Synthesis of a Chiral 3,6T22-Zn-MOF with a T-Shaped Bifunctional Pyrazole-Isophthalate Ligand Following the Principles of the Supramolecular Building Layer Approach

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Synthesis of H_2Isa-az-tmpz

Dimethyl 5-(2-(2,4-dioxopentan-3-ylidene)hydrazineyl)isophthalate
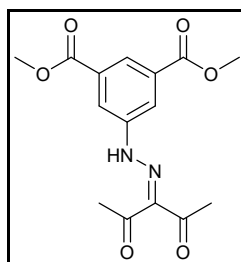
The synthesis of dimethyl 5-(2-(2,4-dioxopentan-3-ylidene)hydrazineyl)isophthalate was carried out following a previously published procedure by Millan et al. Dimethyl 5-aminoisophthalate (2.09 g; 10.0 mmol) was suspended in 20 mL of 3 mol L^{-1} HCL at 0°C. $NaNO_2$ (0.69 g; 10.0 mmol) dissolved in 10 mL of de-ionized (DI) water was slowly added dropwise via a dropping funnel. The diazonium salt solution was then added to a cooled solution of NaOH (0.54 g; 13.5 mmol), NaOAc (4.09 g; 49.9 mmol) and acetylacetone (1.05 mL; 10.0 mmol) in 80 mL of MeOH and 80 mL of DI water, yielding a yellow precipitate. The suspension was stirred for 30 min at 0 °C at first and afterwards for 1 h at room temperature. The yellow precipitate was collected by suction and dried on air and after which the product was recrystallized from ethanole (200 mL). The resulting fibrous yellow product was collected by suction and dried at 60°C under vacuum (2.89 g; 9.0 mmol, 90 %).
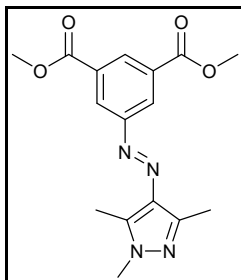
^{1}H-NMR (300 MHz, $CDCl_3$, δ [ppm]): 14.66 (s, 1H, NH), 8.45 (t, J = 1.50 Hz, 1H, Ar H), 8.20 (d, J = 1.50 Hz, 2H, Ar H), 3.96 (s, 6H, -CH_3), 2.61 (s, 3H, -CH_3), 2.52 (s, 3H, -CH_3).
^{13}C-NMR (75 MHz, $CDCl_3$, δ [ppm]): 198.55, 197.10, 165.63, 142.43, 134.23, 132.32, 127.20, 120.94, 52.81, 31.87, 26.82.
EA [%] calc. for $C_{15}H_{16}N_2O_6$, C 56.25, H 5.04, N 8.57; found C 56.49, H 4.92, N 8.69.

ESI-MS (%)**:** [M+H]$^+$ 321.3 (100).

Dimethyl 5-(2-(1,3,5-trimethyl-1H-pyrazol-4-yl)azo)-isophthalate

Methylhydrazine (105 µL; 2.0 mmol) was added to a solution of Dimethyl 5-(2-(2,4-dioxopentan-3-ylidene)hydrazineyl)isophthalate (640.6 mg; 2.0 mmol) in 70 mL EtOH and the mixture was refluxed for 6 h. Afterwards the solution was concentrated under reduced pressure and quenched with DI water. The yellow powder was then filtrated and dried in a vacuum oven over night at 60 °C yielding 638.0 mg (1.93 mmol; 96 %) of Dimethyl 5-(2-(1,3,5-trimethyl-1H-pyrazol-4-yl)azo)-isophthalate. The product was used without further purification.
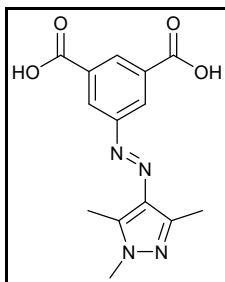
^{1}H-NMR (300 MHz, CDCl$_3$, δ [ppm]): 8.67 (t, J = 1.61 Hz, 1H, Ar H), 8.57 (d, J = 1.71 Hz, 2H, Ar H), 3.98 (s, 6H, -CH$_3$), 3.80 (s, 3H, -NCH$_3$), 2.61 (s, 3H, -CH$_3$), 2.51 (s, 3H, -CH$_3$).
^{13}C-NMR (75 MHz, CDCl$_3$, δ [ppm]): 166.23, 153.93, 142.77, 140.18, 135.39, 131.60, 130.81, 126.98, 52.66, 36.19, 14.12, 10.21.
EA [%] calc. for C$_{16}$H$_{18}$N$_4$O$_4$, C 58.17, H 5.49, N 16.96; found C 58.43, H 5.49, N 16.76.
ESI-MS (%)**:** [M+H]$^+$ 331.3 (100).

5-(2-(1,3,5-trimethyl-1H-pyrazol-4-yl)azo)isophthalic acid (H$_2$Isa-az-tmpz)


Dimethyl 5-(2-(1,3,5-trimethyl-1H-pyrazol-4-yl)azo)-isophthalate (600 mg; 1.82 mmol) was dissolved in 35 mL MeOH, 10 mL of DI-water and 4.08 g (72.8 mmol) of KOH and refluxed for 24 h. MeOH was removed under reduced pressure and the pH of the remaining yellow solution was adjusted to pH 3 with HCL (3 mol L^{-1}). The yellow precipitate was filtrated, washed with DI water and dried at 60 °C in a vacuum oven to yield 485.0 mg (1.60 mmol; 88 %) of H$_2$Isa-az-tmpz.

¹H-NMR (300 MHz, DMSO-d6, δ [ppm]): 8.45 (t, J = 1.61 Hz, 1H, Ar H), 8.36 (d, J = 1.62 Hz, 2H, Ar H), 3.74 (s, 3H, -NCH$_3$), 2.55 (s, 3H, -CH$_3$), 2.36 (s, 3H, -CH$_3$).
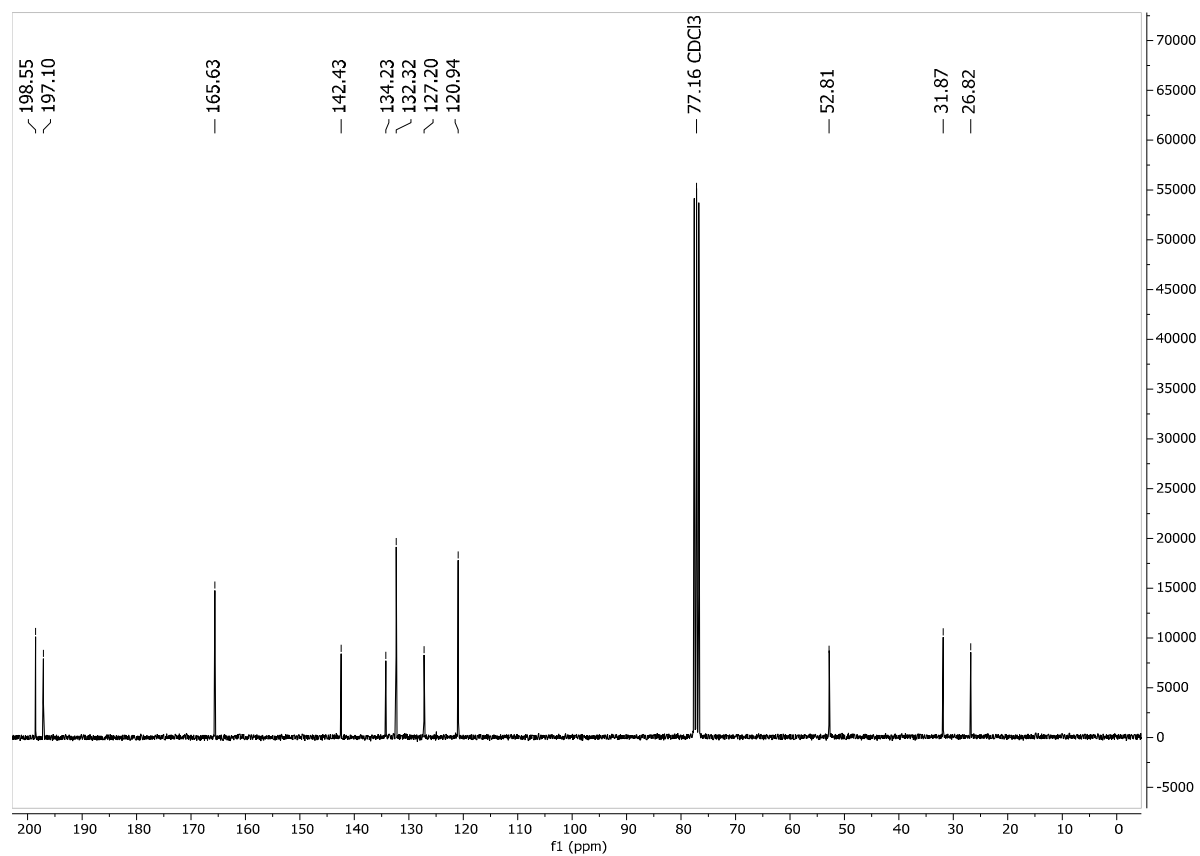
¹³C-NMR (75 MHz, DMSO-d6, δ [ppm]): 166.26, 153.10, 140.85, 140.51, 134.55, 132.37, 130.03, 125.58, 36.00, 13.84, 9.58.

EA [%] calc. for C$_{14}$H$_{14}$N$_4$O$_4$, C 55.63, H 4.67, N 18.53; found C 55.66, H 4.71, N 18.16.
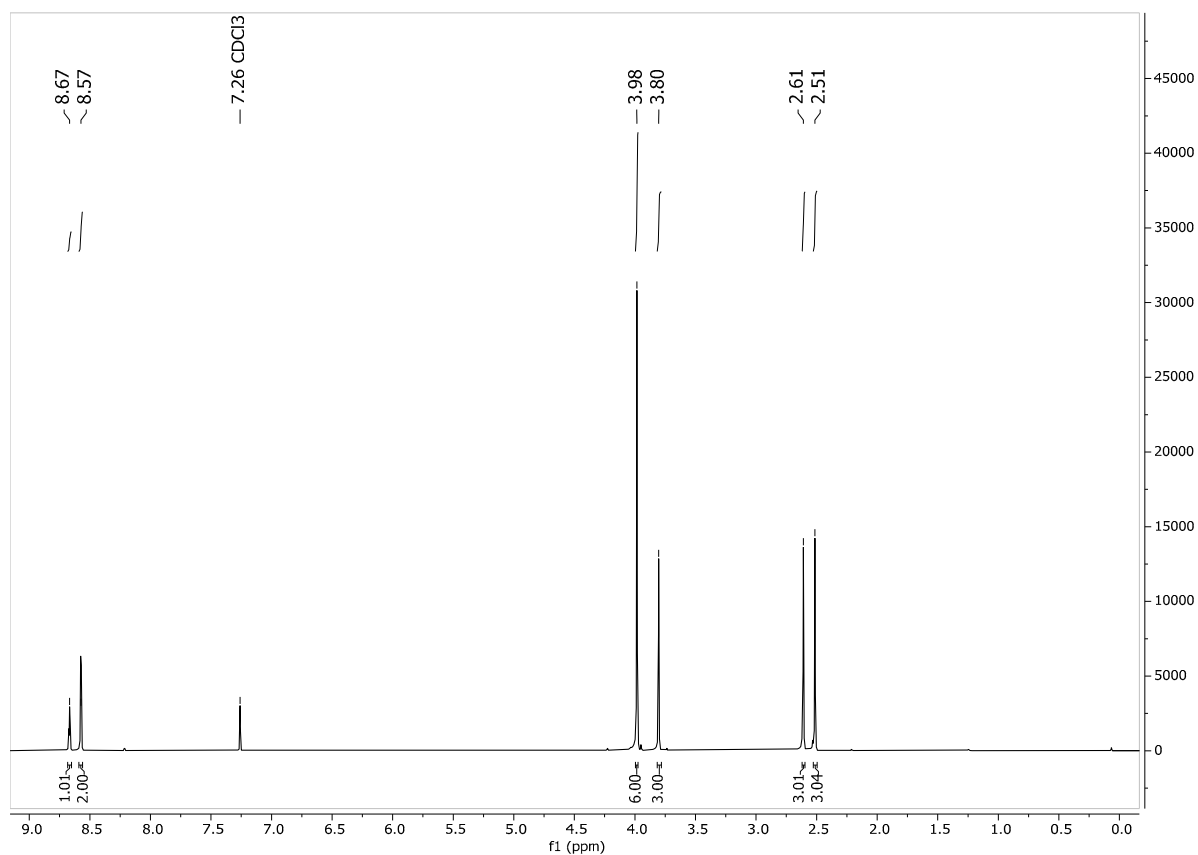
EI-MS (%): [M]$^+$ 302 (36), [Az-tmpz]$^+$ 137 (100), [Tmpz]$^+$ 109 (55).
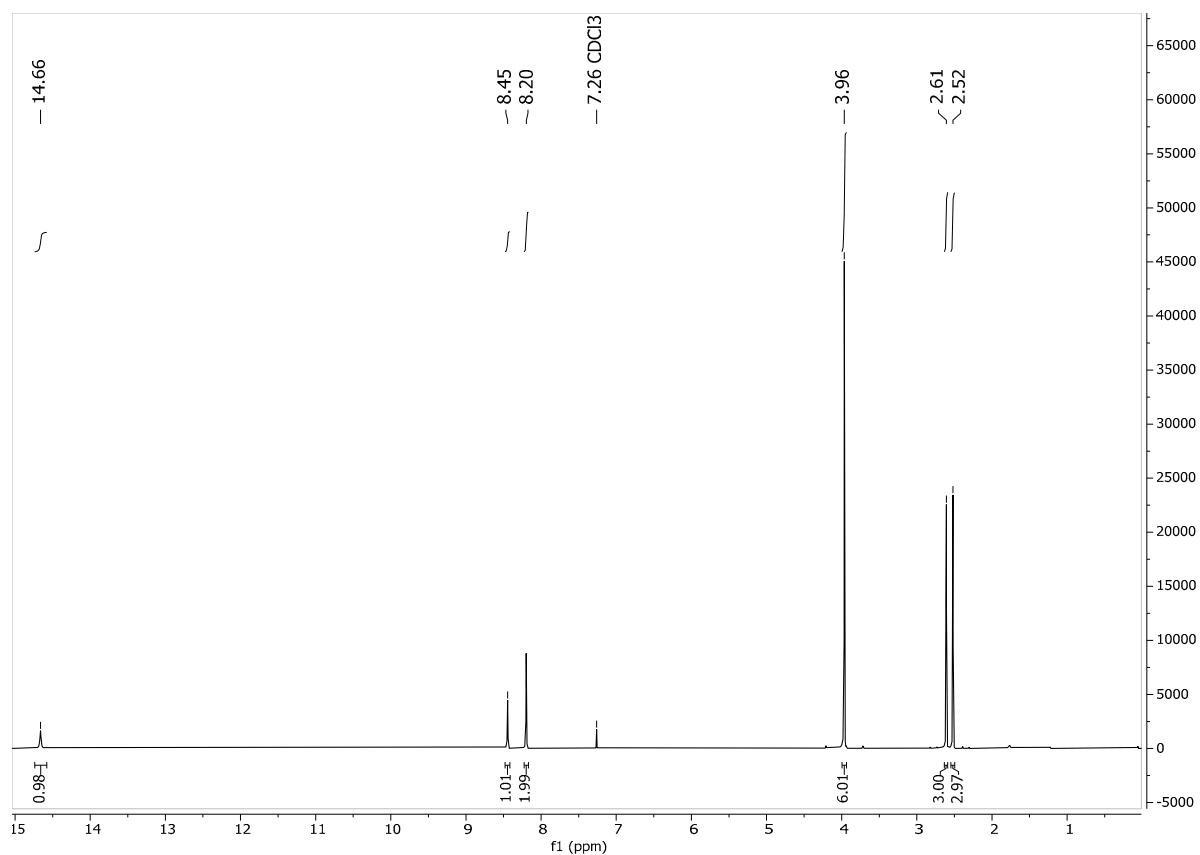
Figure S1. ^{1}H-NMR spectrum of dimethyl 5-(2-(2,4-dioxopentan-3-ylidene)hydrazineyl)-isophthalate in CDCl$_3$.

Figure S2. ^{13}C-NMR spectrum of dimethyl 5-(2-(2,4-dioxopentan-3-ylidene)hydrazineyl)-isophthalate in CDCl$_3$.

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Figure S3. ^{1}H-NMR spectrum of dimethyl 5-(2-(1,3,5-trimethyl-1H-pyrazol-4-yl)azo)-isophthalate in CDCl$_3$.
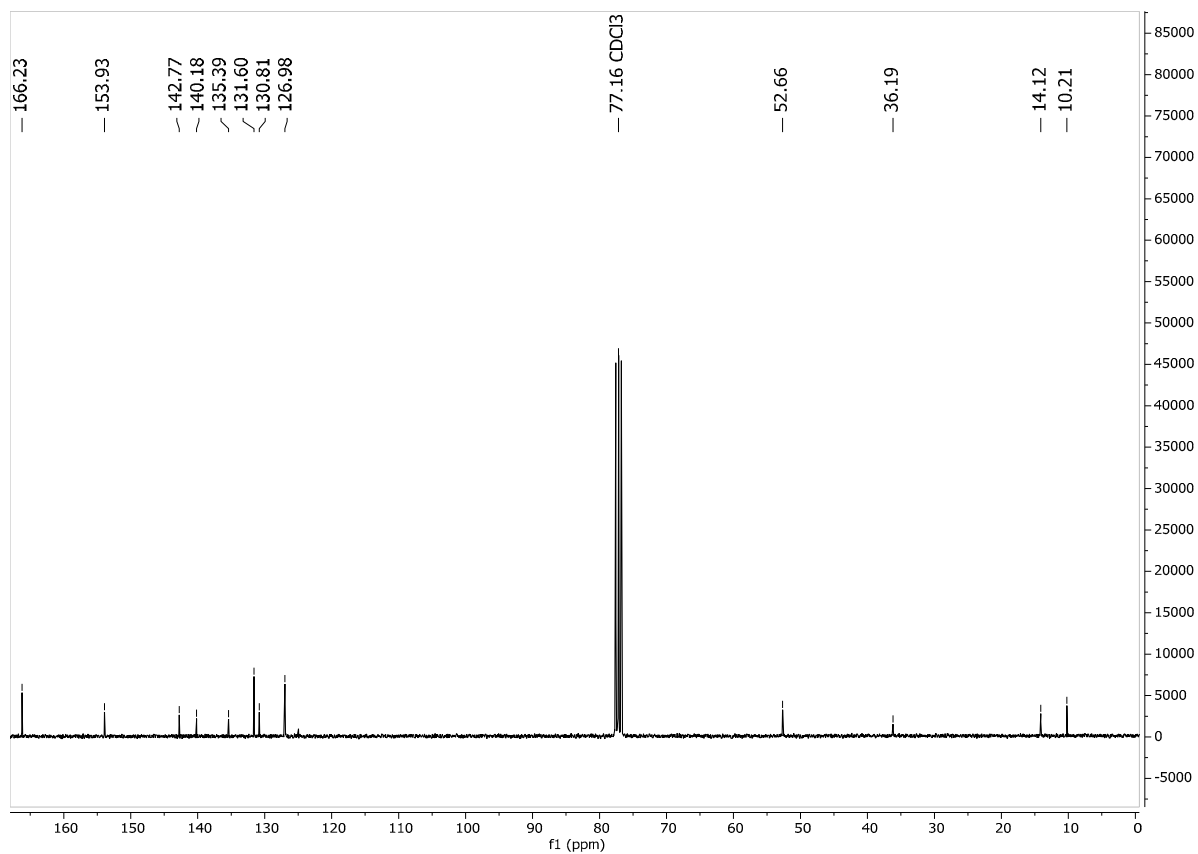
Figure S4. ^{13}C-NMR spectrum of dimethyl 5-(2-(1,3,5-trimethyl-1H-pyrazol-4-yl)azo)-isophthalate in CDCl$_3$.
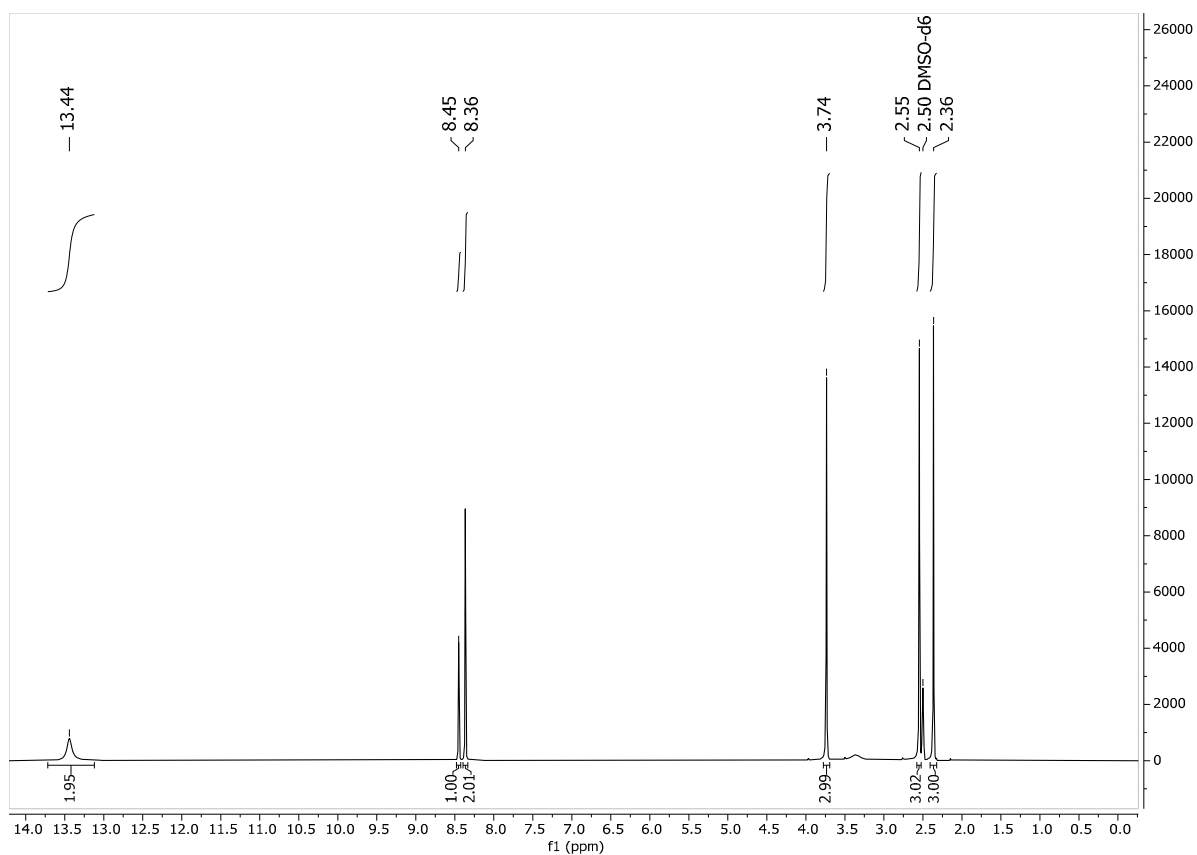
Figure S5. ^{1}H-NMR spectrum of H$_2$Isa-az-tmpz in DMSO-d6.
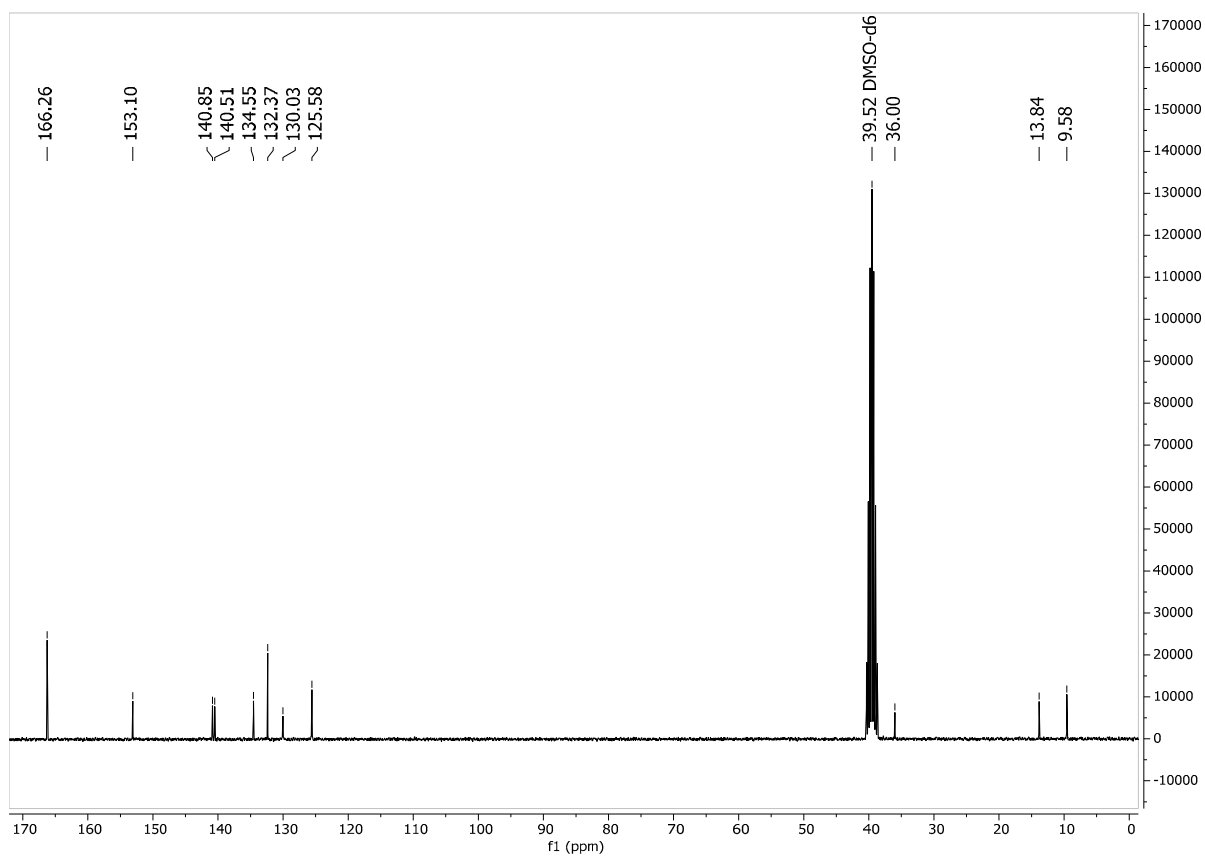
Figure S6. ^{13}C-NMR spectrum of H$_2$Isa-az-tmpz in DMSO-d6.
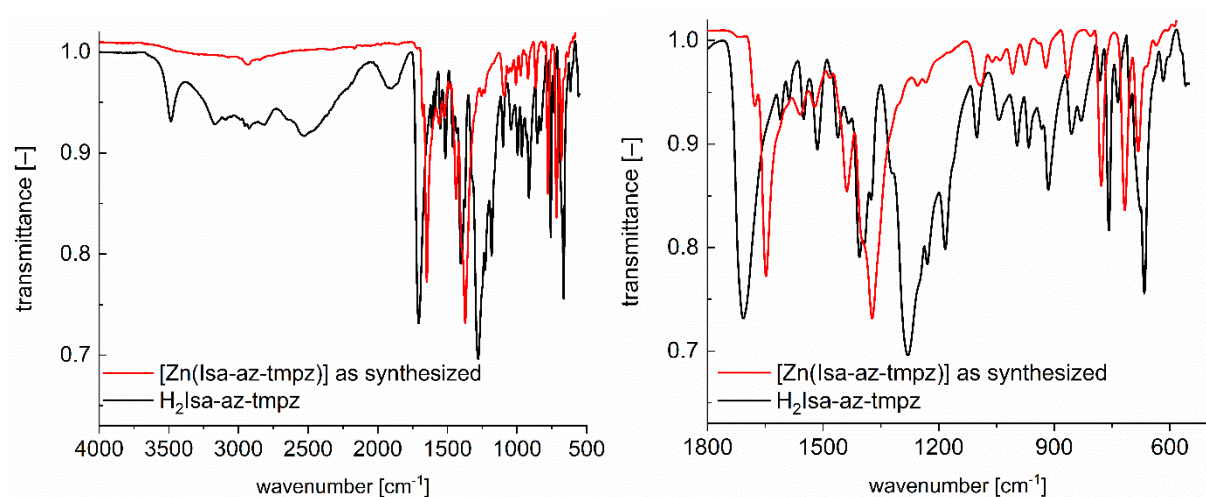
Figure S7. IR-spectra of [Zn(Isa-az-tmpz)]·~1–1.5 DMF and H$_2$Isa-az-tmpz with full range (left) and enlarged section from 1800 to 500 cm^{-1} (right).

Figure S8. Crystals of [Zn(Isa-az-tmpz)]·~1–1.5 DMF obtained from a single crystal synthesis.
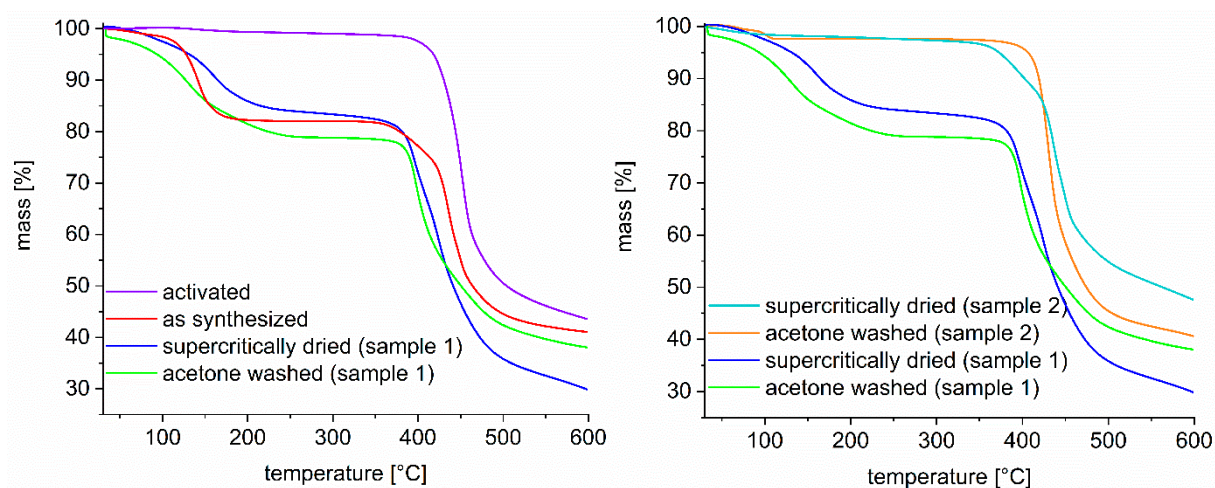
Figure S9. Thermogravimetric analysis (TGA) of [Zn(isa-az-tmpz)] after sequential activation steps. The "activated" material was derived from the supercritically dried sample through additional heating for 3 h at 120 °C under high vacuum.
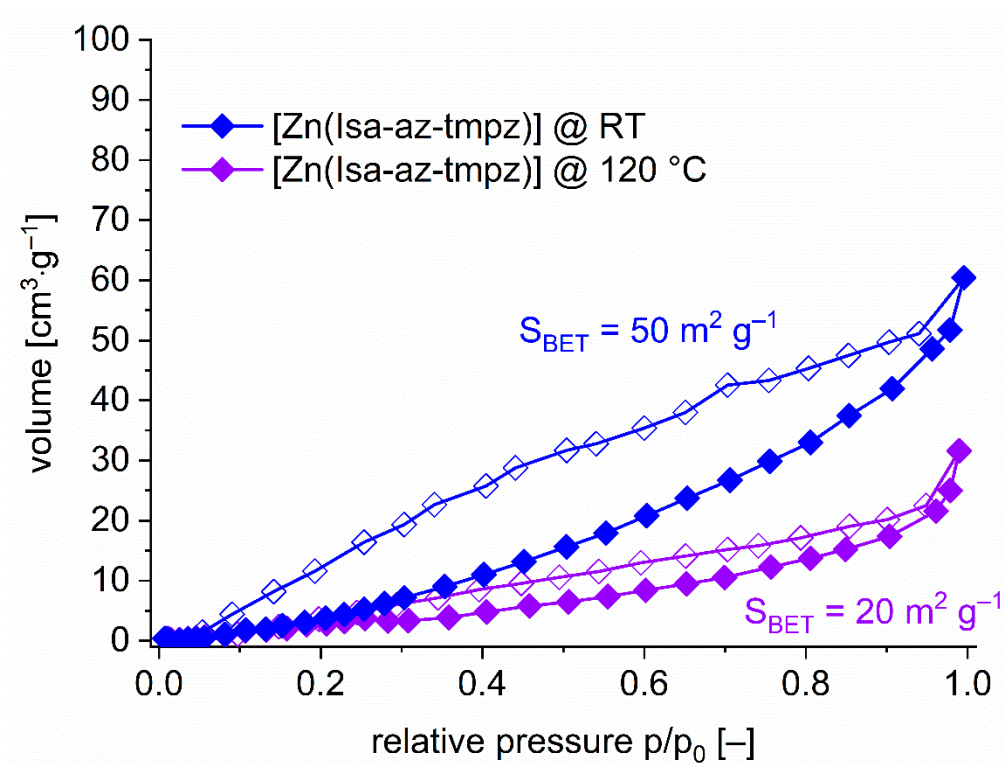
Figure S10. Volumetric nitrogen sorption measurements of [Zn(isa-az-tmpz)] activated at room temperature (RT) and 120 °C.

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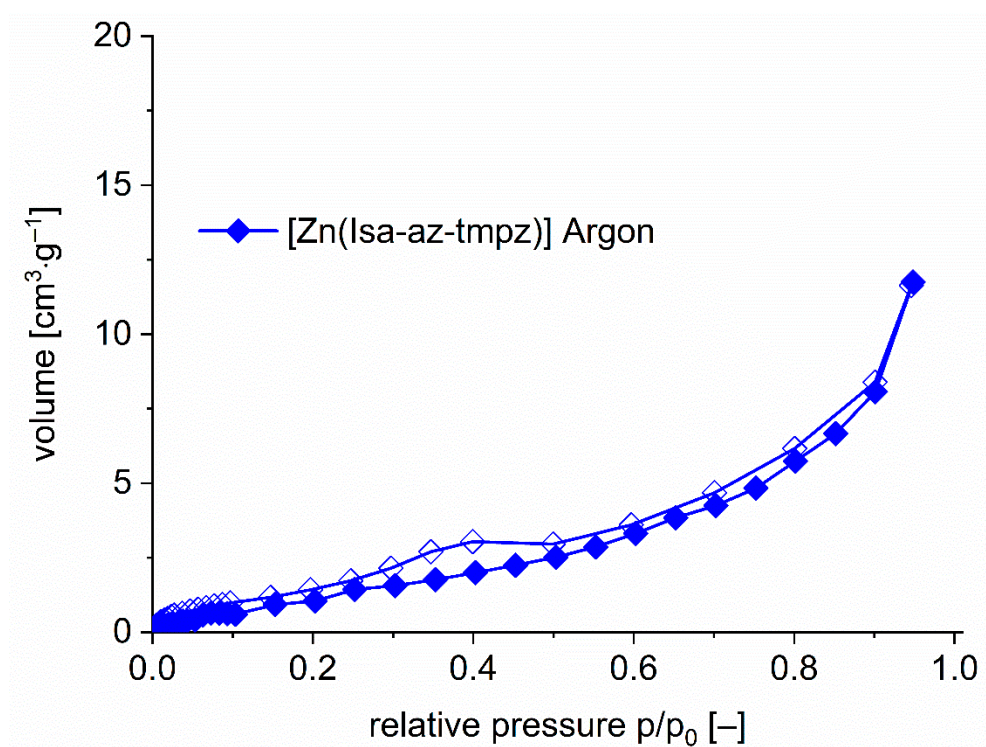
Figure S11. Volumetric argon sorption measurement of [Zn(isa-az-tmpz)] activated at 120 °C.

Table S1. Theoretical surface area and pore volume of [Zn(isa-az-tmpz)]. Calculations are based on structural data obtained from Crystal 1a.

Mercury 'void' calculation[1]	
Probe radius 1.2 Å, grid spacing 0.7 Å Void volume [Å^3] (% of unit cell) specific [cm^3 g^{-1}]	1406 (33) 0.29
Probe radius 0.7 Å, grid spacing 0.7 Å Void volume [Å^3] (% of unit cell) specific [cm^3 g^{-1}]	1693 (40) 0.35
Platon 'Calc Void'[2,3]	
Total potential solvent area [Å^3] (% of unit cell) specific [cm^3 g^{-1}]	1661 (39) 0.34
CrystalExplorer 'Crystal voids' calculation[4,5]	
Surface area $S_{unit\ cell}$ (isovalue 0.002) [Å^2] specific [m^2 g^{-1}]	1672 3442
Surface area $S_{unit\ cell}$ (isovalue 0.003) [Å^2] specific [m^2 g^{-1}]	1747 3596
Pore volume (isovalue 0.002) [Å^2] specific [cm^3 g^{-1}]	1753 0.36
Pore volume (isovalue 0.003) [Å^2] specific [cm^3 g^{-1}]	1983 0.41

Theoretical specific surface areas are calculated according to $(S_{Unit\ Cell} \cdot N_A)/(Z \cdot M)$ and theoretical specific pore volumes are calculated according to $(Void\ Volume \cdot N_A)/(Z \cdot M)$ or $(Solvent\ Accessible\ Volume \cdot N_A)/(Z \cdot M)$;

Z = 8 (number of asymmetric formula units), N_A = Avogadro's constant: $6.022 \cdot 10^{23}$ mol^{-1}, M = 365.65 g mol^{-1} (molecular weight of the asymmetric formula unit).

Topology analysis for [Zn(isa-az-tmpz)] with ToposPro.[6,7] The analysis is based on the structural data obtained from Crystal 1a.

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###################################################
4:C14 H12 N4 O4 Zn/intercluster bonds for rings>6
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Topology for ZA1

Atom ZA1 links by bridge ligands and has

Common vertex with					R(A-A)	
ZB 1	0.1726	-0.1726	0.7500	(-1 0 1)	6.740A	1
ZB 1	0.6726	0.6726	0.5000	(0 0 0)	7.556A	1
ZB 1	0.1726	0.8274	0.7500	(-1 1 1)	8.118A	1

Topology for ZB1

Atom ZB1 links by bridge ligands and has

Common vertex with					R(A-A)	
ZA 1	0.9026	0.2342	0.5854	(0 0 1)	6.740A	1
ZA 1	0.2342	0.9026	0.4146	(0 0-1)	6.740A	1
ZA 1	0.4026	0.2658	0.6646	(0 0 0)	7.556A	1
ZA 1	0.2658	0.4026	0.3354	(0 0 1)	7.556A	1
ZA 1	0.9026	1.2342	0.5854	(0 1 1)	8.118A	1
ZA 1	1.2342	0.9026	0.4146	(1 0-1)	8.118A	1

Structural group analysis

Structural group No 1

Structure consists of 3D framework with ZBZA2

Coordination sequences
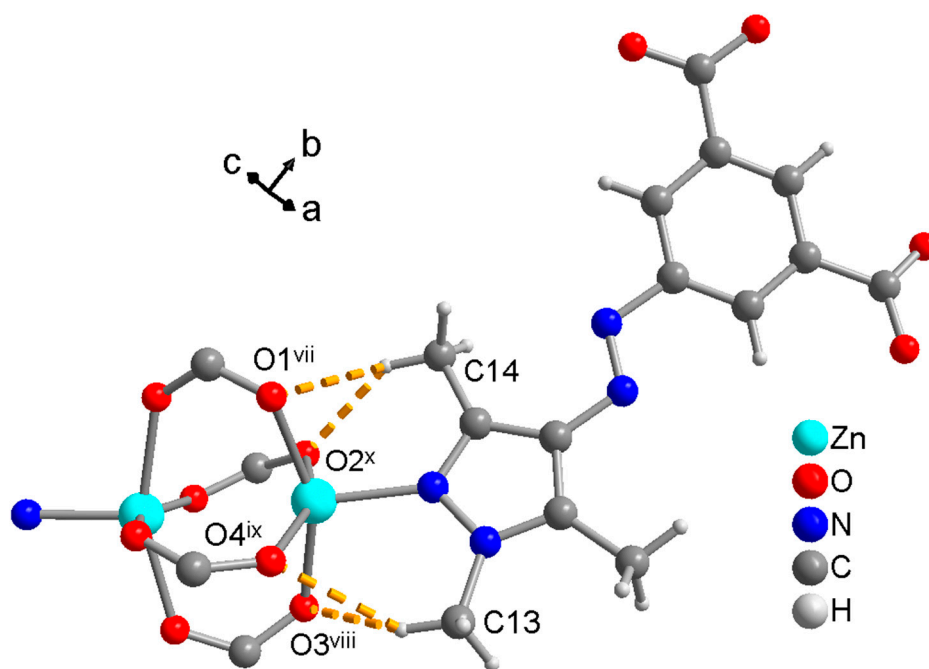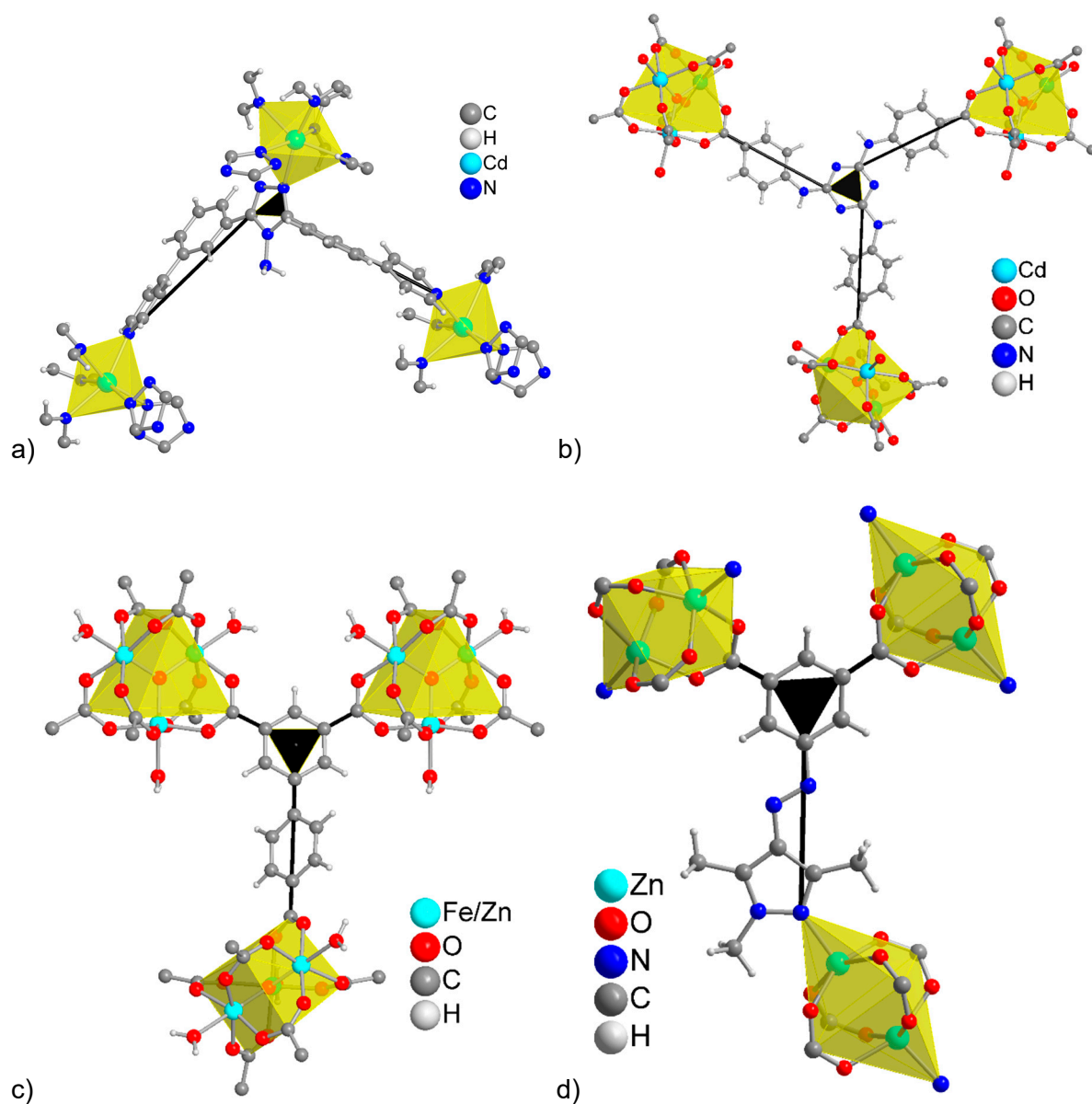
ZA1: 1 2 3 4 5 6 7 8 9 10
```

Num   3 15 22  71  61 167 120 303 199  481

Cum   4 19 41 112 173 340 460 763 962 1443

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ZB1: 1  2  3   4   5   6   7   8   9   10

Num   6 12 44  42 122  92 240 162  398  252

Cum   7 19 63 105 227 319 559 721 1119 1371

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TD10=1419


Vertex symbols for selected sublattice

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ZA1 Point symbol:{6^3}

Extended point symbol:[6(3).6(3).6(3)]

Rings coincide with circuits

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ZB1 Point symbol:{6^11.8^4}

Extended point symbol:[6.6.6.6.6(2).6(2).6(2).6(2).6(2).6(2).6(2).8(5).8(5).8(3).8(3)]

Vertex symbol:      [6.6.6.6.6(2).6(2).6(2).6(2).6(2).6(2).6(2).8.8.*.*]

ATTENTION! Some rings * are bigger than 10, so likely no rings are contained in that angle

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Point symbol for net: {6^11.8^4}{6^3}2

3,6-c net with stoichiometry (3-c)2(6-c); 2-nodal net


New topology, please, contact the authors (17828 types in 4 databases)

Elapsed time: 5.99 sec.


**Result of further analysis in the Topcryst[8,9] database**


Topological type: **3,6T22**

**Figure S12.** Hydrogen bonds in [Zn(Isa-az-tmpz)]. Symmetry transformations: (vii) y-1/2, -x+1/2, z+1/4; (viii) x, y-1, z; (ix) -y+1, -x, -z+3/2; (x) x-1/2, -y+1/2, -z+5/4. Image created from the structural data of crystal 1a.

**Figure S13.** Representations of the metal-linker connectivities in the **3,6T22** MOFs (a) G⊂Cd(L)$_2$ [10,11], (b) [(Me$_2$NH$_2$)Cd$_3$(OH) (H$_2$O)$_3$(Tatab)$_2$] [12], (c) [Fe$_2$M(Bptc)] [13] and (d) [Zn(Isa-az-tmpz)] (this work) The metal SBUs are drawn as yellow 6-c nodes and the linkers are depicted as black 3-c nodes. (L = 4-amino-3,5-bis(4-pyridyl-3-phenyl)-1,2,4-triazole, Tatab = 4,4′,4″-s-triazin-1,3,5-triyltri-p-amino-benzoate, Bptc = biphenyl-3,4′,5-tricarboxylate).

**Table S2.** Selected bond lengths [Å] and angles [°] for [Zn(isa-az-tmpz)] in *Crystal 1a*.

| | | | |
|---|---|---|---|
| Zn1—O1 | 2.0242 (16) | N3—C10 | 1.338 (3) |
| Zn1—N4[i] | 2.0387 (18) | N3—N4 | 1.365 (3) |
| Zn1—O3[ii] | 2.0459 (15) | N3—C13 | 1.464 (3) |
| Zn1—O4[iii] | 2.0575 (15) | O3—C8 | 1.265 (2) |
| Zn1—O2[iv] | 2.0586 (15) | C3—C4 | 1.381 (3) |
| Zn1—Zn1[iv] | 3.0417 (5) | O4—C8 | 1.251 (3) |
| O1—C7 | 1.268 (3) | N4—C11 | 1.342 (3) |
| N1—N2 | 1.259 (3) | C4—C5 | 1.400 (3) |
| N1—C3 | 1.432 (3) | C5—C6 | 1.378 (3) |
| C1—C2 | 1.394 (3) | C5—C8 | 1.496 (3) |
| C1—C6 | 1.395 (3) | C9—C10 | 1.382 (3) |
| C1—C7 | 1.494 (3) | C9—C11 | 1.410 (3) |
| O2—C7 | 1.254 (3) | C10—C12 | 1.494 (4) |
| N2—C9 | 1.397 (3) | C11—C14 | 1.479 (3) |
| C2—C3 | 1.391 (3) | | |
| | | | |
| O1—Zn1—N4i | 100.87 (7) | C4—C3—C2 | 121.1 (2) |
| O1—Zn1—O3ii | 154.84 (6) | C4—C3—N1 | 114.3 (2) |
| N4i—Zn1—O3ii | 104.27 (7) | C2—C3—N1 | 124.6 (2) |
| O1—Zn1—O4iii | 88.19 (7) | C8—O4—Zn1vi | 124.02 (14) |
| N4i—Zn1—O4iii | 105.33 (7) | C11—N4—N3 | 106.07 (18) |
| O3ii—Zn1—O4iii | 84.19 (7) | C11—N4—Zn1vii | 127.34 (16) |
| O1—Zn1—O2iv | 89.04 (6) | N3—N4—Zn1vii | 126.56 (14) |
| N4i—Zn1—O2iv | 99.61 (7) | C3—C4—C5 | 120.1 (2) |
| O3ii—Zn1—O2iv | 87.86 (7) | C6—C5—C4 | 118.9 (2) |
| O4iii—Zn1—O2iv | 154.98 (6) | C6—C5—C8 | 120.8 (2) |
| O1—Zn1—Zn1iv | 79.35 (4) | C4—C5—C8 | 120.2 (2) |
| N4i—Zn1—Zn1iv | 175.22 (6) | C5—C6—C1 | 121.2 (2) |
| O3ii—Zn1—Zn1iv | 75.69 (5) | O2—C7—O1 | 126.2 (2) |
| O4iii—Zn1—Zn1iv | 79.44 (4) | O2—C7—C1 | 117.7 (2) |
| O2iv—Zn1—Zn1iv | 75.61 (4) | O1—C7—C1 | 116.04 (19) |
| C7—O1—Zn1 | 123.78 (15) | O4—C8—O3 | 125.9 (2) |
| N2—N1—C3 | 114.2 (2) | O4—C8—C5 | 117.55 (19) |

| | | | |
|---|---|---|---|
| C2—C1—C6 | 119.7 (2) | O3—C8—C5 | 116.5 (2) |
| C2—C1—C7 | 120.4 (2) | C10—C9—N2 | 121.7 (2) |
| C2—C1—C6 | 119.7 (2) | C10—C9—C11 | 106.5 (2) |
| C2—C1—C7 | 120.4 (2) | N2—C9—C11 | 131.8 (2) |
| C6—C1—C7 | 119.86 (19) | N3—C10—C9 | 106.5 (2) |
| C7—O2—Zn1iv | 127.28 (14) | N3—C10—C12 | 122.5 (2) |
| N1—N2—C9 | 113.6 (2) | C9—C10—C12 | 131.0 (3) |
| C3—C2—C1 | 118.9 (2) | N4—C11—C9 | 109.0 (2) |
| C10—N3—N4 | 111.92 (19) | N4—C11—C14 | 121.7 (2) |
| C10—N3—C13 | 126.7 (2) | C9—C11—C14 | 129.3 (2) |
| N4—N3—C13 | 121.31 (19) | C6—C5—C4 | 118.9 (2) |
| C8—O3—Zn1v | 125.77 (15) | | |

Symmetry codes: (i) -*y*+1/2, *x*+1/2, *z*-1/4; (ii) -*y*+3/2, *x*+1/2, *z*-1/4; (iii) *x*+1/2, -*y*+3/2, -*z*+5/4; (iv) *y*, *x*, -*z*+1; (v) *y*-1/2, -*x*+3/2, *z*+1/4; (vi) *x*-1/2, -*y*+3/2, -*z*+5/4; (vii) *y*-1/2, -*x*+1/2, *z*+1/4.

**Table S3.** Hydrogen bond lengths [Å] and angles [°] for [Zn(isa-az-tmpz)] in *Crystal 1a*.

| D—H⋯A | D—H | H⋯A | D⋯A | D—H⋯A |
|---|---|---|---|---|
| C13—H13B⋯O3viii | 0.98 | 2.51 | 3.370 (3) | 146 |
| C13—H13B⋯O4ix | 0.98 | 2.52 | 3.244 (3) | 130 |
| C14—H14A⋯O1vii | 0.98 | 2.60 | 3.283 (3) | 127 |
| C14—H14A⋯O2x | 0.98 | 2.31 | 3.151 (3) | 144 |

Symmetry codes: (vii) y-1/2, -x+1/2, z+1/4; (viii) x, y-1, z; (ix) -y+1, -x, -z+3/2; (x) x-1/2, -y+1/2, -z+5/4.

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