-300˚C is associated primarily with the loss of DMF. The observed value of 17.3% is relatively well corresponds with the calculated value of 14.5%. According to the TGA there it would be possible to ascribe an additional water molecule, but the good quality SCXRD structure does not confirm that possibility.

[Cd(DMF)$_{0.5}$(H$_2$O)$_{0.5}$(L^3)] · (NH$_2$Me$_2$) · 0.5DMF · 1.5H$_2$O, **2:**

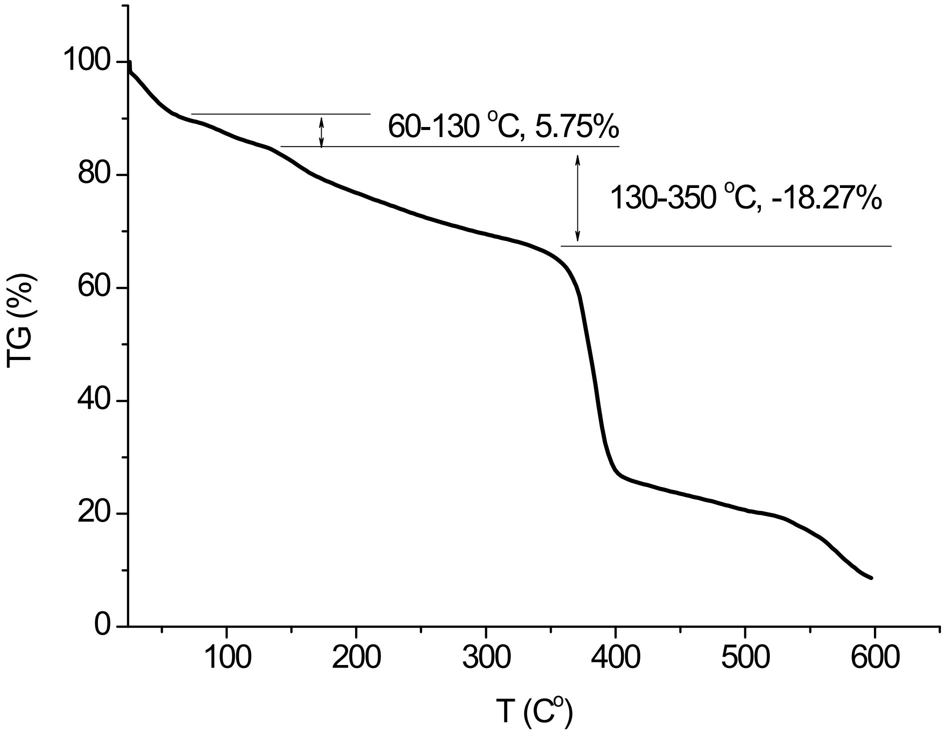


Fig. S11. TGA weight loss curve for $[Cd(DMF)_{0.5}(H_2O)_{0.5}(L^3)] \cdot (NH_2Me_2) \cdot 0.5DMF \cdot 1.5H_2O$, **2**.

There is a rapid weight loss until 60 ˚C, which slows down thereafter. It is interpreted as being related with residual, non-adsorbed solvents, rapidly evaporating in the carrier gas stream, i.e. the sample was evidently not dried thoroughly. The further two, weakly differentiated steps are associated with the loss of water followed by DMF and $NHMe_2$ respectively. The loss of dimethylamine as a result of decomposition of the dimethylammonium cation is not differentiated clearly from DMF, but occurs, as expected, at a significantly higher temperatures (up to 350 ˚C). The total weight loss is 24.0%, or, corrected to the initial unaccounted loss of ~10% weight is 21.6%. The further weight loss is associated with decomposition of the ligand.

The solvent content together with dimethylamine associated with the proposed formula is 20.3%, which corresponds well to the observed value.

$[Mn(DMF)(L^4)] \cdot 2(NH_2Me_2) \cdot 3DMF \cdot 4H_2O$, **3**:

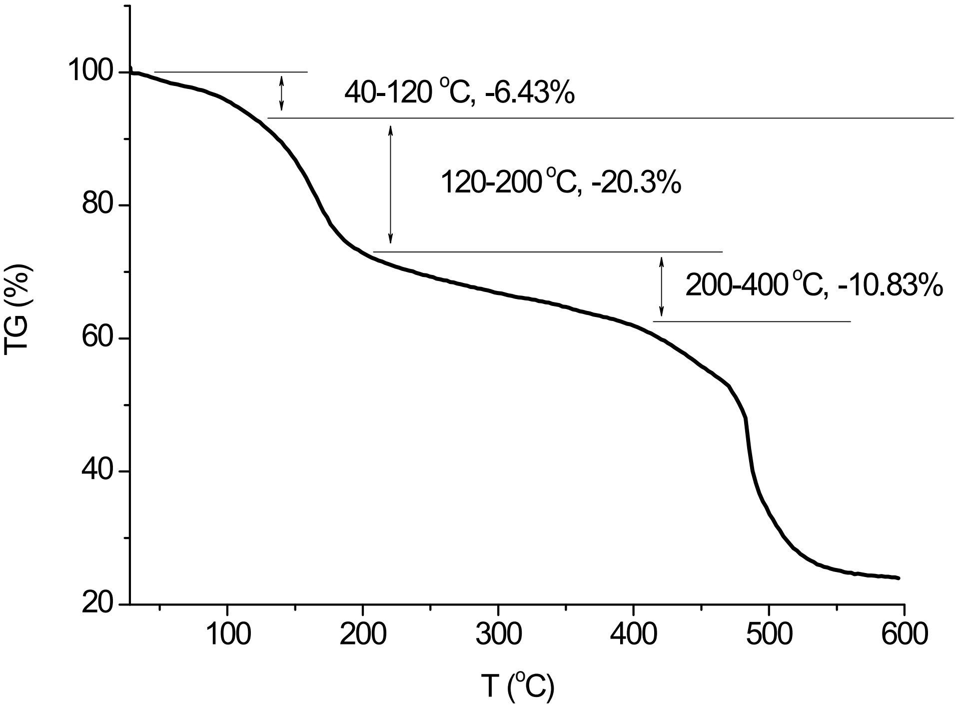


Fig. S12. TGA weight loss curve for [Mn(DMF)(L^4)] · 2(NH_2Me_2) · 3DMF · $4H_2O$, **3**.

The first, relatively slow weight loss stage is interpreted as being associated with the loss of water. It is followed by loss of DMF, which formally ends at around 200 ˚C or somewhat beyond.

However, while it is known that the microporous materials usually lose DMF mostly at a temperatures beyond 250-300 ˚C, even 350 ˚C is a temperature too low for decomposition of the ligand. The relatively small weight loss step in the interval of 200-400 ˚C is only partially associated with the loss of DMF, but mostly with the loss of two dimethylamine molecules per formula unit via decomposition of the respective dimethylammonium cations. This prolonged weight loss wave is one of the main indirect evidences that the compound contains a decomposable cationic component. The same behaviour is also observed in **2**, where the presence of dimethylammonium cations is also observed from the structural data; in the same time there is no such prolonged weight loss wave in the case of **1** (finishes at app. 250 ˚C), where the framework is neutral and no dimethylammonium is present.

The observed 6.43/31.13 weight loss for H_2O / (DMF + $NHMe_2$) corresponds reasonably well to the proposed molecular formula of [Mn(DMF)(L^4)] · 2(NH_2Me_2) · 3DMF · $4H_2O$ with 36.5% of the volatile part.

Free volume check:

- The total solvent accessible space available in the structure is 893 $Å^3$
- The vdW volume of DMF and H_2O in the liquid state is, respectively 127 $Å^3$ and 40 $Å^3$ (in the case of the coordinated DMF the volume is slightly smaller and is estimated to be at 91 $Å^3$). The molecular volume of $NH_2Me_2^+$ is not straightforwardly available, but it may be very approx.. estimated at around ~100 $Å^3$ (a volume of $NHMe_2$ molecule derived from the density of the liquid phase gives a value of 114 $Å^3$)

- The total volume of all guest molecules is ~740 Å^3 with a formal packing index of 0.83. It is higher than the typical Kitaigorodskii packing index, KPI, at 0.65, but the estimates of the molecular volume is already derived from densities of liquid phases and the additional contraction in the case of ionic components, namely dimethylammonium, was not fully accounted.

[Co(DMF)(L^4)] · 2(NH$_2$Me$_2$) · 2DMF · 5H$_2$O, **4**:

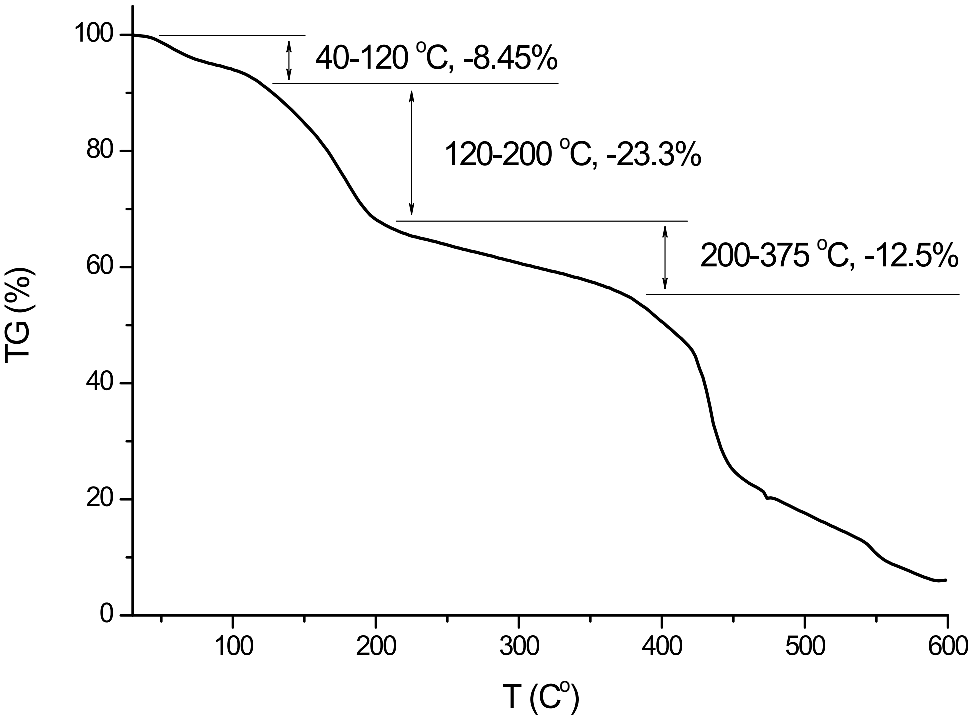


Fig. S13. TGA weight loss curve for [Co(DMF)(L^4)] · 2(NH$_2$Me$_2$) · 2DMF · 5H$_2$O, **4**.

4 is isostructural to **3** and the TGA weight loss curve is very similar (see above). The main difference is the somewhat larger water loss, while the uncertainty in assignment of the loss associated with DMF is similar. The assigned formula, corresponding to 35% of solvent molecules by weight is close alternative to the formula ascribed to **4**, but leans to the lower N-content witnessed by elemental analysis. Ascribing slightly different solvent content to isostructural compounds also reflects the imprecision and compromise at the assignment based on at least two different methods.

FT-IR

The FT-IR spectra were collected by a Bruker Tensor 37 system equipped with an ATR unit (Platinum ATR-QL, diamond) in the 4000-550 cm^{-1} range with a 2 cm^{-1} resolution. Peak intensities were designated as: s – strong, m – medium, w – weak, br – broad, sh – shoulder, v- 'very' prefix.

The comparison of the IR spectra for the ligand and the resulting complex are shown below (the numeric values of the peak positions are given in the respective synthetic sections).

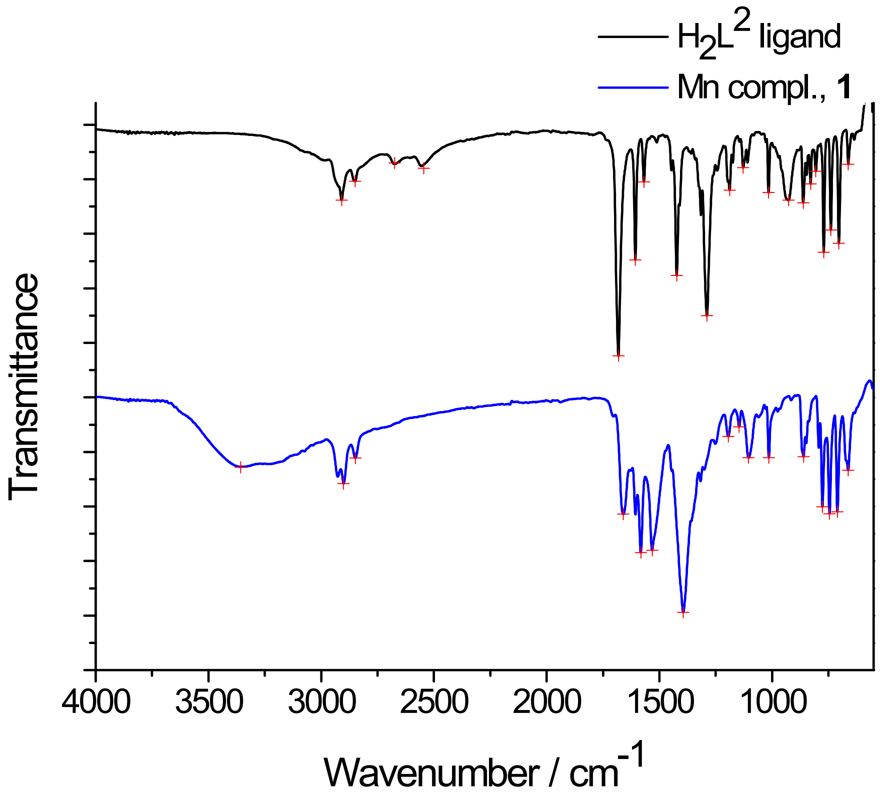


Fig. S14. FT-IR spectra comparison of H_2L^2 and [Mn(DMF)(L^2)], **1**.

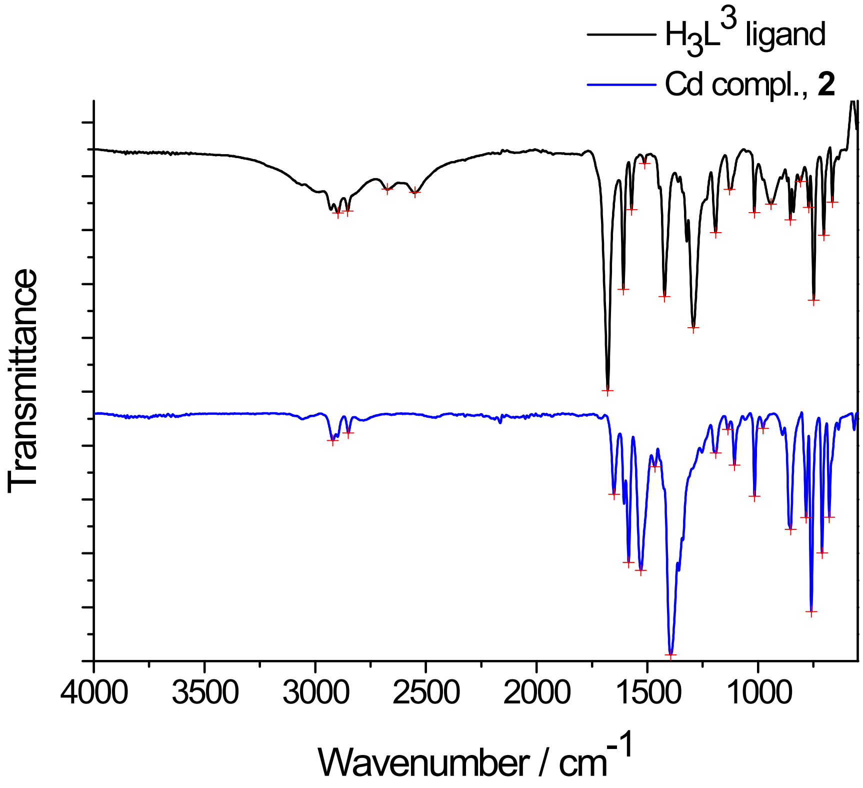


Fig. S15. FT-IR spectra comparison of H_3L^3 and [Cd(DMF)$_{0.5}$(H_2O)$_{0.5}$(L^3)] · (NH_2Me_2) · 0.5DMF · 1.5H_2O, **2**.

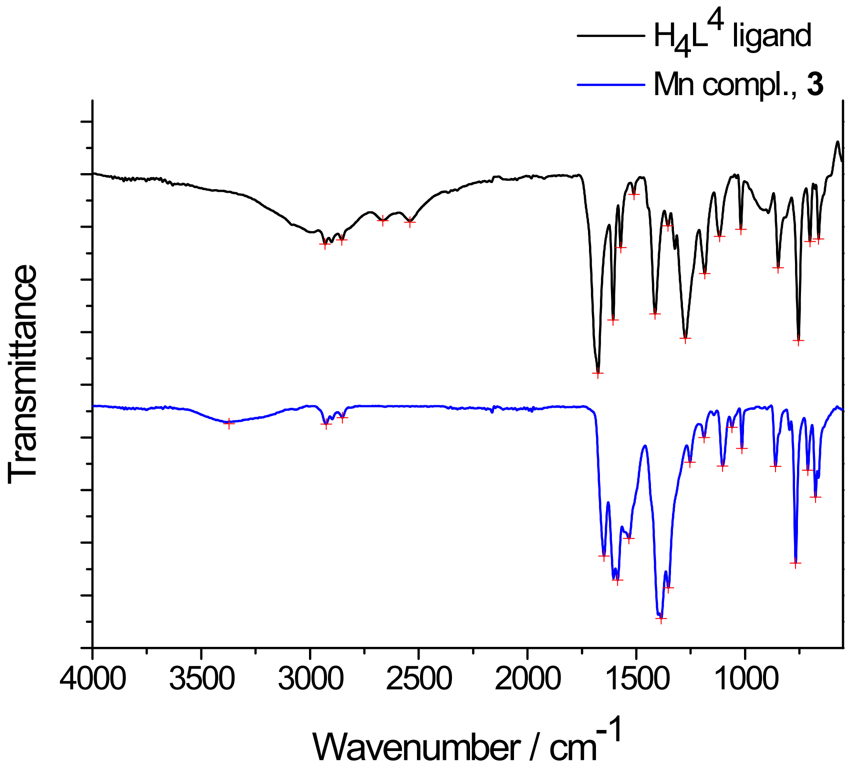


Fig. S16. FT-IR spectra comparison of H_4L^4 and [Mn(DMF)(L^4)] · 2(NH_2Me_2)-· 3DMF · $4H_2O$, **3**

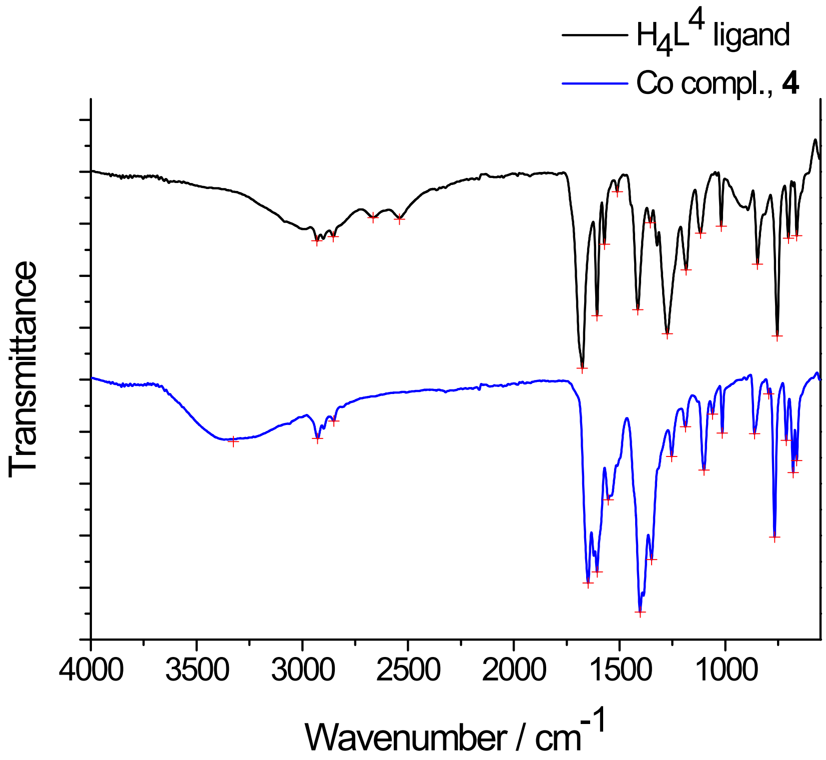


Fig. S17. FT-IR spectra comparison of H_4L^4 and [Co(DMF)(L^4)] · 2(NH_2Me_2)-· 2DMF · $5H_2O$, **4**.

Gas adsorption measurements

The measurements were performed on a Quantachrome NOVA 4000 automatic gas adsorption analyser at 77K. The samples were degassed under high vacuum (10^{-3} Torr) at 200°C for at least 2 h, prior to each measurement.

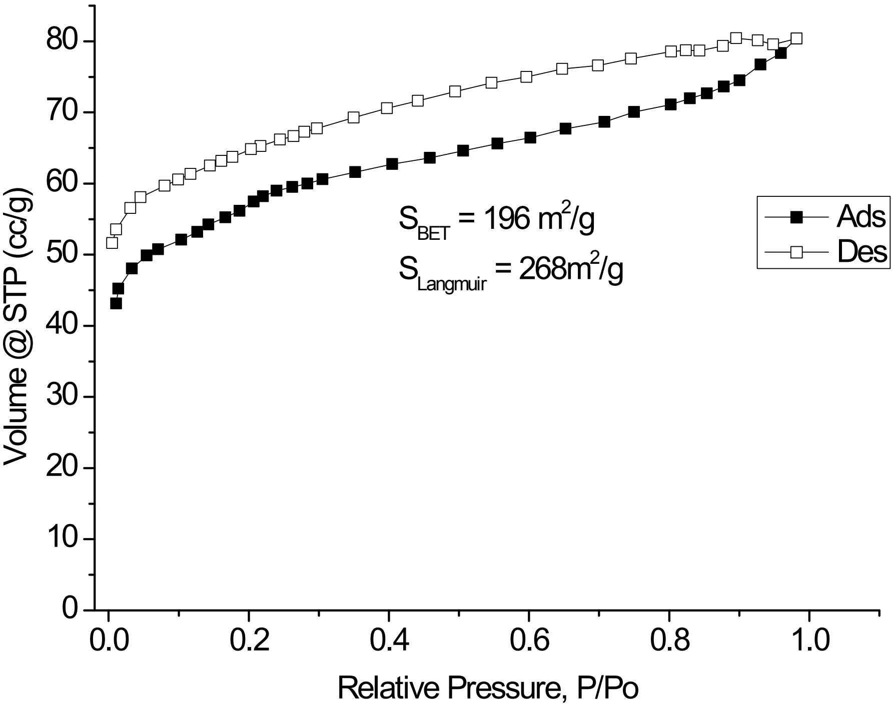


Fig. S18. N_2 adsorption isotherm for the degassed $[Cd(DMF)_{0.5}(H_2O)_{0.5}(L^3)] \cdot (NH_2Me_2) \cdot 0.5DMF \cdot 1.5H_2O$, **2**.

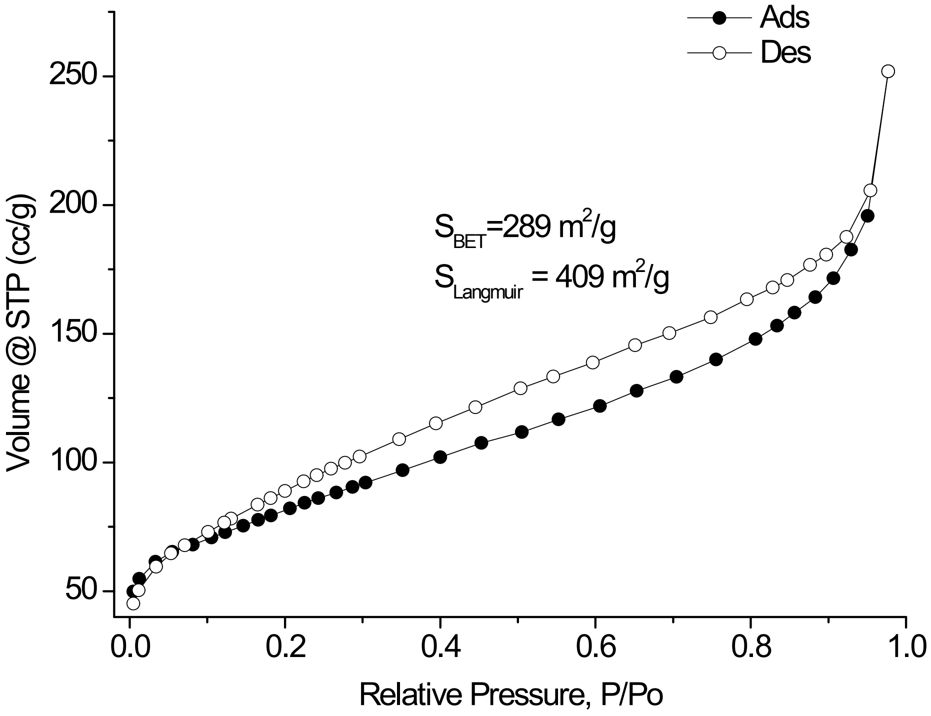


Fig. S19. N_2 adsorption isotherm for the degassed [Mn(DMF)(L^4)] · 2(NH_2Me_2)- · 3DMF · 4H_2O, **3**

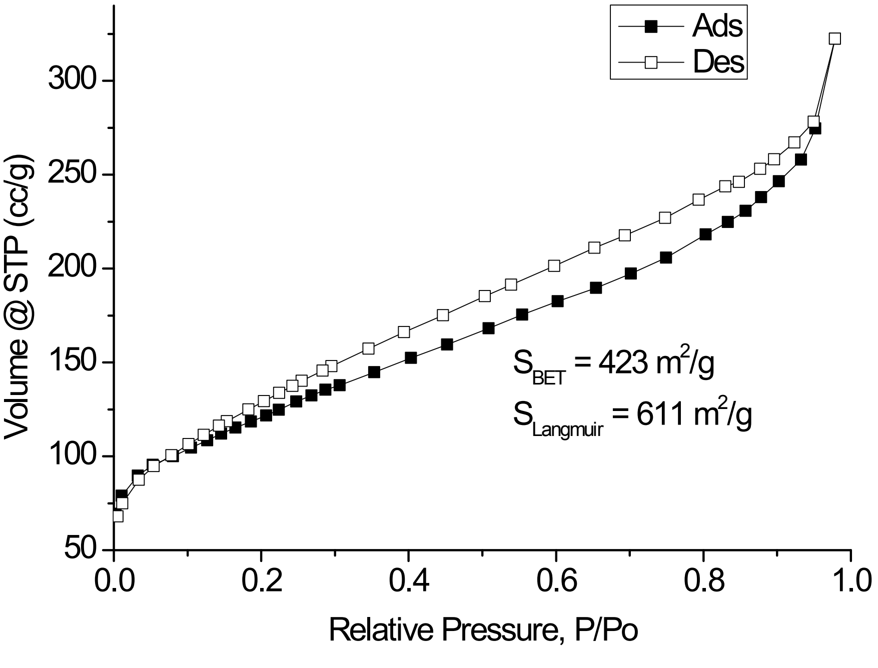


Fig. S20. N_2 adsorption isotherm for the degassed [Co(DMF)(L^4)] · 2(NH_2Me_2)- · 2DMF · 5H_2O, **4**

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