Supporting Information

"*In situ* X-ray study of breathing-like effect in interlocked metal organic nanocages."

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Contents

Materials and Methods.

Single crystal XRD.

The reported single crystal XRD experiments were measured at the NeXt GAME Laboratory of the Politecnico di Milano, co-founded by Regione Lombardia.

The reagents used for the synthesis of **1** (original file name: **se221vt**) and **2** (original file name: **az32vt**) (i. e., TPB, ZnI_2 methanol, chloroform and paraxylene (*p*-xy)) were purchased from chemical suppliers and used without further purification.

All the single crystal X-ray data reported in this work were recorded using a XtaLAB Synergy-S, Dualflex, HyPix-6000HE diffractometer. Suitable crystals of **1** and **2** were selected and mounted on a nylon loop using a magnetic pin on a XtaLAB Synergy-S, Dualflex, HyPix-6000HE diffractometer. The cooling equipment to control the temperature in the X-ray experiments is an Oxford Cryostream 1000. The crystals were cooled to 100 K then raised up to 150 K, 200 K, 250 K, and 300 K for data collection. All the structures were solved with the ShelXT[1] structure solution program using the Intrinsic Phasing solution method and by using Olex2[2] as the graphical interface. The model was refined with version 2014/7 of ShelXL 2014/7[1] using Least Squares minimization. The structures were solved in the space group *R*-3 for **1@100K, 1@150K, 1@200K, 1@250K, 1@300K, 2@150K, 2@200K, 2@250K** and **2@300K** determined by the ShelXT[1] structure solution program using Intrinsic Phasing and refined by Least Squares using version 2014/7 of ShelXL 2014/7.[1] All non-hydrogen atoms were refined anisotropically except for **2@300K**. Hydrogen atom positions were calculated geometrically and refined using the riding model.

Note: The R-factors in **2@300K** have worsened compared to **2@250K** due to a weaker diffraction at high angles (Table S18). The crystal did not move during the measurement at 300 K as the indexing of the spots is correct in the las runs of the **2@300K** structure (Figure S8). However, the data is sufficient to solve the structure to do the structural analysis of the host

substructure. The data has not been deposited in the CCDC but can be obtained upon direct request to the author.

Powder X-Ray diffraction experiments.

All the powder X-ray diffraction (PXRD) experiments were carried out using a Bruker D2-Phaser diffractometer equipped with Cu radiation (λ = 1.54184 Å) using Bragg-Brentano geometry. The experiments were performed at room temperature. The sample exposure time was 0.5 seconds, the scan range is from 4.00 to 30.00 in 2-theta degrees with a step-width of 0.01622 °.

Density Functional Theory (DFT)

The calculations, as in previous studies, have been performed at the PBE/DNP level (where PBE is the functional of Perdew, Burke and Ernzerhof while DNP states for a standard numerical basis as implemented into Dmol3 package[3], and roughly comparable to the 6-31G** gaussian set). The strategy employed in the current work showed good performances in some studies of crystalline systems (including molecules, polymers, and hybrid metal-organic materials).[4] Explicit van der Waals contribution, according to the approach proposed by Grimme was determined.[5] Optimized structures used in the calculations are available upon request.

Synthesis of single crystal XRD of 1 and 2.

Single crystals of **1** and **2** were grown by layering diffusion method. TPB (7.5 mg) is dissolved in a mixture of *p*-xy/methanol (8 mL/1mL) for **1** or in a chloroform/methanol (6 mL/1mL) for **2**. The solutions of **1** and **2**, in two separate crystallization tubes, are placed at the bottom of the tube (Figure S1 and S2). Then a middle layer of methanol (3mL) is added to create a bilayer. Then the metal ions are added dropwise using a ZnI_2 methanol solution (12 mg in 2 mL of methanol). The crystallization tubes were left at room temperature for 7d. Large single crystals suitable for SC-XRD experiments were obtained after one week (Figure S1).

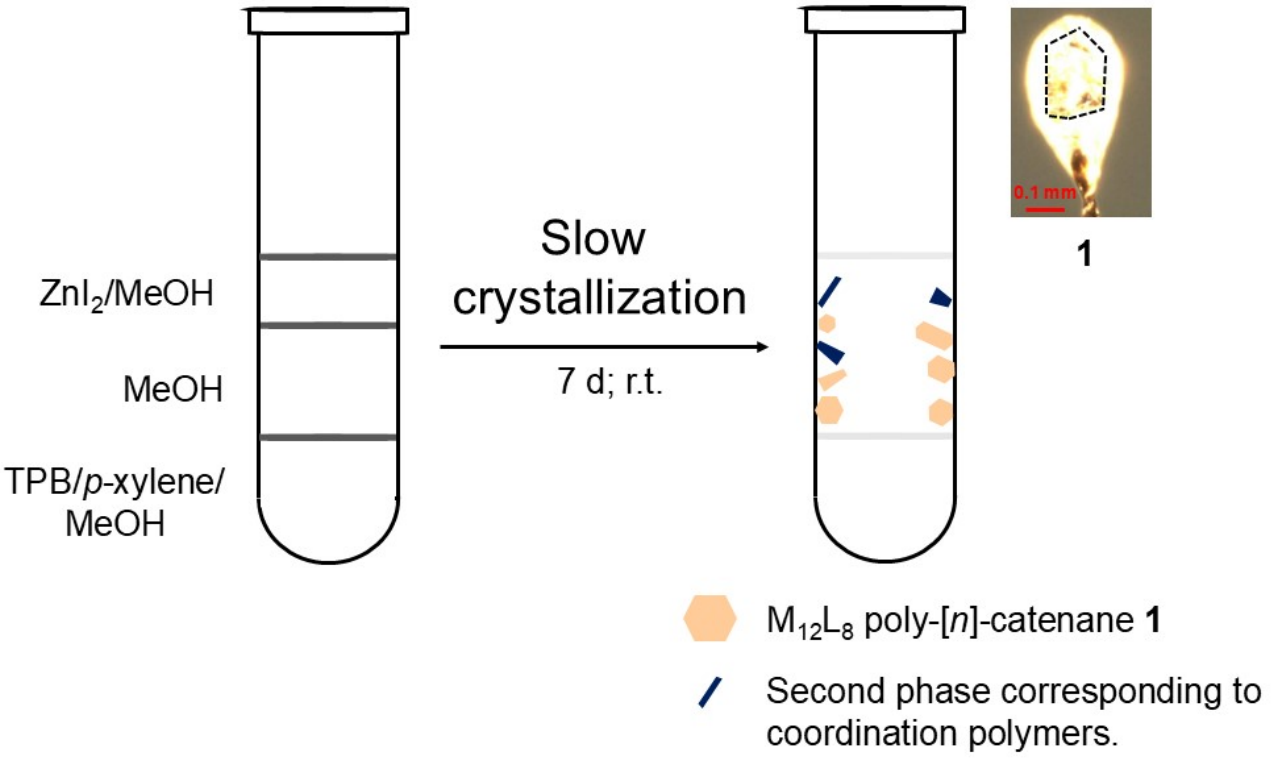

Figure S1. Cartoon showing the slow crystallization of **1**.

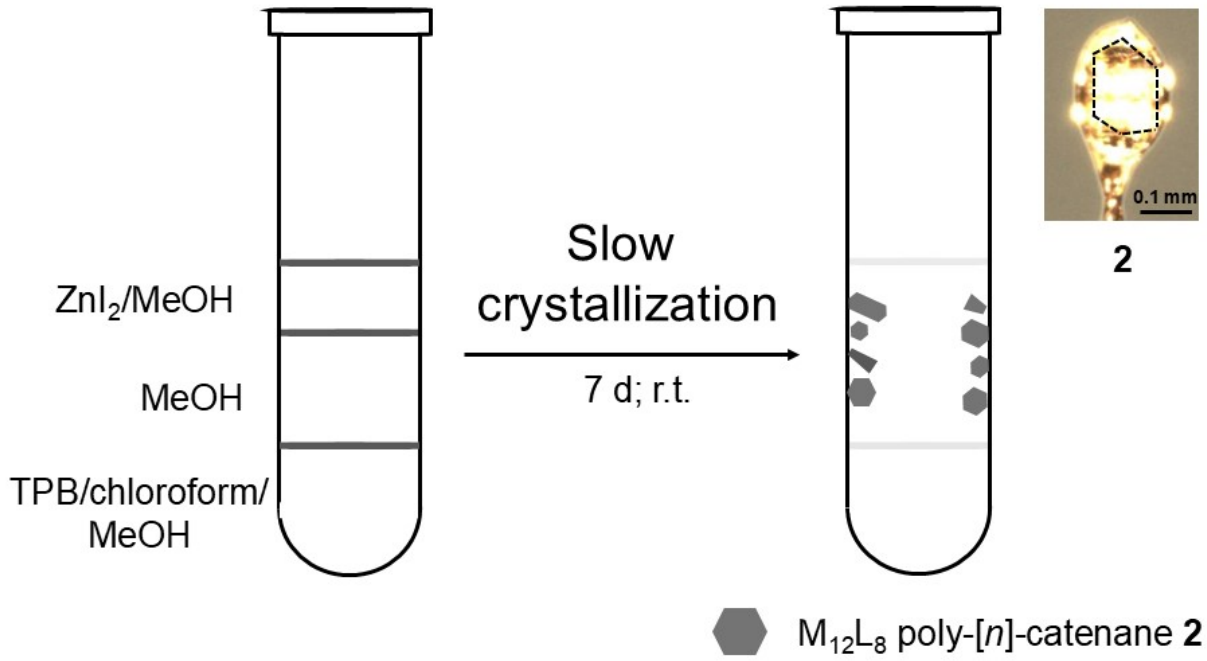

Figure S2. Cartoon showing the slow crystallization of **2**.

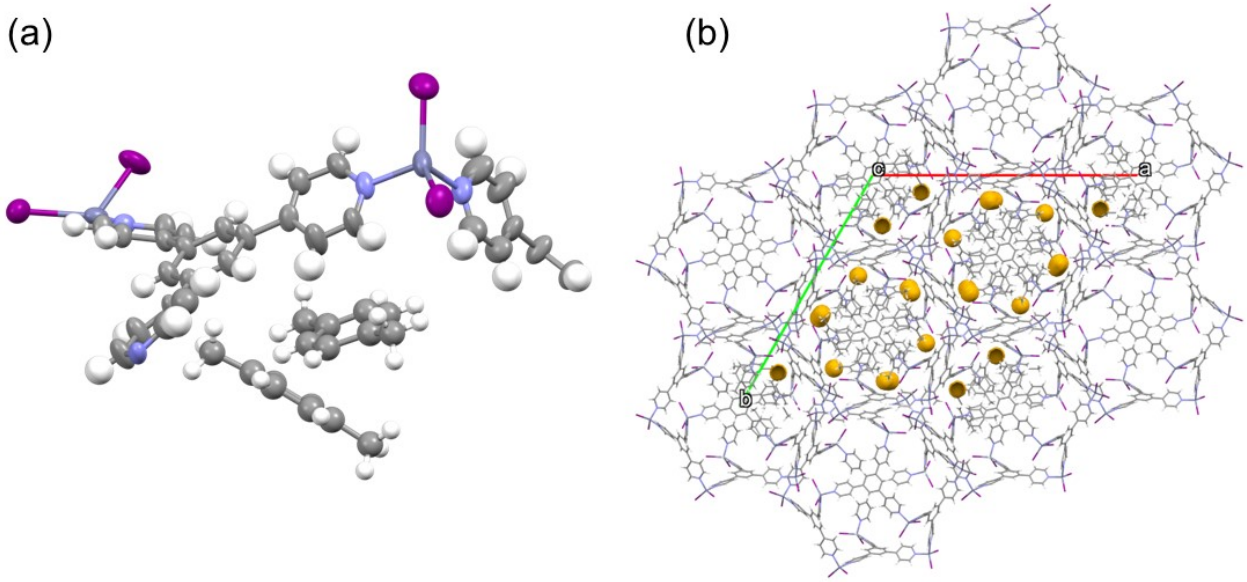

Figure S3. (a) Crystal structure of **1** showing the asymmetric unit including two *p*-xy guest molecules. (b) Crystal packing of **1** viewed along the *c*-axis with the $M_{12}L_8$ residual void space (0.9 % of the total unit cell volume) in yellow surface.

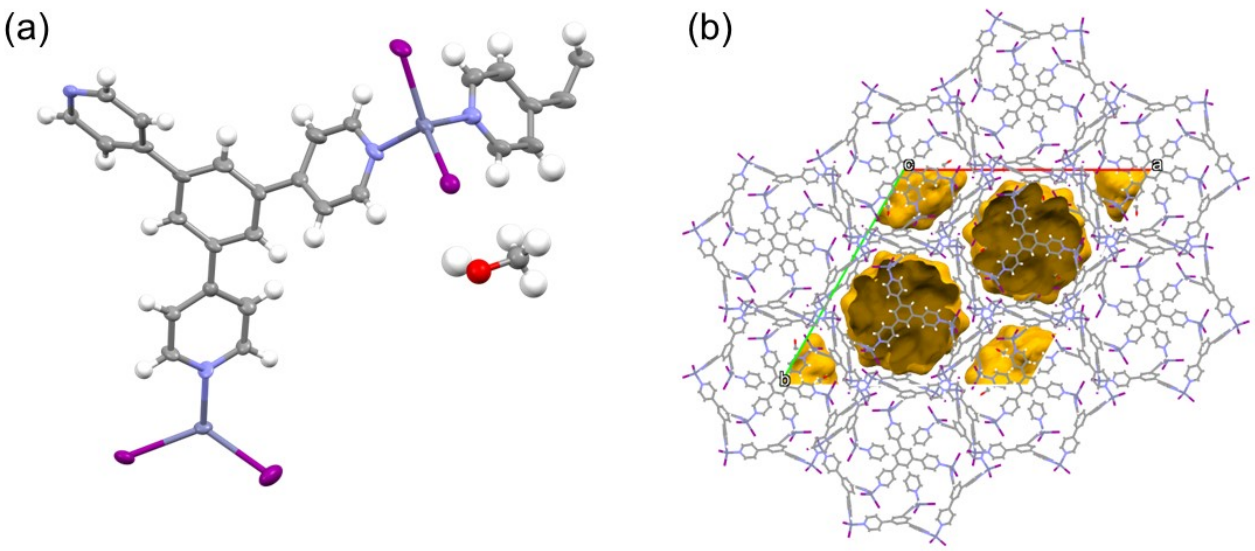

Figure S4. (a) Crystal structure of **2** showing the asymmetric unit including one methanol guest molecule. (b) Crystal packing of **2** viewed along the *c*-axis with the $M_{12}L_8$ void space in yellow surface. The voids shown in yellow correspond to 29 % of the total unit cell volume.

Synthesis of the amorphous phase (a1) of poly-[*n*]-catenane using TPB and ZnI_2 for the crystalline to amorphous transformation by uptaking methanol.

Following our reported solid-state synthesis of the $M_{12}L_8$ polycatenane,[6] the amorphous phase **a1** was obtained griding 30 mg of TPB and 47 mg of ZnI_2 in a mortar and pestle for 15 minutes (Figure S5a). Then **a1**, was immersed in methanol overnight to generate the crystalline phase of **a1** including methanol (Figure S5b). The sample turns amorphous if it is left in contact with air for *ca*. 15 min.

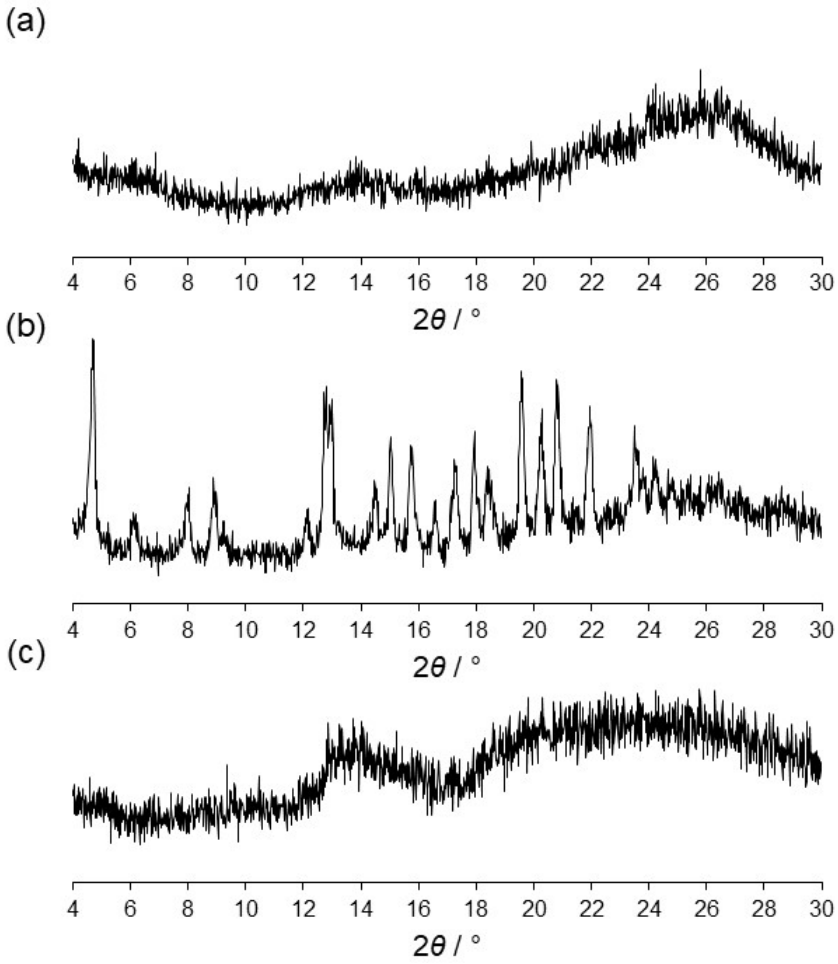

Figure S5. (a) Amorphous phase **a1** of the poly-[*n*]-catenane of $M_{12}L_8$ nanocages obtained after neat grinding TPB and ZnI_2. (b) Diffractogram showing the crystalline phase of the polycatenane obtained after immersing **a1** in methanol overnight. The diffractogram shown in b) was measured right after the sample was filtered. (c) Powder XRD pattern carried out immediately after the measurement shown in b) was finished. Note: One diffractogram takes about 15 minutes to be recorded.

Single-crystal-to-single-crystal (SCSC) guest exchange reaction exposing 1 to vapors of nitrobenzene to give 1'.

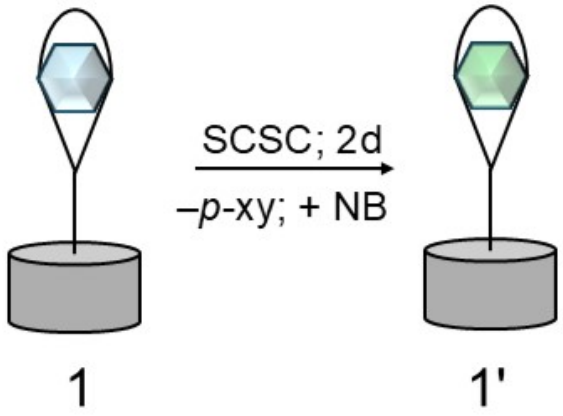

Figure S6. Cartoon depicting the guest exchange via a SCSC reaction by exposing **1** to vapours of nitrobenzene to form **1'**.

The lattice parameters after the guest exchange of **1** to give **1'** in a SCSC are as follows:

Unit cell for **1 (300 K)**: a = 39.0407(16) Å; b = 39.0407(16) Å; c = 16.2780(5) Å; $\alpha = \beta = 90°$; $\gamma = 120°$; V = 21486.6(19) Å^3. Further structural information is given in Table S5.

Unit cell for **1' (173 K)**: a = 38.6444(6) Å; b = 38.6444(6) Å; c = 16.0924(2) Å; $\alpha = \beta = 90°$; $\gamma = 120°$. V= 20812.5(7) Å^3. (CSD Entry: BIWYOZ).[7]

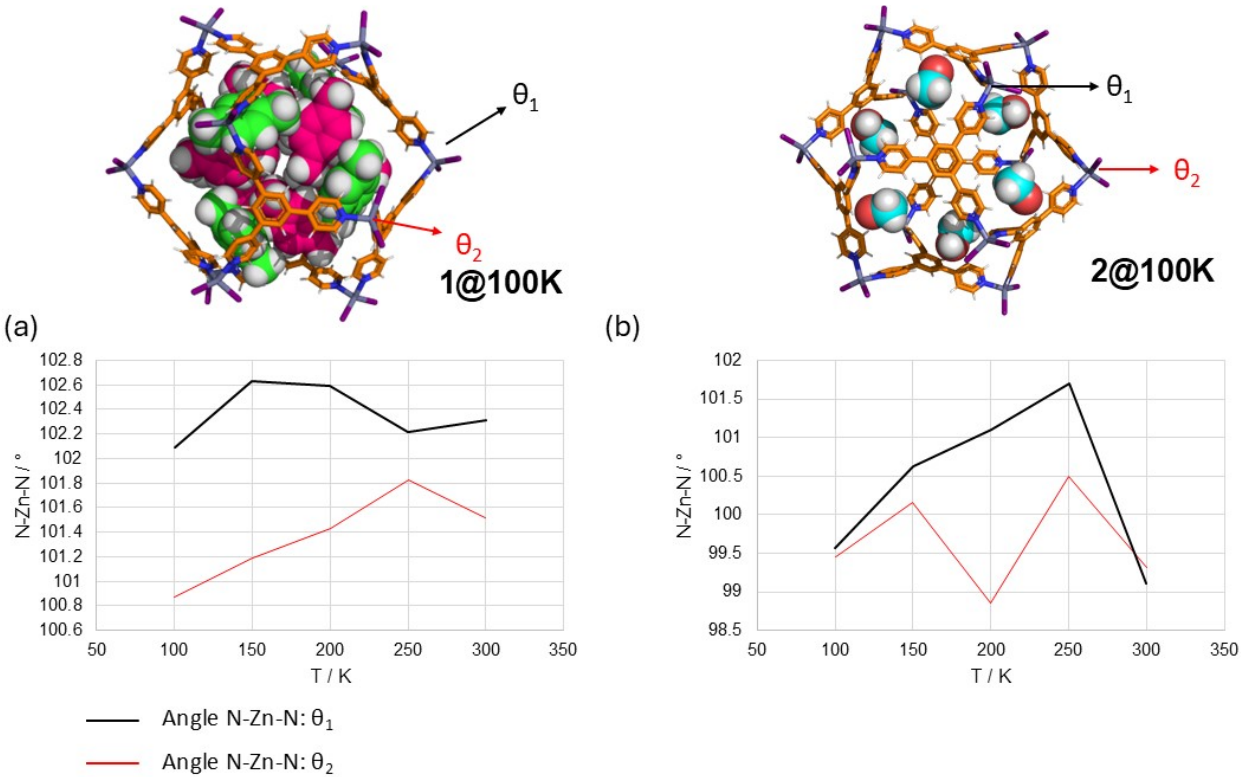

Figure S7. Plots showing the evolution as a function of temperature of the two different coordination angles N-Zn-N in the $M_{12}L_8$ cages in **1@100K** (a) and **2@100K** (b). The measured θ_1 and θ_2 angles are shown in the top of the figure in the $M_{12}L_8$ nanocages. The N-Zn-N angles θ_1 and θ_2 are given in Table S7 and S8.

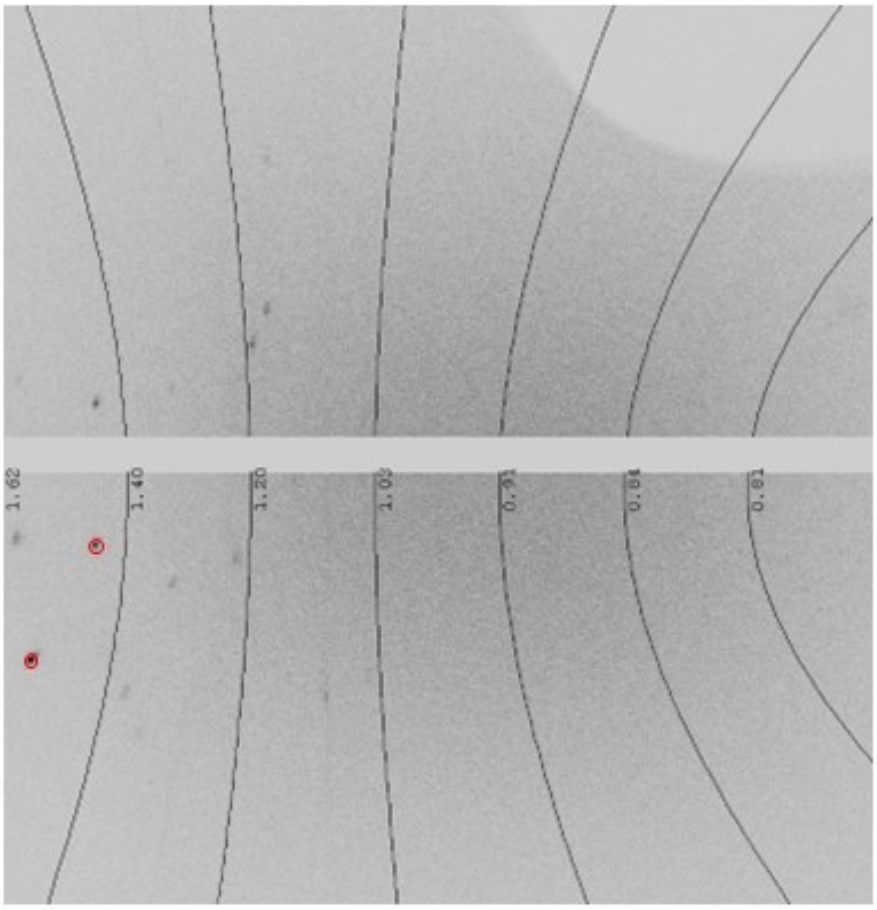

Figure S8. One of the images (image 91) corresponding to the last run in the data collection of **2@300K** showing the overlay spot prediction (red circles) on the diffraction image and the weak diffraction at high angles.

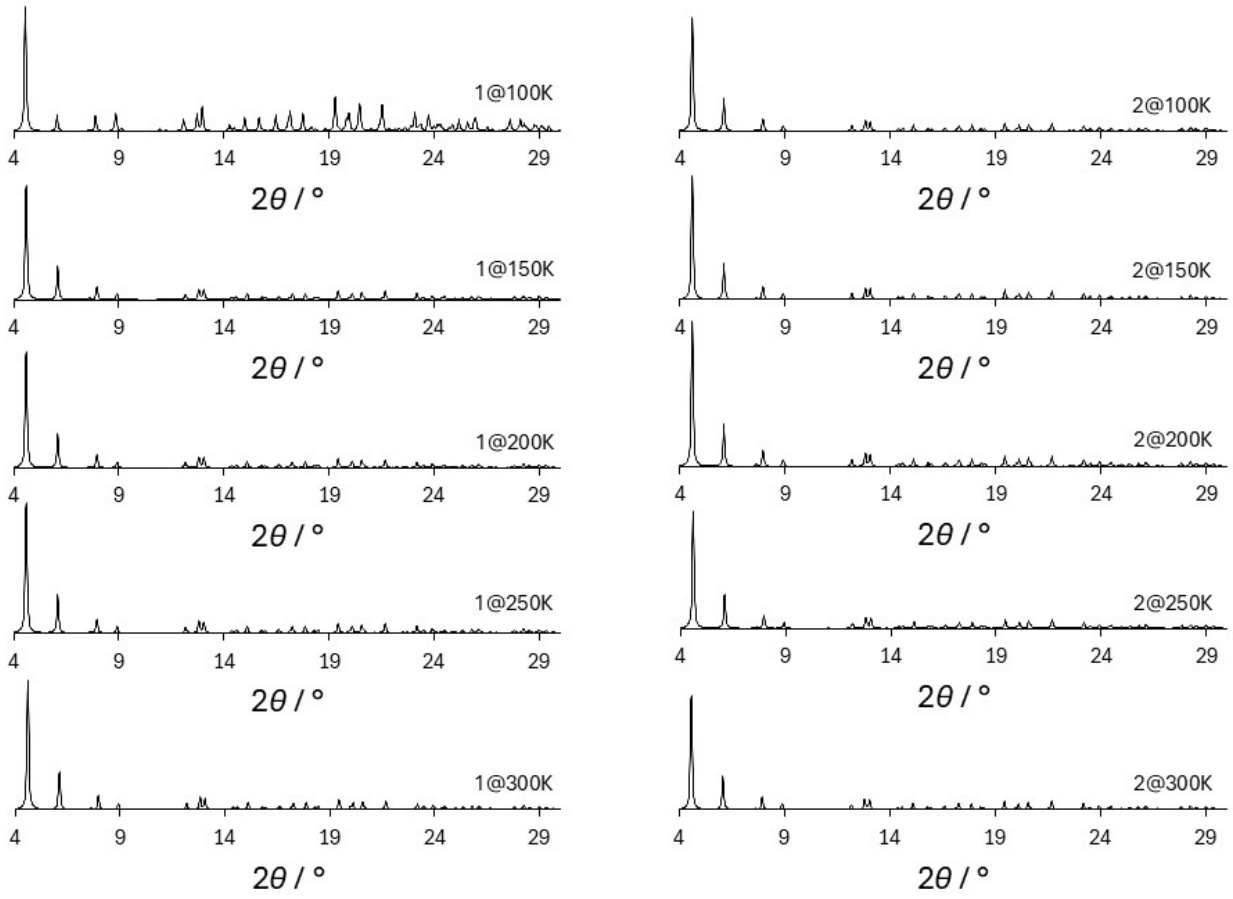

Figure S9. Simulated powder XRD patterns of **1** and **2** at the various temperatures described in this work.

Table S1. Lattice parameters *a* and *b* for crystals **1**, **2** and **1'** at different temperatures.

Temperature (K)	**Lattice vector *a*/*b* of 1 (Å)**	**Lattice vector *a*/*b* of 2 (Å)**	**Lattice vector *a*/*b* of 1' (Å)**
100	38.7577	38.6352	
150	38.8366	38.7388	
173			38.6444
200	38.9215	38.8170	
250	39.0207	38.8579	
300	39.0407	38.452	

Table S2. Lattice parameters *c* for crystals **1**, **2** and **1'** at different temperatures.

Temperature (K)	**Lattice vector *c* of 1 (Å)**	**Lattice vector *c* of 2 (Å)**	**Lattice vector *c* of 1' (Å)**
100	16.161	15.8231	
150	16.2247	15.9128	
173			16.0924
200	16.2503	16.050	
250	16.3353	16.2103	
300	16.278	16.0939	

Table S3. Unit cell volume for crystals **1**, **2** and **1'** at different temperatures.

Temperature (K)	**Cell volume of 1 (Å^3)**	**Cell volume of 2 (Å^3)**	**Cell volume for 1' (Å^3)**
100	21024	20455	
150	21193	20681	
173			20813
200	21319	20943	
250	21540	21197	
300	21487	20608	

Table S4. Distances from the two benzene centroids forming part of the mechanical bonds for crystals **1**, **2** and **1'** at different temperatures.

Temperature (K)	**Mechanical bond π-π distances (Å) for 1**	**Mechanical bond π-π distances (Å) for 2**	**Mechanical bond π-π distances (Å) for 1'**
100	3.970	3.800	
150	3.959	3.753	
173			3.694
200	3.980	3.718	
250	3.957	3.718	
300	3.984	3.820	

Table S5. Unit cell void in % calculated for **1** and **2** after manually removing the guest molecules. The probe used for the void's calculation had a diameter of 1.2 Å. The program used for the determination of the voids was Mercury (Version 2022.1.0).

Temperature (K)	**Unit cell Void (%) for 1**	**Unit cell Void (%) for 2**
100	37.8	35.5
150	38.0	35.9
200	38.4	36.9
250	38.6	37.6
300	39.2	35.9

Table S6. Distances among the centroids of the *p*-xy guest and the pyridine ring of TPB in **1** determined at different temperatures.

Temperature (K)	**p-xy-py-TPB distances (Å)**
100	4.195
150	4.179
200	4.162
250	4.192
300	4.152

Table S7. List of coordination bod angles (Zn-N-Zn) in crystals **1** at different temperatures.

Temperature (K)	**Angle θ_1: N-Zn-N**	**Angle θ_2: N-Zn-N**
100	102.31	100.87
150	102.63	101.19
200	102.59	101.43
250	102.22	101.83
300	102.31	101.52

Table S8. List of coordination bod angles (Zn-N-Zn) in crystals **2** at different temperatures.

Temperature (K)	**Angle θ_1: N-Zn-N**	**Angle θ_2: N-Zn-N**
100	99.46	99.57
150	100.16	100.63
200	98.86	101.10
250	100.49	101.7
300	99.31	99.10

Table S9. Crystal data and structure refinement for **1@100K**. CCDC: **2452216**

Identification code	**1@100K**	
Empirical formula	$C_{264}\ H_{240}\ I_{24}\ N_{24}\ Zn_{12}$	
Formula weight	7578.83	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	R -3 :H	
Unit cell dimensions	a = 38.7577(9) Å	α = 90°.
	b = 38.7577(9) Å	β = 90°.
	c = 16.1610(3) Å	γ = 120°.
Volume	21024.0(11) $Å^3$	
Z	3	
Density (calculated)	1.796 Mg/m^3	
Absorption coefficient	22.265 mm^{-1}	
F(000)	10872	
Crystal size	0.15 x 0.1 x 0.1 mm^3	
Theta range for data collection	3.035 to 76.504°.	
Index ranges	-34<=h<=46, -48<=k<=43, -10<=l<=19	
Reflections collected	26613	
Independent reflections	8971 [R(int) = 0.0726]	
Completeness to theta = 67.684°	98.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8971 / 22 / 397	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0737, wR2 = 0.1973	
R indices (all data)	R1 = 0.0919, wR2 = 0.2141	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.604 and -2.661 $e.Å^{-3}$	

Table S10. Crystal data and structure refinement for **1@150K**. CCDC: **2452217**.

Identification code	**1@150K**	
Empirical formula	$C_{264}\ H_{240}\ I_{24}\ N_{24}\ Zn_{12}$	
Formula weight	7578.83	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	R -3 :H	
Unit cell dimensions	a = 38.8366(13) Å	α = 90°.
	b = 38.8366(13) Å	β = 90°.
	c = 16.2247(10) Å	γ = 120°.
Volume	21192.9(19) $Å^3$	
Z	3	
Density (calculated)	1.781 Mg/m^3	
Absorption coefficient	22.087 mm^{-1}	
F(000)	10872	
Crystal size	0.15 x 0.1 x 0.1 mm^3	
Theta range for data collection	3.024 to 76.638°.	
Index ranges	-35<=h<=47, -47<=k<=47, -19<=l<=7	
Reflections collected	23947	
Independent reflections	9043 [R(int) = 0.0715]	
Completeness to theta = 67.684°	97.3 %	
Absorption correction	"multi-scan"	
Max. and min. transmission	1.00000 and 0.25159	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9043 / 14 / 407	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0690, wR2 = 0.1862	
R indices (all data)	R1 = 0.0938, wR2 = 0.2099	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.412 and -2.104 $e.Å^{-3}$	

Table S11. Crystal data and structure refinement for **1@200K**. CCDC: 2452221.

Identification code	**1@200K**	
Empirical formula	$C_{264}\ H_{240}\ I_{24}\ N_{24}\ Zn_{12}$	
Formula weight	7578.83	
Temperature	200(2) K	
Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	R -3 :H	
Unit cell dimensions	a = 38.9215(14) Å	α = 90°.
	b = 38.9215(14) Å	β = 90°.
	c = 16.2503(6) Å	γ = 120°.
Volume	21319.2(17) $Å^3$	
Z	3	
Density (calculated)	1.771 Mg/m^3	
Absorption coefficient	21.957 mm^{-1}	
F(000)	10872	
Crystal size	0.15 x 0.1 x 0.1 mm^3	
Theta range for data collection	3.779 to 77.156°.	
Index ranges	-44<=h<=45, -45<=k<=47, -7<=l<=19	
Reflections collected	24295	
Independent reflections	9129 [R(int) = 0.0813]	
Completeness to theta = 67.684°	97.1 %	
Absorption correction	"multi-scan"	
Max. and min. transmission	1.00000 and 0.25255	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9129 / 32 / 391	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0763, wR2 = 0.2054	
R indices (all data)	R1 = 0.1051, wR2 = 0.2330	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.595 and -1.905 $e.Å^{-3}$	

Table S12. Crystal data and structure refinement for **1@250K**. CCDC: 2452222.

Identification code	**1@250K**	
Empirical formula	$C_{264}\ H_{240}\ I_{24}\ N_{24}\ Zn_{12}$	
Formula weight	7578.83	
Temperature	250(2) K	
Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	R -3 :H	
Unit cell dimensions	a = 39.0207(18) Å	α = 90°.
	b = 39.0207(18) Å	β = 90°.
	c = 16.3353(6) Å	γ = 120°.
Volume	21540(2) $Å^3$	
Z	3	
Density (calculated)	1.753 Mg/m^3	
Absorption coefficient	21.731 mm^{-1}	
F(000)	10872	
Crystal size	0.15 x 0.1 x 0.1 mm^3	
Theta range for data collection	3.005 to 77.391°.	
Index ranges	-48<=h<=48, -37<=k<=45, -20<=l<=7	
Reflections collected	25079	
Independent reflections	9167 [R(int) = 0.0804]	
Completeness to theta = 67.684°	97.7 %	
Absorption correction	"multi-scan"	
Max. and min. transmission	1.00000 and 0.08144	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9167 / 44 / 386	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0794, wR2 = 0.2196	
R indices (all data)	R1 = 0.1165, wR2 = 0.2523	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.301 and -1.276 $e.Å^{-3}$	

Table S13. Crystal data and structure refinement for **1@300K**. CCDC: 2452242.

Identification code	**1@300K**	
Empirical formula	$C_{264}\ H_{240}\ I_{24}\ N_{24}\ Zn_{12}$	
Formula weight	7578.83	
Temperature	300(2) K	
Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	R -3 :H	
Unit cell dimensions	a = 39.0407(16) Å	α = 90°.
	b = 39.0407(16) Å	β = 90°.
	c = 16.2780(5) Å	γ = 120°.
Volume	21486.6(19) $Å^3$	
Z	3	
Density (calculated)	1.757 Mg/m^3	
Absorption coefficient	21.786 mm^{-1}	
F(000)	10872	
Crystal size	0.15 x 0.1 x 0.1 mm^3	
Theta range for data collection	3.013 to 76.532°.	
Index ranges	-49<=h<=47, -46<=k<=47, -19<=l<=8	
Reflections collected	25846	
Independent reflections	9144 [R(int) = 0.0592]	
Completeness to theta = 67.684°	98.4 %	
Absorption correction	"multi-scan"	
Max. and min. transmission	1.00000 and 0.14631	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9144 / 51 / 381	
Goodness-of-fit on F^2	1.079	
Final R indices [I>2sigma(I)]	R1 = 0.0848, wR2 = 0.2467	
R indices (all data)	R1 = 0.1040, wR2 = 0.2636	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.023 and -1.588 $e.Å^{-3}$	

Table S14. Crystal data and structure refinement for **2@100K**. CCDC: 2452223.

Identification code	**2@100K**	
Empirical formula	$C_{174}\ H_{144}\ I_{24}\ N_{24}\ O_6\ Zn_{12}$	
Formula weight	6497.16	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	R -3 :H	
Unit cell dimensions	a = 38.6352(9) Å	α = 90°.
	b = 38.6352(9) Å	β = 90°.
	c = 15.8231(4) Å	γ = 120°.
Volume	20454.5(11) Å^3	
Z	3	
Density (calculated)	1.582 Mg/m^3	
Absorption coefficient	22.792 mm^{-1}	
F(000)	9108	
Crystal size	0.17 x 0.12 x 0.10 mm^3	
Theta range for data collection	3.845 to 76.750°.	
Index ranges	-43<=h<=45, -47<=k<=45, -13<=l<=19	
Reflections collected	23524	
Independent reflections	8653 [R(int) = 0.1020]	
Completeness to theta = 67.684°	98.4 %	
Absorption correction	"Multi-scan"	
Max. and min. transmission	1.00000 and 0.43824	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8653 / 5 / 341	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.1057, wR2 = 0.2809	
R indices (all data)	R1 = 0.1251, wR2 = 0.2961	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.290 and -2.531 e.Å^{-3}	

Table S15. Crystal data and structure refinement for **2@150K**. CCDC: 2452231.

Identification code	**2@150K**	
Empirical formula	$C_{174}\ H_{144}\ I_{24}\ N_{24}\ O_6\ Zn_{12}$	
Formula weight	6497.16	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	R -3 :H	
Unit cell dimensions	a = 38.7388(8) Å	α = 90°.
	b = 38.7388(8) Å	β = 90°.
	c = 15.9128(3) Å	γ = 120°.
Volume	20680.9(9) $Å^3$	
Z	3	
Density (calculated)	1.565 Mg/m^3	
Absorption coefficient	22.542 mm^{-1}	
F(000)	9108	
Crystal size	0.17 x 0.12 x 0.10 mm^3	
Theta range for data collection	3.953 to 76.453°.	
Index ranges	-45<=h<=47, -47<=k<=44, -19<=l<=12	
Reflections collected	24167	
Independent reflections	8942 [R(int) = 0.0952]	
Completeness to theta = 67.684°	97.9 %	
Absorption correction	"Multi-scan"	
Max. and min. transmission	1.00000 and 0.37919	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8942 / 2 / 353	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0832, wR2 = 0.2337	
R indices (all data)	R1 = 0.0979, wR2 = 0.2495	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.229 and -1.559 e.$Å^{-3}$	

Table S16. Crystal data and structure refinement for **2@200K**. CCDC: 2452232.

Identification code	**2@200K**	
Empirical formula	$C_{174}\ H_{144}\ I_{24}\ N_{24}\ O_6\ Zn_{12}$	
Formula weight	6497.16	
Temperature	200(2) K	
Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	R -3 :H	
Unit cell dimensions	a = 38.8170(7) Å	α = 90°.
	b = 38.8170(7) Å	β = 90°.
	c = 16.0500(3) Å	γ = 120°.
Volume	20943.5(9) $Å^3$	
Z	3	
Density (calculated)	1.545 Mg/m^3	
Absorption coefficient	22.260 mm^{-1}	
F(000)	9108	
Crystal size	0.17 x 0.12 x 0.10 mm^3	
Theta range for data collection	3.808 to 76.205°.	
Index ranges	-31<=h<=45, -48<=k<=47, -13<=l<=19	
Reflections collected	24715	
Independent reflections	9158 [R(int) = 0.1125]	
Completeness to theta = 67.684°	98.6 %	
Absorption correction	"multi-scan"	
Max. and min. transmission	1.00000 and 0.04300	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9158 / 4 / 348	
Goodness-of-fit on F^2	1.276	
Final R indices [I>2sigma(I)]	R1 = 0.1154, wR2 = 0.3192	
R indices (all data)	R1 = 0.1387, wR2 = 0.3357	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.704 and -2.771 $e.Å^{-3}$	

Table S17. Crystal data and structure refinement for **2@250K**. CCDC: 2452233

Identification code	**2@250K**	
Empirical formula	$C_{174}\ H_{144}\ I_{24}\ N_{24}\ O_6\ Zn_{12}$	
Formula weight	6497.16	
Temperature	250(2) K	
Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	R -3 :H	
Unit cell dimensions	a = 38.8579(8) Å	α = 90°.
	b = 38.8579(8) Å	β = 90°.
	c = 16.2103(3) Å	γ = 120°.
Volume	21197.3(10) Å^3	
Z	3	
Density (calculated)	1.527 Mg/m^3	
Absorption coefficient	21.993 mm^{-1}	
F(000)	9108	
Crystal size	0.17 x 0.12 x 0.10 mm^3	
Theta range for data collection	3.941 to 76.390°.	
Index ranges	-48<=h<=47, -44<=k<=46, -19<=l<=7	
Reflections collected	24456	
Independent reflections	8968 [R(int) = 0.0611]	
Completeness to theta = 67.684°	97.6 %	
Absorption correction	"multi-scan"	
Max. and min. transmission	1.00000 and 0.29191	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8968 / 1 / 353	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0979, wR2 = 0.2841	
R indices (all data)	R1 = 0.1135, wR2 = 0.2943	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.669 and -1.568 e.Å^{-3}	

Table S18. Crystal data and structure refinement for **2@300K**.

Identification code	**2@300K**	
Empirical formula	$C_{168}\ H_{120}\ I_{24}\ N_{12}\ Zn_{24}$	
Formula weight	6921.23	
Temperature	300(2) K	
Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	R -3 :H	
Unit cell dimensions	a = 38.452(2) Å	α = 90°.
	b = 38.452(2) Å	β = 90°.
	c = 16.0939(6) Å	γ = 120°.
Volume	20608(2) $Å^3$	
Z	3	
Density (calculated)	1.673 Mg/m^3	
Absorption coefficient	23.656 mm^{-1}	
F(000)	9612	
Crystal size	0.17 x 0.12 x 0.10 mm^3	
Theta range for data collection	3.982 to 76.390°.	
Index ranges	-23<=h<=48, -48<=k<=34, -19<=l<=11	
Reflections collected	21610	
Independent reflections	8555 [R(int) = 0.1890]	
Completeness to theta = 67.684°	96.2 %	
Absorption correction	"multi-scan"	
Max. and min. transmission	1.00000 and 0.18113	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8555 / 0 / 168	
Goodness-of-fit on F^2	1.158	
Final R indices [I>2sigma(I)]	R1 = 0.3170, wR2 = 0.6185	
R indices (all data)	R1 = 0.3550, wR2 = 0.6305	
Extinction coefficient	n/a	
Largest diff. peak and hole	6.068 and -3.953 e.$Å^{-3}$	

Table S19. Computed DFT energies in **2@300K** and **1@300K**.

	2@300K **kcal/mol**	**1@300K kcal/mol**
Interaction energies(***E***) 1 mol of cages	Interlocked: 94.5 kcal/mol Non-Interlocked: 46.8 kcal/mol	Interlocked: 64.7 kcal/mol Non-Interlocked: 33.6 kcal/mol
Lattice energy (***E****) 1 mol of cages / chains	Single cage: 503 kcal/mol Chain: 400 kcal/mol	Single cage: 357 kcal/mol Chain: 306 kcal/mol

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