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Supplementary Information

to

Guest-Dependent Mechanical Anisotropy in Pillared-Layered

Soft-Porous Crystals – A Nanoindentation Study

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1 Syntheses

All DMF-included samples have been synthesized in analogy to previously published procedures.^[S1] Compounds hosting other guest molecules have been prepared via post-synthetic guest exchange as outlined below.

1⊃dmf:

 $Zn(NO_3)_2 \cdot 6H_2O$ (250 mg, 0.84 mmol), 2-nitroterephthalic acid (178 mg, 0.84 mmol), and 1,4-diazabicyclo[2.2.2]octane (49 mg, 0.44 mmol) were suspended in 20 mL *N,N*-dimethylformamide (DMF). After stirring for 15 min the suspension was filtered and the obtained clear solution transferred into a Teflon lined steel autoclave (volume of 45 mL) and heated to 125 °C for 48 h. After cooling to room temperature the crystals were filtered off and rinsed in 20 mL fresh DMF for 3 d. The DMF was exchanged against fresh solvent two times, after 24 h and 48 h. The crystals were kept in the DMF solution prior to further manipulation and analysis.

1⊃dmso:

Several crystals of $1 \supset dmf$ were rinsed in 20 mL fresh dimethyl sulfoxide (DMSO) for 3 d. The DMSO was exchanged against fresh solvent two times, after 24 h and 48 h. The crystals were kept in the DMSO solution prior to further manipulation and analysis.

1⊃mesitylene:

Several crystals of $1 \supset dmf$ were rinsed in 20 mL fresh mesitylene for 3 d. The mesitylene was exchanged against fresh solvent two times, after 24 h and 48 h. The crystals were kept in the mesitylene solution prior to further manipulation and analysis.

1⊃toluene:

Several crystals of 1⊃dmf were rinsed in 20 mL fresh toluene for 3 d. The toluene was exchanged against fresh solvent two times, after 24 h and 48 h. The crystals were kept in the

^[S1] (a) Dybtsev, D. N.; Chun, H.; Kim, K. Angew. Chem. Int. Ed. 2004, 43, 5033; (b) Chun, H.; Dybtsev, D. N.; Kim, H.; Kim, K. Chem. Eur. J. 2005, 11, 3521; (c) Uemura, K.; Onishi, F.; Yamasaki, Y.; Kita, H. J. Solid State Chem. 2009, 182, 2852; (d) Uemura, K.; Yamasaki, Y.; Onishi, F.; Kita, H.; Ebihara, M. Inorg. Chem. 2010, 49, 10133; (e) Furukawa, S.; Hirai, K.; Nakagawa, K.; Takashima, Y.; Matsuda, R.; Tsuruoka, T.; Kondo, M.; Haruki, R.; Tanaka, D.; Sakamoto, H.; Shimomura, S.; Sakata, O.; Kitagawa, S. Angew. Chem. Int. Ed. 2009, 48, 1766.

toluene solution prior to further manipulation and analysis.

2⊃dmf:

 $Zn(NO_3)_2 \cdot 6H_2O$ (250 mg, 0.84 mmol), terephthalic acid (140 mg, 0.84 mmol), and 1,4diazabicyclo[2.2.2]octane (49 mg, 0.44 mmol) were suspended in 20 mL DMF. After stirring for 15 min the suspension was filtered and the obtained clear solution transferred into a Teflon lined steel autoclave (volume of 45 mL) and heated to 125 °C for 48 h. After cooling to room temperature the crystals were filtered off and rinsed in 20 mL fresh DMF for 3 d. The DMF was exchanged against fresh solvent two times, after 24 h and 48 h. The crystals were kept in the DMF solution prior to further manipulation and analysis.

3⊃dmf:

 $Zn(NO_3)_2 \cdot 6H_2O$ (250 mg, 0.84 mmol), 1,4-naphthalenedicarboxylic acid (182 mg, 0.84 mmol), and 1,4-diazabicyclo[2.2.2]octane (49 mg, 0.44 mmol) were suspended in 20 mL DMF. After stirring for 15 min the suspension was filtered and the obtained clear solution transferred into a Teflon lined steel autoclave (volume of 45 mL) and heated to 125 °C for 48 h. After cooling to room temperature the crystals were filtered off and rinsed in 20 mL fresh DMF for 3 d. The DMF was exchanged against fresh solvent two times, after 24 h and 48 h. The crystals were kept in the DMF solution prior to further manipulation and analysis.

4⊃dmf:

 $Zn(NO_3)_2 \cdot 6H_2O$ (250 mg, 0.84 mmol), 2-bromoterephthalic acid (206 mg, 0.84 mmol), and 1,4-diazabicyclo[2.2.2]octane (49 mg, 0.44 mmol) were suspended in 20 mL DMF. After stirring for 15 min the suspension was filtered and the obtained clear solution transferred into a Teflon lined steel autoclave (volume of 45 mL) and heated to 125 °C for 48 h. After cooling to room temperature the crystals were filtered off and rinsed in 20 mL fresh DMF for 3 d. The DMF was exchanged against fresh solvent two times, after 24 h and 48 h. The crystals were kept in the DMF solution prior to further manipulation and analysis.

2 Single Crystal X-ray Diffraction

Single-crystal X-ray diffraction measurements were performed on an Oxford Diffraction Gemini E Ultra diffractometer with an Eos CCD detector using Cu K_{α} ($\lambda = 1.5418$ Å) or Mo K_{α} radiation ($\lambda = 0.7107$ Å). The crystals were harvested directly from solution and mounted on a cryoloop or a glass fiber using perfluorinated oil. Data were collected using ω scans at a temperature between 250 K and 290 K in a nitrogen stream. Data collection and data reduction were performed with CrysAlisPro (Version 1.171.36.28) from Agilent Technologies. An empirical absorption correction was applied to all data using spherical harmonics as implemented in SCALE3 ABSPACK scaling algorithm. The structures were solved with ShelXS-97^[S2] using direct methods and refined against F^2 with ShelXL-97^[S2] by a least squares minimization algorithm using the Olex2 program package^[S3].

All non-hydrogen atoms, except for the NO_2 -groups of the crystal structures of 1, have been refined anisotropically. Hydrogen atoms have been added at idealized positions and refined isotropically using a riding model. The NO₂-substituents in the four crystal structures of 1 are disordered over two $(1 \supset dmf)$, four $(1 \supset dmso)$ or eight positions $(1 \supset mesitylene)$, **1⊃toluene**). This is accompanied by disorder of the phenyl ring of the NO₂-bdc linker over two positions for 1Ddmso, 1Dmesitylene, and 1Dtoluene. As a consequence the atoms of the NO₂-groups have only been refined isotropically and the corresponding bond lengths have been restrained to typical bond lengths found in other Zn-based NO₂-bdc coordination polymers.^[S4]

The dabco pillar is highly disordered (four-fold in most structures) over the main symmetry axis in all crystal structures reported herein. Bond distance restrains for the C-N distances have been used to tackle the disorder. For further details regarding the used constrains and restrains please see the individual cifs.

All compounds feature a certain amount of guest molecules in the pores. However, the guests could only be localized in the electron density map of compound $2 \supset dmf$. In all other compounds the guests are highly disordered and their atomic positions could not be refined. Moreover, the structures of compounds 1, 3, and 4 feature varying degrees of disorder of the substituents connected to the phenyl ring of the linker (NO₂-, Br-groups or the additional

^[S2] Sheldrick, G. M. Acta Cryst. 2008, A64, 112.

^[S3] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.; J. Appl. Cryst. 2009, 42, ^[S4] Guo, M.-L.; Guo, C.-H. Acta Cryst. 2007, C63, m352.

phenyl ring of ndc) as well as the central phenyl ring of the linker L itself. The electron density of the disordered guest molecules was subtracted from the data using the SQUEEZE algorithm implemented in the Platon program package.^[S5] However, the calculated number of electrons in the guest accessible voids of the structures of **1**, **3**, and **4** (see Table S1 and S2) is significantly lower than the expected values based on TG/DTA data (see Chapter 5 of the Supporting Information). This is explained by the high disorder of the substituents at L, which leads to an artificial reduction of the accessible void space for each crystal structure – the derived void space is decreasing significantly with increasing disorder of the substituents) and complicates a reliable determination of the number of guest molecules present. Hence, with the exception of **2dmf**, atoms belonging to guest molecules have not been included in the reported molecular formula and molecular weight.

For compound 1 only the guest-free structure, which is similar to the structures of 1⊃mesitylene and 1⊃toluene, has been reported so far.^[S1c] The guest responsive fitting of 1 upon adsorption of DMF or DMSO is reported here for the first time. The crystal structures of 2⊃dmf, 3⊃dmf, and 4⊃dmf have been reported previously.^[S1a,b,c,e] However, we redetermined these structures at a temperature between 270 K and 290 K to obtain the exact structures of the materials at (almost) ambient conditions, which are the conditions where the nanoindentation experiment was conducted. The structures of 2⊃dmf and 4⊃dmf are in very good agreement with the literature reference data. 3⊃dmf, however, crystallizes in the space group *P4/mbm* (lattice parameters: *a* = 15.4195(4) Å, *c* = 9.6416(4) Å; *T* = 290 K). To the best of our knowledge two structures of **3**⊃dmf have been reported so far. Both structures feature a four-fold disorder of the ndc linker and crystallize either in *P4/mmm* (lattice parameters: *a* = 15.4631(7) Å, *c* = 9.6840(5) Å; *T* = 293 K)^[S1e]. The structure we report here features only a two-fold disorder of the ndc linker, which we ascribe to the excellent quality of the examined single crystals.

^[S5] Spek, A. L.; Acta Cryst. 2009, D65, 148.

Table S1: Crystallograph	ic data of compounds	1⊃dmf, 1⊃dmso, 1⊐	Omesitylene, and 1⊃toluene.

Compound	1⊃dmf	1⊃dmso	1⊃mesitylene	1⊃toluene
Empirical formula	$C_{22}H_{18}N_4O_{12}Zn_2\\$	$C_{22}H_{18}N_4O_{12}Zn_2$	$C_{22}H_{18}N_4O_{12}Zn_2\\$	$C_{22}H_{18}N_4O_{12}Zn_2$
Formula weight	661.14	661.14	661.14	661.14
Radiation used	Cu Ka	Cu Ka	Cu Kα	Cu Kα
Т / К	270	250	250	290
Crystal system	orthorhombic	tetragonal	tetragonal	tetragonal
Space group	Pban	I4/mcm	P4/mmm	P4/mmm
<i>a</i> / Å	16.2647(5)	15.25553(12)	10.94325(7)	10.90313(18)
b / Å	14.5206(5)	15.25553(12)	10.94325(7)	10.90313(18)
c / Å	9.6475(3)	19.3129(2)	9.67577(10)	9.6490(3)
α / °	90	90	90	90
β/°	90	90	90	90
γ/°	90	90	90	90
$V/\text{\AA}^3$	2278.50(14)	4494.72(8)	1158.719(15)	1147.06(4)
Ζ	2	4	1	1
$ ho_{ m calc}$ / mg mm ⁻³	0.964	0.977	0.947	0.957
μ / mm ⁻¹	1.66	1.683	1.632	1.649
F(000)	668	1336	334	334
Crystal size / mm ³	$0.17 \times 0.16 \times 0.15$	$0.31 \times 0.26 \times 0.25$	$0.35 \times 0.23 \times 0.17$	$0.42 \times 0.37 \times 0.28$
2θ range for data collection	9.16 to 140.74°	11.6 to 140.6°	12.22 to 140.66°	12.24 to 140.26°
Index ranges	$\begin{array}{l} -17 \leq h \leq 19, \\ -17 \leq k \leq 17, \\ -6 \leq l \leq 11 \end{array}$	$\begin{array}{l} -17 \leq h \leq 18, \\ -18 \leq k \leq 18, \\ -23 \leq l \leq 23 \end{array}$	$\begin{array}{c} -13 \leq h \leq 13, \\ -12 \leq k \leq 13, \\ -11 \leq l \leq 11 \end{array}$	$\begin{array}{c} -10 \leq h \leq 13, \\ -12 \leq k \leq 13, \\ -11 \leq l \leq 11 \end{array}$
Reflections collected	6716	27069	22618	4246
Independent reflections	2178 [<i>R</i> (int) = 0.0362]	1172 [R(int) = 0.0288]	698 [<i>R</i> (int) = 0.0185]	689 [<i>R</i> (int) = 0.0202]
Data/restraints/parameters	2178/44/121	1172/38/84	698/17/56	689/17/56
Goodness-of-fit on F^2	1.160	1.162	1.312	1.153
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0627,$ $wR_2 = 0.2025$	$R_1 = 0.0606,$ $wR_2 = 0.1995$	$R_1 = 0.0470,$ $wR_2 = 0.1619$	$R_1 = 0.0544,$ $wR_2 = 0.1607$
Final <i>R</i> indexes [all data]	$R_1 = 0.0704,$ $wR_2 = 0.2116$	$R_1 = 0.0615, wR_2 = 0.2012$	$R_1 = 0.0470,$ $wR_2 = 0.1619$	$R_1 = 0.0548,$ $wR_2 = 0.1615$
Largest diff. peak/hole / e Å ⁻³	0.68/-0.56	0.54/-0.37	0.67/-0.34	0.95/-0.53
Calculated void space using "Calc Solv" in Platon ^{S5}	48%	30%	26%	26%
Counted electrons in the void per unit cell/per zinc paddle wheel using SQEEZE (Platon)	180/90	250/62.5	21/21	24/24
Number of guest molecules per zinc paddle wheel calculated from the electron count of SQUEEZE	2.25 (DMF)	1.49 (DMSO)	0.32 (mesitylene)	0.48 (toluene)
Number of guest molecules calculated from TG/DTA data	4.3 (DMF)	4.8 (DMSO)	2.5 (mesitylene)	2.7 (toluene)

Compound	2⊃dmf	3⊃dmf	4⊃dmf
Empirical formula	$C_{34}H_{48}N_6O_{12}Zn_2$	$C_{30}H_{24}N_2O_8Zn_2$	$C_{22}H_{18}Br_2N_2O_8Zn_2$
Formula weight	862.42	671.26	728.94
Radiation used	Μο Κα	Μο Κα	Cu Kα
Т / К	270	290	270
Crystal system	tetragonal	tetragonal	orthorhombic
Space group	I4/mcm	P4/mbm	Pban
<i>a</i> / Å	15.0609(8)	15.4195(4)	16.3684(4)
b / Å	15.0609(8)	15.4195(4)	14.4237(3)
<i>c</i> / Å	19.2433(13)	9.6416(4)	9.6406(2)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
$V/ Å^3$	4365.0(4)	2292.39(13)	2276.07(9)
Ζ	4	2	2
$ ho_{ m calc}$ / mg mm ⁻³	1.314	0.972	1.064
μ / mm^{-1}	1.159	1.080	3.598
F(000)	1800	684	716
Crystal size / mm ³	$0.25 \times 0.17 \times 0.12$	$0.27 \times 0.27 \times 0.14$	$0.31 \times 0.26 \times 0.18$
2θ range for data collection	6.4 to 54.98°	6.76 to 61.44°	9.18 to 140.72°
Index ranges	$\begin{array}{l} -19 \leq h \leq 9, \\ -19 \leq k \leq 16, \\ -22 \leq l \leq 24 \end{array}$	$\begin{array}{l} -21 \leq h \leq 20, \\ -20 \leq k \leq 20, \\ -13 \leq l \leq 13 \end{array}$	$\begin{array}{l} -19 \leq h \leq 19, \\ -10 \leq k \leq 17, \\ -10 \leq l \leq 11 \end{array}$
Reflections collected	5404	12583	6928
Independent reflections	1349 [R(int) = 0.0445]	1827 [R(int) = 0.0313]	2175 [<i>R</i> (int) = 0.0260]
Data/restraints/parameters	1349/14/70	1827/30/91	2175/17/105
Goodness-of-fit on F^2	1.114	1.232	1.123
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0568,$ $wR_2 = 0.1558$	$R_1 = 0.0407,$ $wR_2 = 0.1598$	$R_1 = 0.0554,$ $wR_2 = 0.1571$
Final R indexes [all data]	$R_1 = 0.0844,$ $wR_2 = 0.1811$	$R_1 = 0.0622,$ $wR_2 = 0.1704$	$R_1 = 0.0594,$ $wR_2 = 0.1612$
Largest diff. peak/hole / e Å ⁻³	0.67/-0.47	0.59/-0.43	0.62/-0.87
Calculated void space using "Calc Solv" in Platon ^{S5}	_	31%	44%
Counted electrons in the void per unit cell/per zinc paddle wheel using SQEEZE (Platon)	-	58/29	166/83
Number of DMF molecules per zinc paddle wheel calculated from the electron count of SQUEEZE	_	0.73	2.08
Number of DMF molecules calculated from the TG/DTA data	4.4	4.3	4.3



Figure S1: Representation of the asymmetric unit of the crystal structure of $1 \supseteq dmf$. All non-hydrogen atoms are shown with principal ellipses representing the 50% probability level. Hydrogen atoms are shown as spheres with fixed radii. The C atoms of the dabco pillar are disordered and possess occupancy of 0.3. The NO₂-group is disordered over two positions by symmetry. The corresponding N and O atoms of the NO₂-group are half occupied and have been refined isotropically. The half occupied H atom bonded to the C atom where the half occupied NO₂-group is connected, has not been added to the model. However, the H atom has been included in the molecular formula and weight.



Figure S2: Representation of the asymmetric unit of the crystal structure of $1 \supset dmso$. All non-hydrogen atoms are shown with principal ellipses representing the 50% probability level. Hydrogen atoms are shown as spheres with fixed radii. The C atoms of the dabco pillar are disordered and possess occupancy of 0.25. The phenyl ring of the NO₂-bdc linker is disordered over two positions leading to a disorder of the NO₂-group over four positions by symmetry. The corresponding N and O atoms of the NO₂-group have been refined isotropically. The 0.25-fold occupied H atom bonded to the C atom where the partly occupied NO₂-group is connected, has not been added to the model. However, the H atom has been included in the molecular formula and weight.



Figure S3: Representation of the asymmetric unit of the crystal structure of $1 \supset$ mesitylene. All non-hydrogen atoms are shown with principal ellipses representing the 50% probability level. Hydrogen atoms are shown as spheres with fixed radii. The C atoms of the dabco pillar are disordered and possess occupancy of 0.25. The phenyl ring of the NO₂-bdc linker is disordered over two positions leading to a disorder of the NO₂-group over eight positions by symmetry. The corresponding N and O atoms of the NO₂-group have been refined isotropically. The H atoms of the NO₂-bdc linker have not been added to the model. However, the H atoms have been included in the molecular formula and weight.



Figure S4: Representation of the asymmetric unit of the crystal structure of **1Dtoluene**. All non-hydrogen atoms are shown with principal ellipses representing the 50% probability level. Hydrogen atoms are shown as spheres with fixed radii. The C atoms of the dabco pillar are disordered and possess occupancy of 0.25. The phenyl ring of the NO₂-bdc linker is disordered over two positions leading to a disorder of the NO₂-group over eight positions by symmetry. The corresponding N and O atoms of the NO₂-group have been refined isotropically. The H atoms of the NO₂-bdc linker have not been added to the model. However, the H atoms have been included in the molecular formula and weight.



Figure S5: Representation of the asymmetric unit of the crystal structure of $2 \supseteq dmf$. All non-hydrogen atoms are shown with principal ellipses representing the 50% probability level. Hydrogen atoms are shown as spheres with fixed radii. The C atoms of the dabco pillar are disordered and possess occupancy of 0.375. Atoms belonging to DMF guests have been refined isotropically. The O atom of DMF is disordered over two positions by space group symmetry. Following, the aldehydic H atom has not been added to the structural model. However, the H atom has been included in the molecular formula and weight.



Figure S6: Representation of the asymmetric unit of the crystal structure of $3 \supseteq dmf$. All non-hydrogen atoms are shown with principal ellipses representing the 50% probability level. Hydrogen atoms are shown as spheres with fixed radii. The C atoms of the dabco pillar are disordered and possess occupancy of 0.25. Furthermore, the ndc linker is disordered over two positions by space group symmetry.



Figure S7: Representation of the asymmetric unit of the crystal structure of $4 \supseteq dmf$. All non-hydrogen atoms are shown with principal ellipses representing the 50% probability level. Hydrogen atoms are shown as spheres with fixed radii. The C atoms of the dabco pillar are disordered and possess occupancy of 0.25. The Br-group is disordered over four positions with mixed occupancies (see cif-file for details).



Figure S8: Photographs of representative examples of face-indexed single crystals of $1 \supset dmf$ (a), $1 \supset dmso$ (b), $1 \supset mesitylene$ (c), $1 \supset toluene$ (d), $2 \supset dmf$ (e), $3 \supset dmf$ (f), and $4 \supset dmf$ (g).

3 Powder X-ray Diffraction

Powder X-ray diffraction (PXRD) measurements of all samples were performed on a Bruker D8 Advance powder diffractometer using Cu K_{α} ($\lambda = 1.5418$ Å) radiation and a LynxEye position sensitive detector in Bragg-Brentano (θ - θ) geometry in a 2θ range from 5° - 50° at room temperature. The solvated samples were taken out of the respective solvent (DMF, DMSO, mesitylene, or toluene), gently ground, and placed on a polished zero-background silicon substrate. The patterns were analysed (Pawley fitting) with the TOPAS program package (academic version). Cell parameters, sample offset, and background function were refined simultaneously using a least square algorithm. Space group symmetry and starting values for the cell parameters were taken from the single crystal X-ray diffraction data. All compounds were found to be phase pure. The unit cell parameters and space group symmetry are in excellent agreement with the single crystal data.



Figure S9: Pawley fit to the PXRD pattern of **1Ddmf**. The black crosses, red lines, and green lines represent the experimental, calculated, and difference profiles, respectively. The blue tick marks indicate the positions of allowed Bragg reflections in the space group *Pban*. The cell parameters were determined to be a = 16.693(2) Å, b = 13.972(2) Å, c = 9.6768(7) Å. Final R_p and R_{wp} values are 3.56% and 5.16% ($R_{exp} = 2.81\%$).



Figure S10: Pawley fit to the PXRD pattern of $1 \supset dmso$. The black crosses, red lines, and green lines represent the experimental, calculated, and difference profiles, respectively. The blue tick marks indicate the positions of allowed Bragg reflections in the space group *I4/mcm*. The cell parameters were determined to be a = b = 15.3521(4) Å, c = 19.3834(6) Å. Final R_p and R_{wp} values are 2.60% and 3.40% ($R_{exp} = 2.69\%$).



Figure S11: Pawley fit to the PXRD pattern of **1Dmesitylene**. The black crosses, red lines, and green lines represent the experimental, calculated, and difference profiles, respectively. The blue tick marks indicate the positions of allowed Bragg reflections in the space group *P4/mmm*. The cell parameters were determined to be a = b = 10.9566(4) Å, c = 9.6960(3) Å. Final R_p and R_{wp} values are 2.14% and 2.97% ($R_{exp} = 2.72\%$).



Figure S12: Pawley fit to the PXRD pattern of **1Dtoluene**. The black crosses, red lines, and green lines represent the experimental, calculated, and difference profiles, respectively. The blue tick marks indicate the positions of allowed Bragg reflections in the space group *P*4/*mmm*. The cell parameters were determined to be a = b = 10.9012(5) Å, c = 9.6585(4) Å. Final R_p and R_{wp} values are 3.52% and 4.86% ($R_{exp} = 2.95\%$).



Figure S13: Pawley fit to the PXRD pattern of $2 \supset \text{dmf}$. The black crosses, red lines, and green lines represent the experimental, calculated, and difference profiles, respectively. The blue tick marks indicate the positions of allowed Bragg reflections in the space group *I4/mcm*. The cell parameters were determined to be a = b = 15.1407(5) Å, c = 19.3023(4) Å. Final R_p and R_{wp} values are 5.80% and 8.37% ($R_{exp} = 3.03\%$).



Figure S14: Pawley fit to the PXRD pattern of **3Ddmf**. The black crosses, red lines, and green lines represent the experimental, calculated, and difference profiles, respectively. The blue tick marks indicate the positions of allowed Bragg reflections in the space group *P4/mbm*. The cell parameters were determined to be a = b = 15.4557(5) Å, c = 9.6654(4) Å. Final R_p and R_{wp} values are 6.18% and 8.36% ($R_{exp} = 2.70\%$).



Figure S15: Pawley fit to the PXRD pattern of **4Ddmf**. The black crosses, red lines, and green lines represent the experimental, calculated, and difference profiles, respectively. The blue tick marks indicate the positions of allowed Bragg reflections in the space group *Pban*. The cell parameters were determined to be a = 16.2185(9) Å, b = 14.6187(8) Å, c = 9.6570(5) Å. Final R_p and R_{wp} values are 3.12% and 4.25% ($R_{exp} = 2.81\%$).

4 Nanoindentation

Single crystals for nanoindentation have been mounted as reported in the literature.^[S6] Untwined single crystals with well-defined rectangular shape were taken out of the respective solvent (DMF, DMSO, mesitylene, or toluene), face-indexed using single crystal X-ray diffraction and subsequently glued onto flat aluminium chips (~5 mm x 5 mm, 1 mm thick) using a small amount of cyanoacrylate glue. The crystals were glued onto the chips so that either the {110} or {001} facets (compounds 1 \supset dmf, 1 \supset dmso, 2 \supset dmf, 3 \supset dmf, and 4 \supset dmf) or the {100} or {001} facets (compounds 1 \supset mesitylene and 1 \supset toluene) were in contact with the aluminium chips. The samples were then cold-mounted using Epofix resin (Struers Ltd.). Afterwards, the mounted samples were carefully grinded using Si/C grinding papers to remove the aluminium chips followed by gentle polishing with a polishing cloth using oil based diamond suspensions. A diamond suspension with a particle size of 1 µm was used in the final step in order to minimize the surface roughness.

The nanoindentation experiments were performed at room temperature on a MTS Nanoindenter XP immediately after polishing in order to minimize effects of guest evaporation and crystal degradation. The instrument was placed in an isolation cabinet in order to minimize thermal instability and acoustic interference. The indenter (three-sided pyramidal Berkovich tip, end radius ~100 nm) was aligned normal to the respective crystal facets. A minimal number of 10 indents were performed on each crystal facet. The interindent spacing was guaranteed to be at least 25 μ m. A fused silica standard, with elastic modulus of 72 GPa and hardness of 9 GPa, was used for calibration of the indenter.

Nanoindentation was performed under the dynamic displacement controlled *continuous stiffness measurement* (CSM) mode, where a sinusoidal displacement of 2 nm at a frequency of 45 Hz is superimposed onto the primary loading curve. This allows for the determination of elastic modulus (*E*) and indentation hardness (*H*) as a function of indentation depth using the method proposed by Oliver and Pharr.^[S7] The load (*P*) was monitored as a function of indentation depth (*h*) until a maximum indentation depth of 1000 nm was reached. The indenter was held for 30 s at the maximum depth without increasing the load further

^[S6] (a) Tan, J. C.; Merrill, C. A.; Orton, J. B.; Cheetham, A. K. *Acta Mater.* 2009, *57*, 3481; (b) Tan, J. C.;
Furman, J. D.; Cheetham, A. K. *J. Am. Chem. Soc.* 2009, *131*, 14252; (c) Tan, J. C.; Bennett, T. D.; Cheetham, A. K. *Proc. Natl. Acad. Sci. USA* 2010, *107*, 9938; (d) Li, W.; Barton, P. T.; Kiran, M. S.; Burwood, R. P.;
Ramamurty, U.; Cheetham, A. K. *Chem. Eur. J.* 2011, *17*, 12429; (e) Tan, J. C.; Jain, P.; Cheetham, A. K. *Dalton Trans.* 2012, *41*, 3949; (f) Li, W.; Kiran, M. S.; Manson, J. L.; Schlueter, J. A.; Thirumurugan, A.;
Ramamurty, U.; Cheetham, A. K. *Chem. Commun.* 2013, *49*, 4471.

^[S7] (a) Oliver, W. C.; Pharr, G. M. J. Mater. Res. **1992**, 7, 1564; (b) Oliver, W. C.; Pharr, G. M. J. Mater. Res. **2004**, 19, 3; (c) Pharr, G. M.; Strader, J. H.; Oliver, W. C. J. Mater. Res. **2011**, 24, 653.

followed by unloading. The strain rate for loading and unloading was set to be 0.05 s⁻¹. The *Ph* curves were analysed as described in previous reports^[S6b,f] to yield the depth dependent elastic moduli and hardnesses. The elastic modulus and the Poisson's ratio (v) of the indenter tip are $E_{tip} = 1141$ GPa and $v_{tip} = 0.07$. The elastic moduli of the MOF samples were calculated using an isotropic Poission's ratio of 0.3. In order to minimize effects of surface roughness average values for *E* and *H* were calculated based on the indentation data in the range from 200 to 1000 nm.

Notice, that the Oliver and Pharr Method requests the elastic properties of the samples to be isotropic in order to extract *intrinsic* (absolute) elastic moduli.^[S7] Since this is not the case for the single crystals analysed in this work, the obtained elastic moduli should not be regarded as absolute values. Nevertheless, the obtained values allow us to compare the relative stiffness of the different MOF samples and to derive important structure-property relationships.

Notice also, that the calculated value of the elastic modulus is sensitive to the Poission's ratio.^[S6a,b] Density functional theory calculations of the elastic properties of guestfree $[Zn_2(bdc)_2(dabco)]_n$ (2), either featuring the idealized square grid or the idealized rhomb shaped grid, showed that the Poission's ratio of this material is highly anisotroptic and can be in the range from 0.0 to 1.0 (for the square grid structure as shown by 1)mesitylene, 1 \supset toluene, and 3 \supset dmf) or -0.4 to 3.2 (for the rhomb shaped structure as shown by 1 \supset dmf or **4**⊃**dmf**).^[S8] Thereby the Poission's ratio is continuously changing with the direction of the transverse vector when the direction of compression (indentation) is kept constant. As already mentioned the Oliver and Pharr method is only valid for strictly isotropic materials, where the Poission's ratio is constant for all transverse directions of a given compression axis. Similar to former nanoindentation studies on MOFs and dense hybrid frameworks^[S6a,b,c,f], we decided to set the Poission's ratio to 0.3 for the calculation of the elastic modulus. This allows us to get unbiased moduli, which are suitable for a comparative discussion. It is noted, that calculation of E using a Poission's ratio of 0.2 instead of 0.3 results in a change of only $\sim 5\%$ in E. Overall, despite the above shortcomings, nanoindentation provides an excellent first-order estimate of the intrinsic Young's modulus for MOF single crystals.^[S9]

^[S8] Ortiz, A.; Boutin, A.; Fuchs, A.; Coudert, F.-X. Phys. Rev. Lett. 2012, 109, 195502.

^[S9] Tan, J.-C.; Civalleri, B.; Lin, C.-C.; Valenzano, L.; Galvelis, R.; Chen, P.-F.; Bennett, T.; Mellot-Draznieks, C.; Zicovich-Wilson, C.; Cheetham, A. K. *Phys. Rev. Lett.* **2012**, *108*, 095502.

To evaluate the elastic behaviour of these soft porous crystals we determined the so-called plasticity index^[S10] (Ψ) from representative *P*-*h* curves according to the following equation:

$$\Psi = \frac{W_{\rm tot} - W_{\rm e}}{W_{\rm tot}}$$

where W_{tot} is the total indentation work (equal to the area under the loading segment of the *P*-*h* curve including the 30 s holding segment) and W_e is the elastic indentation work (equal to the area under the unloading segment of the *P*-*h* curve). Hence, Ψ is a measure for the extent of plastic deformation of the material. When $\Psi = 1$ the material solely deforms plastically and the deformation under the indenter tip is completely irreversible. While when $\Psi = 0$ the material exclusively deforms elastically and the deformation is fully reversible. For $0 < \Psi < 1$ an intermediate behaviour is apparent.

After the indentation measurements the residual indents have been examined using the optical microscope implemented in the nanoindentation apparatus. Representative micrographs for the $\{110\}$ and $\{001\}$ facets of $1 \supset dmf$ are shown in Figure S16. As expected for porous MOFs it is evident that no pile-up is occurring. Moreover, there are no cracks apparent as a result of the indentations.



Figure S16: Optical micrograph of the residual indents on (a) the {110} facet and (b) the {001} facet of 1⊃dmf.

^[S10] (a) Du, B. Y.; Tsui, O. K. C.; Zhang, Q. L.; He, T. B. *Langmuir* **2001**, *17*, 3286; (b) Yahyaei, H.; Mohseni, M. *Tribol. Int.* **2013**, *57*, 147.



Figure S17: Representative *P*-*h* curves for compounds $1 \supseteq dmf$, $2 \supseteq dmf$, $3 \supseteq dmf$, and $4 \supseteq dmf$. (a) Indentation along the dabco axis on the {001}-oriented facet. (b) Indentation orthogonal to the dabco-linker plane on the {110}-oriented facet.



Figure S18: Evolution of the hardness (i.e. nano-hardness) measured orthogonal to the dabco-linker plane of $1 \supseteq dmf$ (indentation on the {110} facet), $1 \supseteq dmso$ (indentation on the {110} facet), $1 \supseteq mesitylene$ (indentation on the {100} facet), and $1 \supseteq toluene$ (indentation on the {100} facet) in dependence on the indentation depth. The data are based on 25 indents for $1 \supseteq dmf$, 10 for $1 \supseteq dmso$, 18 for $1 \supseteq mesitylene$, and 20 for $1 \supseteq toluene$. The average data reported in Table S3 have been calculated for the depth region from 200 to 1000 nm.



Figure S19: Evolution of the hardness (i.e. nano-hardness) measured along the dabco axis of $1 \supseteq dmf$, $1 \supseteq dmso$, $1 \supseteq mesitylene$, and $1 \supseteq toluene$ (all indentations on the {001} facet) in dependence on the indentation depth. The data are based on 25 indents for $1 \supseteq dmf$, 16 for $1 \supseteq dmso$, 19 for $1 \supseteq mesitylene$, and 15 for $1 \supseteq toluene$. The average data reported in Table S3 have been calculated for the depth region from 200 to 1000 nm.



Figure S20: Evolution of the hardness (i.e. nano-hardness) measured orthogonal to the dabco-linker plane of $1 \supseteq dmf$, $2 \supseteq dmf$, $3 \supseteq dmf$, and $4 \supseteq dmf$ (all indentations on the {110} facet) in dependence on the indentation depth. The data are based on 25 indents for $1 \supseteq dmf$, 10 for $2 \supseteq dmf$, 11 for $3 \supseteq dmf$, and 13 for $4 \supseteq dmf$. The average data reported in Table S3 have been calculated for the depth region from 200 to 1000 nm.



Figure S21: Evolution of the hardness (i.e. nano-hardness) measured along the dabco axis of 1 dmf, 2 dmf, 3 dmf, and 4 dmf (all indentations on the {001} facet) in dependence on the indentation depth. The data are based on 25 indents for 1 dmf, 10 for 2 dmf, 22 for 3 dmf, and 16 for 4 dmf. The average data reported in Table S3 have been calculated for the depth region from 200 to 1000 nm.

Table S3: Number of indents, average elastic modulus (*E*) and average hardness (*H*), as well as the elastic anisotropy $(E_{\{001\}}/E_{\{110\}})$ or $E_{\{001\}}/E_{\{100\}})$ and the hardness anisotropy $(H_{\{001\}}/H_{\{110\}})$ or $H_{\{001\}}/H_{\{100\}})$ determined in the region from 200 nm to 1000 nm indentation depth of all compounds investigated in this work.

Compound	Orientation	Number of indents	E / GPa	Elastic anisotropy	H / GPa	Hardness anisotropy
1⊃dmf	{110}	25	$2.08\pm\!\!0.09$	4.5	0.173 ± 0.011	2.0
	{001}	25	9.26 ± 0.18		0.351 ± 0.018	
1 > dmaa	{110}	10	3.68 ± 0.19	2.2	0.190 ± 0.014	- 1.8
	{001}	16	8.16 ± 0.44		0.341 ± 0.012	
1 magitulana	{100}	18	6.06 ± 0.21	1.7	0.375 ± 0.017	1.2
	{001}	19	10.17 ± 0.26		0.460 ± 0.020	1.2
1 Dtoluono	{100}	20	6.53 ± 0.20	1.3	0.361 ± 0.017	1.0
Toluene	{001}	15	8.69 ± 0.29		0.370 ± 0.019	
2 dmf	{110}	10	$4.36\pm\!\!0.19$	1.8	0.186 ± 0.019	2.0
2_ami	{001}	10	8.01 ± 0.17		0.368 ± 0.029	2.0
2 dmf	{110}	11	7.39 ± 0.22	1.1	0.319 ± 0.017	1.2
3 Jumi	$\{001\}$ 22 8.04 ± 0.22	1.1	0.389 ± 0.018	1.2		
17 dmf	{110}	13	2.88 ±0.15	2 1	0.112 ± 0.006	4.2
4_ami	{001}	16	8.93 ±0.28	3.1	0.470 ± 0.024	4.2

Table S4: Total indentation work (W_{tot}), elastic indentation work (W_e), and plasticity index (Ψ) of all compounds investigated in this work. The data have been calculated based on representative *P*-*h* curves obtained for the respective crystal facets.

Compound	Orientation	W _{tot} / nJ	W _e / nJ	Ψ
1⊃dmf	{110}	1.26	0.59	0.53
	{001}	3.36	0.56	0.83
1 > dmga	{110}	1.60	0.61	0.62
	{001}	3.25	0.65	0.80
1 magitulana	{100}	2.87	1.11	0.61
I _ mesityiene	{001}	3.91	0.91	0.77
1 Dtoluono	{100}	3.10	1.31	0.58
Toluene	{001}	3.65	0.51	0.86
2 - J £	{110}	1.69	0.38	0.78
2_dmi	{001}	3.42	0.95	0.72
2	{110}	2.92	0.58	0.80
3 Jami	{001}	3.35	0.71	0.79
47 days	{110}	1.04	0.38	0.64
4_ami	{001}	3.81	0.97	0.75

5 Thermogravimetric and Differential Thermal Analysis

Thermogravimetric and differential thermal analysis (TG-DTA) was performed on a TA Instruments Q600 (sample weight approximately 5 mg) under nitrogen flow (flow rate 100 mL min^{-1}) in the temperature range from 25 °C to 600 °C with a heating rate of 10 °C min^{-1} . The solvated samples were taken out of the respective solvent (DMF, DMSO, mesitylene, or toluene), air-dried for approximately 1 h and placed in alumina crucibles.



Figure S22: TG/DTA trace of 1**Ddmf**. 32% weight loss up to a temperature of ~200 °C corresponds to 4.3 DMF molecules per formula unit of $[Zn_2(NO_2-bdc)_2(dabco)]_n$.



Figure S23: TG/DTA trace of **1Ddmso**. 36% weight loss up to a temperature of ~230 °C corresponds to 4.8 DMSO molecules per formula unit of $[Zn_2(NO_2-bdc)_2(dabco)]_n$.



Figure S24: TG/DTA trace of 1**Dmesitylene**. 29% weight loss up to a temperature of ~350 °C corresponds to 2.5 mesitylene molecules per formula unit of $[Zn_2(NO_2-bdc)_2(dabco)]_n$.



Figure S25: TG/DTA trace of 1**D**toluene. 27% weight loss up to a temperature of ~230 °C corresponds to 2.7 toluene molecules per formula unit of $[Zn_2(NO_2-bdc)_2(dabco)]_n$.



Figure S26: TG/DTA trace of $2 \supset \text{dmf}$. 36% weight loss up to a temperature of ~220 °C corresponds to 4.4 DMF molecules per formula unit of $[\text{Zn}_2(\text{bdc})_2(\text{dabco})]_n$. The mismatch of 0.4 DMF molecules to the quantity determined by single crystal X-ray diffraction (four DMF molecules per formula unit) may be explained by additional DMF molecules, which are located in the inter-particle voids. The second step at ~300 °C (weight loss of ~13%) can be ascribed to the complete loss of dabco pillars prior to framework decomposition.



Figure S27: TG/DTA trace of **3Ddmf**. 32% weight loss up to a temperature of ~220 °C corresponds to 4.3 DMF molecules per formula unit of $[Zn_2(ndc)_2(dabco)]_n$.



Figure S28: TG/DTA trace of $4 \supseteq dmf$. 30% weight loss up to a temperature of ~230 °C corresponds to 4.3 DMF molecules per formula unit of $[Zn_2(Br-bdc)_2(dabco)]_n$.

6 IR spectra

IR spectroscopy was carried out on air-dried samples on a Bruker Tensor 27 FT-IR spectrometer ($\tilde{v} = 520 \text{ cm}^{-1} - 4000 \text{ cm}^{-1}$) in reflection mode using a diamond ATR (attenuated total reflectance) unit.



Figure S29: ATR-FTIR spectra of $1 \supseteq dmf$, $1 \supseteq dmso$, $1 \supseteq mesitylene$, and $1 \supseteq toluene$. Left: Spectral region from 2500 to 4000 cm⁻¹. Right: Spectral region from 500 to 2000 cm⁻¹. The specific vibrational bands of the respective guest molecules are observed, while the peaks associated to the framework are barely affected by the nature of the guest molecule.



Figure S30: ATR-FTIR spectra of $2 \supseteq dmf$, $3 \supseteq dmf$, and $4 \supseteq dmf$. Left: Spectral region from 2500 to 4000 cm⁻¹. Right: Spectral region from 500 to 2000 cm⁻¹. The specific vibrational bands of the DMF guests are observed.