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Topological transformations in metal-organic frameworks: a prospective design route?

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Supplementary information

Table S1. Examples of structural transformations with the change of internal coordinates, pores dimensions, and placement of structural groups interacting through H-bonds and van der Waals contacts

Compound	Net	Component undergoing change	Stimuli	Changing property	Ref.
$Co(N(CN)_2)_2$	3D **rtl**	Rotation of coordination polyhedra	Pressure	Negative linear compressibility, magnetic response	[1]
MIL-68(In)	3D 4,4,6,6T1	Rotation of coordination polyhedra, H-bonds, pores	Gas pressure,	CO_2 adsorption	[2]
$[Fe^{II}Pd(CN)_4(thiome)_2]\cdot 2H_2O$	**sql**	Ligand rotation, H-bonds, pores	Pressure, temperature, solvent	High-spin- to low-spin transition	[3]
$[Ni(L\text{-aspartate})(H_2O)_2]\cdot H_2O$	2C1	Rotation of coordination polyhedra, H-bonds	Pressure	Anisotropic compression	[4]
PCN-167	3D **stp**	Bending of ligand	Temperature, solvent	Stability, dyes uptake	[5]
PCN-168	3D **stp**	Rotation of coordination polyhedra, bending of ligand	Temperature, solvent	Stability, Anion exchange-based selective uptake of organic dyes	[5]
$[Co(NCS)_2(tpomm)]\cdot 2H_2O\cdot CH_3OH$	2-f 3D **pts**	Distortion of coordination polyhedra, ligand conformation, collapsing pores	Solvents, vapors	Solvatochromic and vapochromic behavior, magnetic response	[6]
PCN-250 or MIL-127	3D **soc**	Distortion of coordination polyhedra, ligand conformation, pores	Pressure	CH_4 adsorption	[7]
X-pcu-1-Zn-3i-α to X-pcu-1-Zn-3i-β to X-pcu-1-Zn-3i-γ	3-f 3D **pcu**	Distortion of coordination polyhedra, ligand conformation, pores	Temperature, vacuum, solvent	Free volume	[8]
X-pcu-1-Zn-3i-α to X-pcu-1-Zn-3i-δ	3-f 3D **pcu**	Networks slip, pores	Temperature, solvent	Free volume	[8]
$Zn(CN)_2$ (*Pn*$\bar{3}$*m*) to $Zn(CN)_2$-II (*Pbca*)	2-f 3D **dia**	Rotation of coordination polyhedra, displacement of ligand	Pressure	-	[9,10]
$[Co(4,4\text{-pba})_2]_4\cdot 3DMF\cdot 0.25EtOH\cdot 4H_2O$ to $[Co(4,4\text{-pba})_2]\cdot 2.5MeOH\cdot H_2O$	4-f 3D **dia**	Distortion of coordination polyhedra, ligand conformation, pores	Solvent	Color	[11]
α-Cu(tcm) to β-Cu(tcm)	3-f 3D **ths**	Distortion of coordination polyhedra, ligand conformation, pores	Temperature	Magnetic response	[12]
$[Cd(2\text{-eiba})_2]$(solvent)	4-f 3D **dia**	irreversible rotation of 2-eiba ligand	Temperature, solvent	Luminescent sensing of nitrobenzene and Fe^{3+}	[13]

MIL-68(In) – [In(OH)terephthalate]

thiome - 4-[(E)-2-(5-methyl-2-thienyl)vinyl]-1,2,4-triazole)

PCN-167 - tris(μ-4,4',4",4'"-(9,9'-spirobi[fluorene]-2,2',7,7'-tetrayl)tetrabenzoato)-bis(μ-oxo)-hexa-aqua-hexa-indium(iii) dinitrate

PCN-168 - tris(μ-4,4',4",4'"-(9,9'-spirobi[fluorene]-2,2',7,7'-tetrayl)tetrabenzoato)-bis(μ-oxo)-hexa-aqua-hexa-iron(iii) dichloride

tpomm - tetrakis(4-pyridyloxymethylene)methane

PCN-250 or MIL-127 - catena-[hexakis(μ-5,5'-((E)-diazenediyl)bis(benzene-1,3-dicarboxylato))-tetrakis(μ-oxo)-dodeca-aqua-dodeca-iron]

X-pcu-1-Zn-3i-α to X-pcu-1-Zn-3i-β to X-pcu-1-Zn-3i-γ - [Zn2(4,4′-biphenyldicarboxylate)2(4,4′-bis(4-pyridyl)biphenyl)]

4,4-pba - 4-(4-pyridyl)benzoate

α-Cu(tcm), β-Cu(tcm) - copper(I) tricyanomethanide

Heiba - 4-(2-ethyl-1H-imidazol-1-yl)benzoic acid

Table S2. Examples of structural transformations with the change of coordination modes of ligands and/or metal cations

Compound	Net1	Net2	Component undergoing change	Stimuli	Properties	Ref.
$[Cd(tppbda)(NO_3)_2]\cdot DMF\cdot 4H_2O$	4-f **pts**	4-f **pts**	Coordination mode of nitrate-anion, orientation of ligands, pores	Solvent	Luminescence	[14]
X-pcu-1-Zn-3i-α to X-pcu-2-Zn-3i	3-f **pcu**	3-f **pcu**	square coordination of Zn(II) transform to tetrahedral	Tempera ture, solvent	Free volume	[8]

tppbda - N^1,N^1,N^4,N^4-tetrakis[4-(pyridin-4-yl)phenyl]benzene-1,4-diamine

X-pcu-1-Zn-3i-α, X-pcu-2-Zn-3i - $[Zn_2(4,4'\text{-biphenyldicarboxylate})_2(4,4'\text{-bis(4-pyridyl)biphenyl})]$

Table S3. Examples of structural transformations with the change of bonds inside of ligand

Compound	Net1	Net2	Component undergoing change	Stimuli	Properties	Ref.
$[Zn_2(hfcpbetdp)(odb)]$ to $[Zn_2(dehfthibtdp)(odb)]$	**3D fsx**-3,4-C2	3D 3,4,4,5T65	cyclization of ligand, formation of one coordination bond, pores	UV and vis. light	UV-vis spectra, CO_2 capture	[15]

hfcpbetdp - 4,4'-[(3,3,4,4,5,5-hexafluorocyclopent-1-ene-1,2-diyl)bis(5-ethylthiene-4,2-diyl)]dipyridine

dehfthibtdp - 4,4'-(9a,9b-diethyl-4,4,5,5,6,6-hexafluoro-5,6,9a,9b-tetrahydro-4H-indeno[5,4-b:6,7-b']bisthiene-2,8-diyl)dipyridine

odb - 4,4'-oxydibenzoate

Table S4. Examples of structural transformations with the change of network connectivity

Composition	Net 1	Net 2	Component undergoing change	Stimuli	Properties	Ref.
$[Zn_3(TBIB)_2Cl_6]\cdot 11H_2O$ to $[Zn_3(TBIB)_2Cl_6]\cdot 6H_2O$	1D 2,2,3C6	2D **hcb**	Zn-N bonds, conformation of ligand	Solvent	Proton conductivity	[16]
$[Zn_2(\mu_4\text{-mtbpc})(DMF)_4]\cdot DMF\cdot 4H_2O$ to $[Zn_2(\mu_4\text{-mtbpc})(DMF)_4]\cdot X$*solv*	2D 2,4L2 (**sql**)	3D 4-f **dia**	Dimerization of metals, pores	Solvent	H_2 adsorption	[17]
$[Ag(pptap)(NO_2)](CHCl_3)$, $[Ag(pptap)](NO_2)(H_2O)_{2.25}$ to $[Ag(pptap)](CF_3CO_2)(H_2O)$	1D (4,4)(0,2)	3D **sra**	4-Py group replaces NO_2^- group in coordination sphere of Ag^+, pores	Solvent, vapor, anion	$Cr_2O_7^{2-}$ cupture	[18]
AlTz-53 to AlTz-68	**bpq**	4,4,6,6T1	Coordination bonds rearrangement through defective structures	Solvent	Free volume, enzyme immobilization, catalytic ester hydrolysis	[19]
$[H_2tmen][Er(HCOO)_4]_2$	**vmd**	**vmt**	Coordination bonds rearrangement, linkage of Er^{3+}	Pressure	Luminescence	[20]
Cu(TCNQ)-I to Cu(TCNQ)-II	2-f **dmh**	2-f **tfi**	Coordination bonds rearrangement	Solvent, electric field	Magnetic response, charge-transport	[21]
$[ZnCl_2(\mu\text{-bipy})]$ to $[Zn(\mu\text{-Cl})_2(\mu\text{-bipy})]$	1D 2C1	2D **sql**	Coordination bonds rearrangement, linkage of Zn^{2+}	Low temperature	-	[22]
Cd(abdc)(bpy)·4.5H2O·3DMF (*P*6/*m*) to Cd(abdc)(bpy)·4H2O·2.5DMF (*Pbam*)	**kag**	**pcu**	Coordination bonds rearrangement	Solvent, pressure	Luminescence, dye separation	[23]
UPC-601 to UPC-602	3D **fit**	3D 5,6,11T4	Rearrangement of 1D SBU to 2D SBU	Temperature	Gas adsorption	[24]

TBIB - 1,3,5-tri(1H-benzo[d]imidazol-1-yl)benzene

mtbpc - methanetetrakis(biphenyl-4'-carboxylate)

pptap - (5-(pyridin-3-yl)-4-(pyridin-4-yl)-4H-1,2,4-triazol-3-yl)pyridine

AlTz-53, AlTz-68 - [Al(OH)(TzDB)] (TzDB = 4,4'-(1,2,4,5-tetrazine-3,6-diyl)dibenzoate)

H_2tmen^{2+} - N,N,N',N'-tetramethylethylenediammonium

TCNQ - 5 7,7,8,8-tetracyanoquinodimethane

abdc - 2-amino-1,4-benzenedicarboxylate

UPC-601, UPC-602 - $[Ba_2(BIPA\text{-}TC)(DMF)(H_2O)]\cdot H_2O$ ($H_4BIPA\text{-}TC$ = 5,5'-(1,3,6,8-tetraoxobenzo[Imn][3,8] phenanthroline-2-7-diyl)bis-1,3-benzenedicarboxylic acid)

Table S5. Examples of structural transformations with the change of entanglement pattern

Compound	Net 1	Net 2	Component undergoing change	Stimuli	Properties	Ref.
[Ni(HBTC)(bipy)]	3D **hms**	2-f 3D **hms-c**	Coordination bonds rearrangement, rotation and translation of pillars and layers, pores	Temperature	N_2 sorption, removal linkers	[25]
[Ni(HBTC)(bipy)]	3D **gra**	2-f 3D **hms-c**	Coordination bonds rearrangement, rotation and translation of pillars and layers, pores	Temperature	N_2 sorption, removal linkers	[25]
[Ni(hatco)]$_3$[(Ni(hatco)(H_2O)$_2$][(Ni(hatco)(TATAB)$_2$]$_2$·46H2O to [(Ni hatco)$_3$(TATAB)$_2$]·5DMF	0D	**2D hcb** Borromean	Coordination bonds rearrangement, coordination environment of metal	Solvents	Free volume	[26]
[Ba$_2$(H_2O)$_2$(BIPATC)(DMF)(H_2O)]·DMF·H2O (UPC-600) to [Ba(BIPA-TC)$_{0.5}$(H_2O)$_2$]·3H_2O (UPC-601)	2-f 3D 6,8T1562	3D **fit**	Rearrangement of 1D SBUs	Temperature	Gas adsorption	[24]
X-pcu-1-Zn-3i-β to X-pcu-1-Zn-4i	3-f 3D **pcu**	4-f 3D **pcu**	Coordination bonds rearrangement, degree of interpenetration, pores	Temperature	Free volume	[8]
Zn(CN)$_2$	2-f 3D **dia**	3D **dia**	Coordination bonds rearrangement, degree of interpenetration, pores	Pressure, solvent	Free volume	[9,10]
Zn(CN)$_2$	2-f 3D **dia**	3D **lon**	Coordination bonds rearrangement, degree of interpenetration, network topology, pores	Pressure, solvent	Free volume	[9,10]
Zn(CN)$_2$	2-f 3D **dia**	3D **pyr**	Coordination bonds rearrangement, degree of interpenetration, network topology, pores	Pressure, solvent	Free volume	[9,10]
Zn(CN)$_2$	3D **lon**	3D **pyr**	Coordination bonds rearrangement, degree of interpenetration, network topology, pores	Pressure, solvent	Free volume	[9,10]
[Co(4,4-pba)$_2$]·(MeOH)$_{2.5}$·(H_2O) to [Co(4,4-pba)$_2$(MeOH)$_2$]$_2$·(MeOH)$_{2.5}$·(H_2O)$_2$	4-f 3D **dia**	2-f 3D **pts**	Coordination bonds rearrangement, coordination modes of ligands, degree of interpenetration, network topology, pores	Solvent	Color	[11]
[Co(4,4-pba)$_2$(MeOH)$_2$]$_2$·(MeOH)$_{2.5}$·(H_2O)$_2$ to [Co(4,4-pba)$_2$(MeOH)$_2$]·(MeOH)$_{0.5}$·(H2O)$_{0.5}$	2-f 3D **pts**	3-f 3D **qtz**	Coordination bonds rearrangement, coordination modes of ligands, degree of interpenetration, network topology, pores	Solvent	Color	[11]
[Co(4,4-pba)$_2$(MeOH)$_2$]·(MeOH)$_{0.5}$·(H2O)$_{0.5}$ to [Co(4,4-pba)$_2$]$_4$·(DMF)$_3$·(EtOH)$_{0.25}$·(H_2O)$_4$	3-f 3D **qtz**	4-f 3D **dia**	Coordination bonds rearrangement, coordination modes of ligands, degree of interpenetration, network topology, pores	Solvent	Color	[11]
α-MUF-9 to β-MUF-9	3D **pcu**	2-f 3D **pcu**	Coordination bonds rearrangement, degree of interpenetration, pores	Temperature, desolvation, mechanical shearing	Mechanical response, dyes adsorption	[27]
α-MUF-10 to β-MUF-10 (enantiopure R-H_2L or S-H_2L)	3D **pcu**	2-f 3D **pcu**	Coordination bonds rearrangement, degree of interpenetration, pores	Temperature, desolvation, mechanical shearing	Mechanical response, dyes adsorption	[27]
[Zn$_2$(ndc)$_2$(bpy)]	2-f 3D **pcu**	3-f 3D **pcu**	Coordination bonds rearrangement, degree of interpenetration, pores	Desolvation	Free volume	[28]
[Co$_2$(ndc)$_2$(bpy)]	2-f 3D **pcu**	3-f 3D **pcu**	Coordination bonds rearrangement, degree of interpenetration, pores	Desolvation	Free volume	[29]
[Zn(pvb)$_2$]·DMF - [Zn(pvb)$_2$]	7-f 3D **dia**	8-f 3D **dia**	Coordination bonds rearrangement, degree of interpenetration, pores	Desolvation	Second harmonic generation, pores	[30]
[Cd(2-eiba)$_2$](solvent)	4-f 3D **dia**	5-f 3D **dia**	Coordination bonds rearrangement, degree of interpenetration, pores	Temperature, solvent	Luminescent sensing of nitrobenzene and Fe^{3+}	[13]

HBTC - singly protonated 1,3,5-benzene tricarboxylate

hatco - 1,3,6,9,11,14-hexaazatricyclo[12.2.1.16,9]octadecane

H_3TATAB - 4,4',4''-triazine-1,3,5-triyltriaminobenzoic acid

H_4BIPA-TC - 5,5'-(1,3,6,8-tetraoxobenzo[Imn][3,8] phenanthroline-2-7-diyl)bis-1,3-benzenedicarboxylic acid

X-pcu-1-Zn-3i-β to X-pcu-1-Zn-4i - [Zn$_2$(4,4′-biphenyldicarboxylate)$_2$(4,4′-bis(4-pyridyl)biphenyl)]

4,4-pba - 4-(4-pyridyl)benzoate

α-MUF-9, β-MUF-9 - [Zn$_4$O(rac-L)$_3$] (L^{2-} = 6,7-bis(4-methylphenyl)dibenzo[e,g][1,4]diazocine-3,10-dicarboxylate)

H_2ndc - 2,6-naphthalene dicarboxylic acid

bpy - 4,4′-bipyridine

pvb - trans-2-(4-pyridyl)-4-vinylbenzoate

Heiba - 4-(2-ethyl-1H-imidazol-1-yl)benzoic acid

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