

## Supplementary Information

### Aftermath of Irradiation: The Stacking Faults in Crystal of Giant Supramolecule Unexpectedly Mended before Total Decay

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## Experimental

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Crystals of **1** were taken from a Schlenk flask under a stream of argon and immediately covered with perfluorinated Fomblin<sup>®</sup> mineral oil to prevent both decomposition and a loss of solvent. However, the crystals quickly lose solvent and are prone to quick amorphization out of mother solution even being so protected. X-ray diffraction studies faced many challenges, since the crystals have relatively small size and decompose rapidly losing solvent molecules. Moreover, the crystals are prone to twinning irrespective of size and shape (plates and prisms are twinned alike) and slowly decay when irradiated.

The quickly chosen single crystals covered by a drop of the oil were taken to the pre-centered goniometer head with CryoMount<sup>®</sup> and directly placed on diffractometer into a stream of cold nitrogen. The data for **1A** and three datasets for **1B** were collected on a Rigaku SuperNova diffractometer equipped with Titan<sup>S2</sup> CCD detector and a SuperNova Cu K $\alpha$  microfocus source using 0.5°  $\omega$  scans. The measurements were performed at 123 K. The datasets for **1B** were collected one after another without any change in the experimental setup, no recentering or other actions that change orientation of the crystal were used to maintain exactly the same measurement conditions. The same strategy used for all measurements of the crystal **1B** is presented in Figure S3.

Data collection, reduction and absorption correction based on were performed in *CrysAlisPRO*.<sup>1</sup> Absorption correction for **1B** was used with the same crystal faces found for the first (**1B-1**) measurement.

The structures of **1** were solved by *SHELX97*.<sup>2</sup> The structures were refined by full-matrix least-squares method against  $|F|^2$  in anisotropic approximation using *SHELXL97* or the multiprocessor and variable memory version *SHELXL2013* and *SHELXL2018*. All non-hydrogen atoms were refined in anisotropic approximation, while the hydrogen atoms were set in calculated positions and refined riding on pivot atoms. The solvent molecules in **1** are not fully localized due to disorder and featureless residual electron density map. No procedures modifying original dataset (like SQUEEZE) were used.

ORTEP drawings were generated in Olex2.<sup>3</sup> The supplementary crystallographic data for this publication (Tables S1: CCDC-2183584 – CCDC-2183586) can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033).

**Table S1. Experimental details for deteriorated compound 1: Crystals 1A and 1B**

Compound	<b>1</b> ·5.4(C <sub>2</sub> H <sub>3</sub> N)·0.4(CH <sub>2</sub> Cl <sub>2</sub> )	<b>1</b> ·4.8(C <sub>2</sub> H <sub>3</sub> N)	<b>1</b> ·4.8(C <sub>2</sub> H <sub>3</sub> N)
CCDC-Codes	CCDC-2183584	CCDC-2183586	CCDC-2183585
Crystal data	<b>1A</b>	<b>1B-2</b>	<b>1B-3</b>
Chemical formula	C <sub>150</sub> H <sub>210</sub> Cu <sub>14</sub> I <sub>14</sub> O <sub>20</sub> P <sub>40</sub> Ta <sub>10</sub> ·5.4(C <sub>2</sub> H <sub>3</sub> N)·0.4(CH <sub>2</sub> Cl <sub>2</sub> )	C <sub>150</sub> H <sub>210</sub> Cu <sub>14</sub> I <sub>14</sub> O <sub>20</sub> P <sub>40</sub> Ta <sub>10</sub> ·4.8(C <sub>2</sub> H <sub>3</sub> N)	C <sub>150</sub> H <sub>210</sub> Cu <sub>14</sub> I <sub>14</sub> O <sub>20</sub> P <sub>40</sub> Ta <sub>10</sub> ·4.8(C <sub>2</sub> H <sub>3</sub> N)
<i>M<sub>r</sub></i>	8303.29	8244.69	8244.69
Crystal system, space group	Monoclinic, <i>C2/m</i>	Monoclinic, <i>C2/m</i>	Monoclinic, <i>C2/m</i>
Temperature (K)	123	123	123
<i>a</i> , <i>b</i> , <i>c</i> (Å)	32.9318 (18), 26.330 (2), 20.9841 (9)	32.9341 (14), 26.3182 (14), 20.9738 (7)	32.9254 (14), 26.3712 (12), 21.0009 (6)
β (°)	126.265 (5)	126.718 (4)	126.930 (4)
<i>V</i> (Å <sup>3</sup> )	14670.6 (17)	14572.3 (12)	14576.3 (12)
<i>Z</i>	2	2	2
<i>F</i> (000)	7767	7707	7707
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	1.880	1.879	1.878
Radiation type	Cu <i>K</i> α	Cu <i>K</i> α	Cu <i>K</i> α
μ (mm <sup>-1</sup> )	21.72	21.80	21.81
Crystal shape and colour	Orange→brown prism	Orange→brown prism	Orange→brown prism
Crystal size (mm)	0.06 × 0.05 × 0.03	0.07 × 0.06 × 0.04	0.07 × 0.06 × 0.04
Data collection			
Diffractometer	SuperNova, Titan <sup>S2</sup>	SuperNova, Titan <sup>S2</sup>	SuperNova, Titan <sup>S2</sup>
Absorption correction	Gaussian	Gaussian	Gaussian
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.267, 0.518	0.327, 0.497	0.355, 0.520
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	28895, 14492, 8606	25766, 14128, 9310	26518, 14327, 8427
<i>R<sub>int</sub></i>	0.058	0.040	0.043
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.624	0.623	0.622
Range of <i>h</i> , <i>k</i> , <i>l</i>	<i>h</i> = -40→40, <i>k</i> = -17→32, <i>l</i> = -19→25	<i>h</i> = -40→34, <i>k</i> = -32→20, <i>l</i> = -23→25	<i>h</i> = -39→34, <i>k</i> = -32→20, <i>l</i> = -23→25
<b>Refinement</b>			
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.081, 0.251, 1.05	0.077, 0.243, 1.07	0.074, 0.235, 0.97
No. of reflections	14492	14128	14327
No. of parameters	697	685	694
No. of restraints	5	8	5
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Δ <sub>max</sub> , Δ <sub>min</sub> (e Å <sup>-3</sup> )	3.34, -2.77	4.58, -2.57	4.46, -2.24

Computer programs: *CrysAlis PRO* 1.171.38.41 (Rigaku OD, 2015), *SHELXL*T (Sheldrick, 2014), *SHELXL2014/7* (Sheldrick, 2014), *SHELXL2018/3* (Sheldrick, 2018).

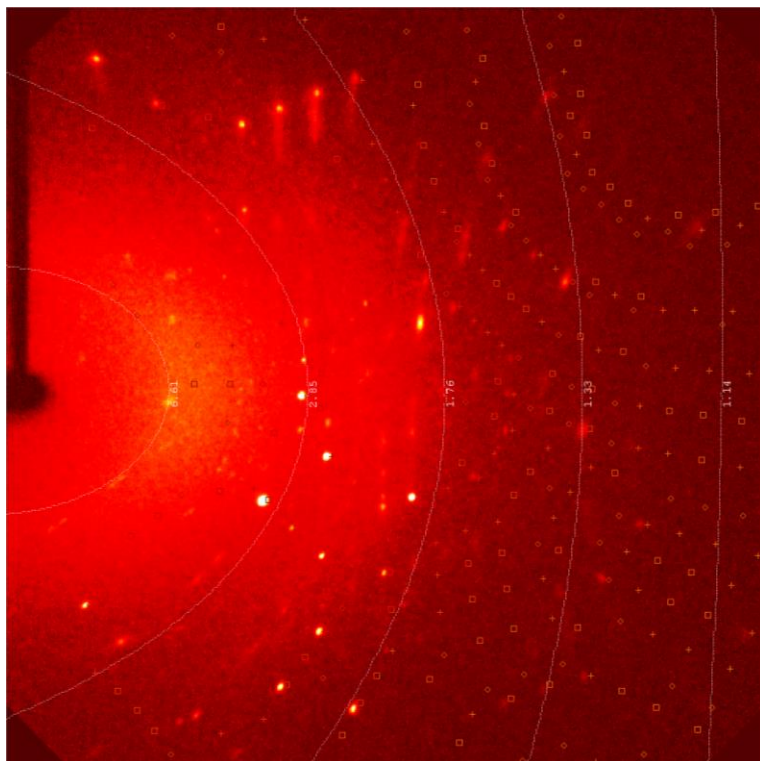


Figure S1. Slight streaking on the diffraction pattern of **1A**. Indexation is shown in a subcell, CrysAlisPro.<sup>1</sup>

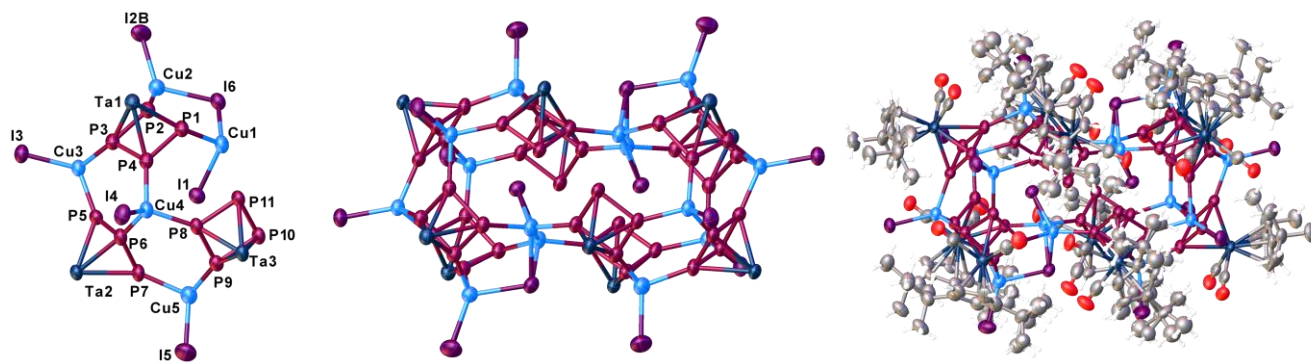
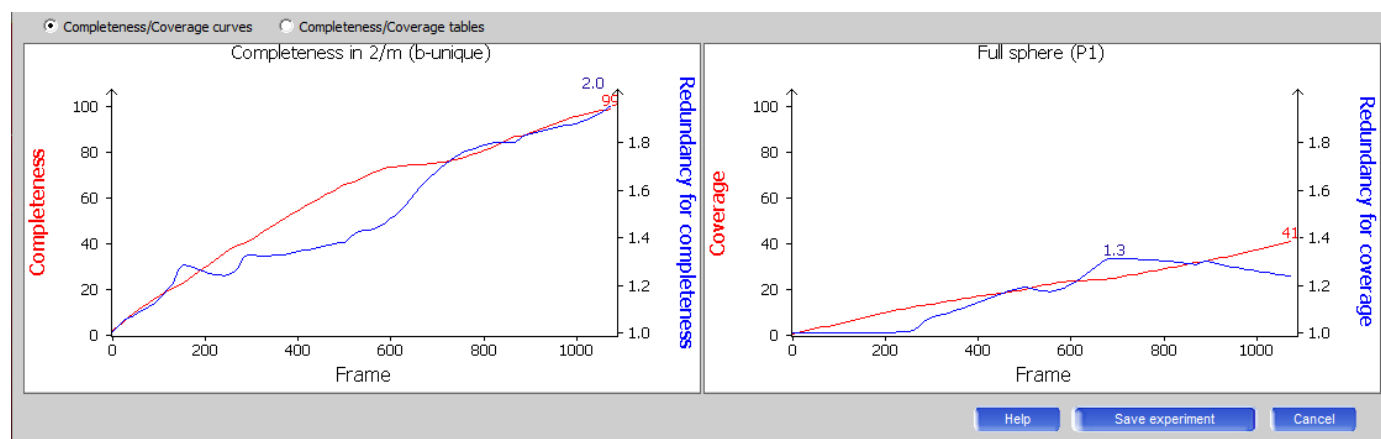


Figure S2. ORTEP drawings of supramolecule in crystal **1A**: (left) a crystallographically unique part (cf. **Table S4** for geometric characteristics), (middle) inorganic core and (right) overall view are shown (a.d.p. ellipsoids at 50% probability).<sup>3</sup>

## Crystal 1B

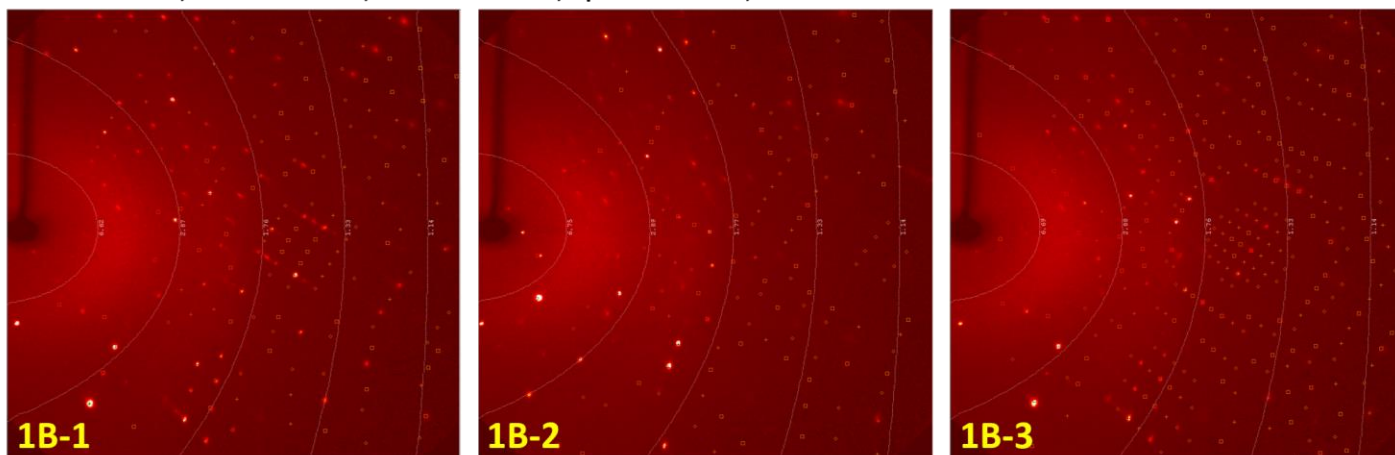


**Figure S3.** Data collection strategy for all repeated experiments from the crystal **1B** (CrysAlisPro output).<sup>[1]</sup>

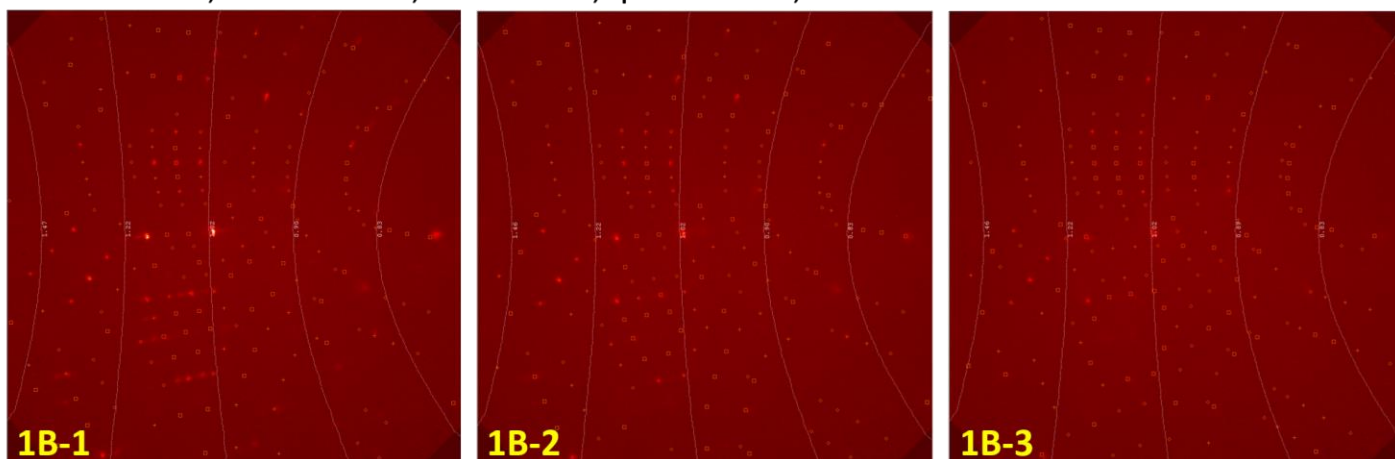
**Table S2.** List of runs (angles in degrees, time in seconds).

#Run	Type	$\omega$ , start	$\omega$ , end	Width	$t_{\text{exposure}}$	$\theta$	$\kappa$	$\phi$	Frames
1	$\omega$	-24.00	62.00	0.50	15.00	44.92	-57.00	60.00	172
2	$\omega$	26.00	118.00	0.50	15.00	44.92	19.00	-120.00	184
3	$\omega$	33.00	133.00	0.50	40.00	104.50	-15.00	-90.00	200
4	$\omega$	49.00	127.00	0.50	40.00	104.50	-45.00	-120.00	156
5	$\omega$	82.00	173.00	0.50	40.00	104.50	45.00	-90.00	182
6	$\omega$	32.00	128.00	0.50	40.00	104.50	-30.00	90.00	192

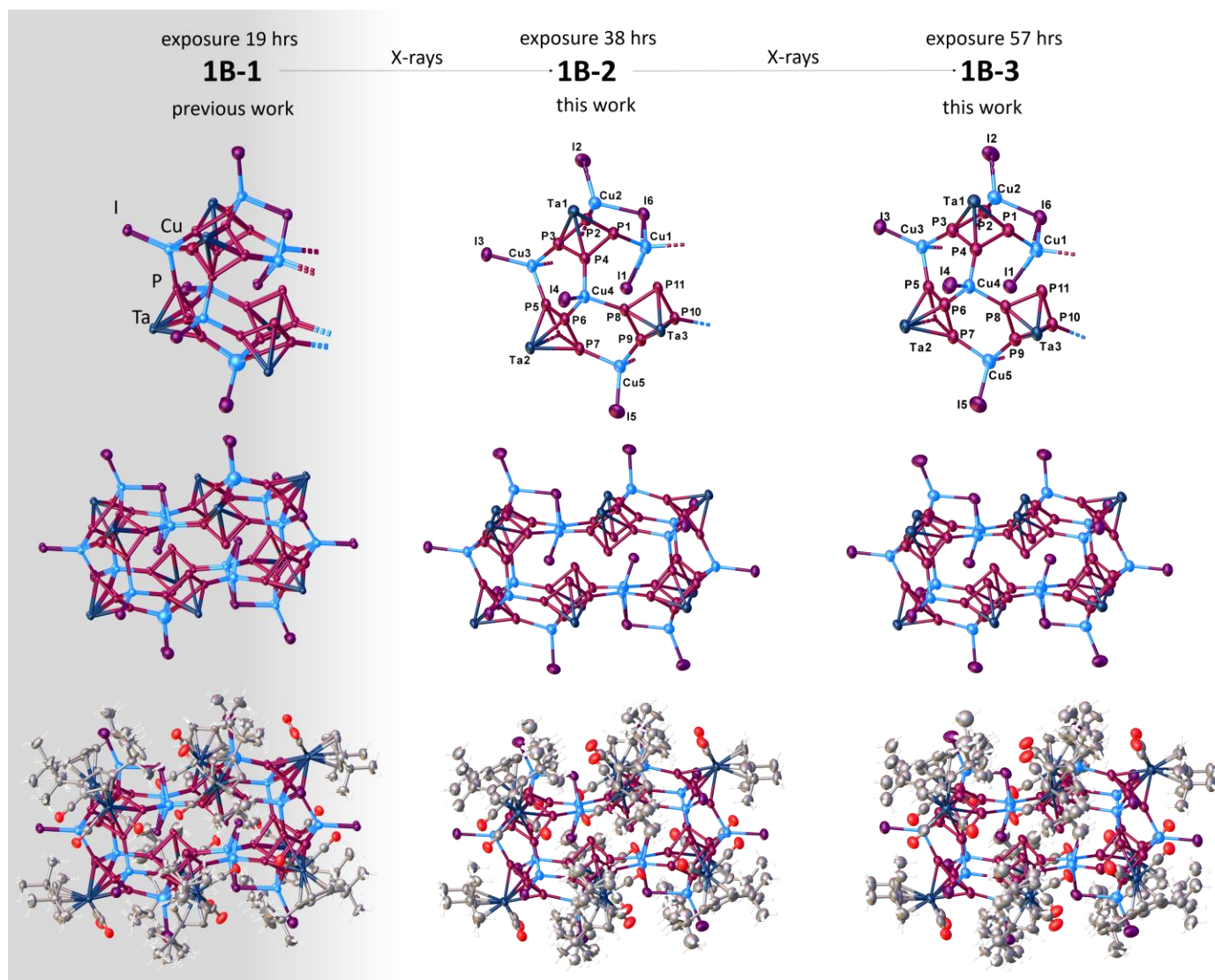
$\omega = -4.00^\circ$ ;  $\theta = 44.02^\circ$ ;  $\kappa = -57.00^\circ$ ;  $\phi = 60.00^\circ$ ; DD = 60 mm



$\omega = 121.50^\circ$ ;  $\theta = 104.50^\circ$ ;  $\kappa = 45.00^\circ$ ;  $\phi = -90.00^\circ$ ; DD = 60 mm



**Figure S4.** Slight streaking on the diffraction pattern of **1B** changing with exposure to X-rays. Indexation is shown in a subcell, CrysAlisPro.<sup>[1]</sup>



**Figure S5.** ORTEP drawings of supramolecule in crystal **1B**: (left) the ‘overlapping’ molecules in crystal after 1<sup>st</sup> experiment (**1B-1** <sup>[4]</sup>), (middle) after 2<sup>nd</sup> experiment (**1B-2**) and (right) and after 3<sup>rd</sup> experiment (**1B-3**) (a.d.p. ellipsoids at 50% probability). For each supramolecule a crystallographically unique part, inorganic core and overall view are shown (up-middle-down, respectively).<sup>[3]</sup>



## Comparison of 1A, 1B-2 and 1B-3

**Table S3.** Intensities of the structural and superstructural reflections of general type for crystals of 1\*

Type of refl.*	Crystal 1A					Crystal 1B-2					Crystal 1B-3				
	Total	N>3 $\sigma$	N>10 $\sigma$	I av.	$\sigma$ av.	Total	N>3 $\sigma$	N>10 $\sigma$	I av.	$\sigma$ av.	Total	N>3 $\sigma$	N>10 $\sigma$	I av.	$\sigma$ av.
GGG	20474	10274	5442	10.8	1.0	12682	7290	4070	9.9	0.5	13332	6722	3478	8.0	0.5
UGG	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
GUG	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
UUG	20724	5923	2203	3.5	0.9	12706	3118	1227	1.6	0.5	13526	1950	404	0.7	0.5
GGU	20721	6036	2190	3.5	0.9	12729	3227	1224	1.6	0.5	12729	3227	1224	0.7	0.5
UGU	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
GUU	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
UUU	20483	10350	5396	10.5	1.0	12660	7211	4090	9.8	0.5	13336	6664	3424	7.9	0.5
$\langle I_{\text{sub.}} \rangle$				10.65	1.0				9.85	0.5				7.95	0.5
$\langle I_{\text{super.}} \rangle$				3.5	0.9				1.6	0.5				0.7	0.5
$\langle I_{\text{super.}}/I_{\text{sub.}} \rangle$				0.33					0.16					0.09	
$\langle I_{\text{sub.}}/I_{\text{super.}} \rangle$				3.04					6.16					11.3	

\* Integration in supercell; G = even (gerade), U = odd (ungerade); N = number of reflections;  $\langle I_{\text{sub.}} \rangle$  and  $\langle I_{\text{super.}} \rangle$  = respective average intensity of sub- and superstructural reflections.

**Table S4.** Selected geometric parameters for 1B-2 (Å, °)

Bond, Å	1A	1B-2	1B-3	Bond, Å	1A	1B-2	1B-3
Cu1—I1	2.589(3)	2.591(3)	2.592(3)	Cu4—P6	2.304(5)	2.302(5)	2.299(5)
Cu1—I6	2.674(3)	2.673(3)	2.673(3)	Cu4—P4	2.310(5)	2.305(4)	2.307(4)
Cu2—I2 <sup>ii</sup>	2.507(4)	2.503(4)	2.512(4)	Cu5—P9	2.361(5)	2.345(4)	2.352(4)
Cu2—I2	2.507(4)	2.503(4)	2.512(4)	Cu5—P9 <sup>ii</sup>	2.361(5)	2.345(4)	2.352(4)
Cu3—I3	2.527(3)	2.534(3)	2.538(3)	Cu5—P7	2.373(6)	2.379(6)	2.378(6)
Cu4—I4	2.521(3)	2.522(2)	2.526(2)	P1—P2	2.142(6)	2.149(6)	2.139(6)
Cu5—I5	2.534(4)	2.539(4)	2.539(4)	P1—P4	2.165(6)	2.175(5)	2.175(5)
Cu1—P1	2.439(5)	2.443(5)	2.436(5)	P2—P3	2.136(6)	2.149(5)	2.147(5)
Cu1—P10 <sup>i</sup>	2.245(4)	2.253(4)	2.251(4)	P3—P4	2.163(6)	2.164(6)	2.165(6)
Cu2—P2	2.278(5)	2.272(5)	2.274(4)	P5—P6	2.142(6)	2.139(6)	2.140(6)
Cu2—P2 <sup>ii</sup>	2.278(5)	2.272(5)	2.274(4)	P5—P6 <sup>ii</sup>	2.142(6)	2.139(6)	2.140(6)
Cu2—I6	2.700(4)	2.707(4)	2.705(4)	P6—P7	2.151(6)	2.163(6)	2.160(6)
Cu3—P5	2.289(6)	2.298(6)	2.303(6)	P8—P9	2.140(6)	2.149(6)	2.143(6)
Cu3—P3	2.328(5)	2.334(4)	2.332(4)	P8—P11	2.148(5)	2.153(4)	2.150(5)
Cu3—P3 <sup>ii</sup>	2.328(5)	2.334(4)	2.333(4)	P9—P10	2.165(5)	2.172(5)	2.169(5)
Cu4—P8	2.284(4)	2.287(4)	2.287(4)	P10—P11	2.176(6)	2.167(6)	2.175(6)
Bond angle, °	1A	1B-2	1B-3	Bond angle, °	1A	1B-2	1B-3
P10 <sup>i</sup> —Cu1—P1	118.3(2)	118.17(19)	118.60(18)	P9—Cu5—P9 <sup>ii</sup>	109.0(3)	108.5(2)	108.2(2)
P2—Cu2—P2 <sup>ii</sup>	94.6(3)	94.7(2)	95.1(2)	P9—Cu5—P7	102.51(17)	102.47(15)	102.68(16)
P5—Cu3—P3	97.19(16)	96.77(15)	96.94(15)	P9 <sup>ii</sup> —Cu5—P7	102.52(17)	102.48(15)	102.68(16)
P5—Cu3—P3 <sup>ii</sup>	97.19(16)	96.77(15)	96.94(15)	Cu1—I1—Cu1 <sup>ii</sup>	67.85(13)	67.39(12)	67.72(12)
P3—Cu3—P3 <sup>ii</sup>	101.0(3)	101.6(2)	102.0(2)	Cu1 <sup>ii</sup> —I6—Cu1	65.42(13)	65.05(12)	65.41(12)
P8—Cu4—P6	102.47(18)	102.56(17)	102.62(16)	Cu1 <sup>ii</sup> —I6—Cu2	99.86(9)	99.82(8)	99.46(9)
P8—Cu4—P4	103.97(16)	103.97(14)	104.00(15)	Cu1—I6—Cu2	99.86(9)	99.82(8)	99.46(9)
P6—Cu4—P4	99.62(18)	99.14(17)	99.38(16)				

Symmetry code(s): (i) -x+2, y, -z; (ii) x, -y, z; (iii) -x+1, y, -z-1.

## References

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- <sup>1</sup> CrysAlisPRO, different versions 2015-2022, Rigaku Oxford Diffraction.
- <sup>2</sup> G. M. Sheldrick. *Acta Cryst.* **C71**, 3-8 (2015).
- <sup>3</sup> O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Cryst.* **42**, 339-341 (2009).
- <sup>4</sup> F. Dielmann, E. V. Peresypkina, B. Kraemer, F. Hastreiter, B. P. Johnson, M. Zabel, C. Heindl and M. Scheer, *Angew. Chem. Int. Ed.*, 2016, **55**, 14833.