Negative X-ray expansion in cadmium cyanide

Supplementary Information

Chloe S. Coates,[a,b] Claire A. Murray,[c] Hanna L. B. Boström,[a,d] Emily M. Reynolds[a,e] and Andrew L. Goodwin*[a]

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[a]Inorganic Chemistry Laboratory, South Parks Road, Oxford, U. K., OX1 3QR.
[b]Department of Chemistry, Lensfield Road, Cambridge, U. K.
[c]Diamond Light Source, Harwell Campus, Didcot, Oxfordshire, U. K. OX11 0DE.
[d]Nanochemistry Department, Max Planck Institute for Solid State Research, Heisenbergstr. 1, Stuttgart, Germany, 70569
[e]ISIS Facility, STFC Rutherford Appleton Laboratory, Didcot, Oxfordshire OX11 0QX, U. K.
*Electronic address: andrew.goodwin@chem.ox.ac.uk

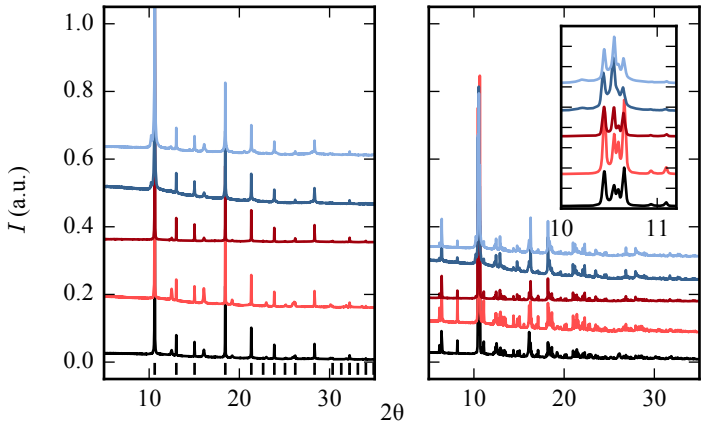

Figure S1 Left: Five samples of $Cd(CN)_2$ measured at 300 K; the positions of Bragg reflections corresponding to $Pn\bar{3}m$ symmetry are shown as tick marks; peaks corresponding to impurities are shown with an asterisk. Right: The same five samples of $Cd(CN)_2$ measured at 100 K. The intensity distribution at 100 K varies between samples, suggesting there are multiple competing phases at low temperature. Shown magnified for $10^\circ < 2\theta < 11^\circ$ in the inset. $\lambda = 0.82538$ Å.

Table S1 Supplmentary information for Figure 2 in the main text. X-ray irradiation dependence of the lattice parameters for $Cd(CN)_2$ with a $KMn[Ag(CN)_2]_3$ standard, obtained from Pawley refinements collected in 10 K increments on heating between 100 K and 160 K. The sample was translated at each temperature point in order to irradiate pristine $Cd(CN)_2$.

		$Cd(CN)_2$	$KMn[Ag(CN)_2]_3$		
T (K)	Radiation (s)	a (Å)	a (Å)	c (Å)	R_{wp} (%)
100.0	10.5	6.34294(45)	6.82229(9)	8.2313(2)	14.568
100.0	22.0	6.33957(31)	6.82233(8)	8.23152(17)	12.707
100.0	33.5	6.33437(21)	6.82229(7)	8.23164(14)	10.524
100.0	46.0	6.32682(15)	6.82250(6)	8.23173(12)	9.136
100.0	57.0	6.32139(9)	6.82250(5)	8.23177(11)	8.104
100.0	68.0	6.31903(6)	6.82265(5)	8.23182(10)	7.198
100.0	78.5	6.31745(5)	6.82255(4)	8.23189(9)	6.456
100.0	90.0	6.31602(4)	6.82265(4)	8.23174(8)	5.887
100.0	101.4	6.31455(3)	6.82258(4)	8.23169(7)	5.492
100.0	113.4	6.31313(3)	6.82261(3)	8.23157(7)	5.251
100.0	124.9	6.31188(3)	6.82265(3)	8.23167(7)	5.154
100.0	136.5	6.31052(3)	6.82261(3)	8.23167(7)	5.080
100.0	148.4	6.30908(3)	6.82261(3)	8.23163(7)	5.063
100.0	160.4	6.30776(3)	6.82258(3)	8.23162(7)	5.050
100.0	170.9	6.30666(3)	6.82269(3)	8.23182(7)	5.049
100.0	181.9	6.30536(3)	6.82265(3)	8.23166(7)	5.084
100.0	192.9	6.30413(3)	6.82260(3)	8.23165(7)	5.064
100.0	203.5	6.30304(3)	6.82263(3)	8.23170(7)	5.069
100.0	213.1	6.30201(3)	6.82268(3)	8.23169(7)	5.047
100.1	224.5	6.30102(3)	6.82273(3)	8.23179(7)	5.047
110.2	11.2	6.31235(3)	6.82590(4)	8.22808(7)	5.086
110.2	23.8	6.31096(3)	6.82596(4)	8.22798(7)	5.065
110.2	35.3	6.30964(3)	6.82597(4)	8.22781(7)	5.045
110.1	45.8	6.30868(3)	6.82622(4)	8.22787(7)	5.035
110.1	58.3	6.30755(3)	6.82627(4)	8.22794(7)	5.005
110.1	68.8	6.30620(3)	6.82601(4)	8.22752(7)	5.043
110.1	79.8	6.30534(3)	6.82617(4)	8.22776(7)	4.949
110.1	91.8	6.30435(3)	6.82624(4)	8.22787(7)	4.948
110.1	103.4	6.30326(3)	6.82624(4)	8.22779(7)	4.945
110.1	113.9	6.30232(3)	6.82619(4)	8.22768(7)	4.915
110.1	125.4	6.30143(3)	6.82624(4)	8.22778(7)	4.913
110.1	135.0	6.30065(3)	6.82624(4)	8.22776(7)	4.925
110.0	145.5	6.29977(3)	6.82624(4)	8.22770(7)	4.913
110.1	157.0	6.29895(3)	6.82623(4)	8.22770(7)	4.928
110.0	168.6	6.29810(3)	6.82630(4)	8.22767(7)	4.895
110.0	180.5	6.29723(3)	6.82625(4)	8.22772(7)	4.923
110.0	190.5	6.29646(3)	6.82624(4)	8.22770(7)	4.881
110.0	201.0	6.29580(3)	6.82621(4)	8.22769(7)	4.907
110.0	213.0	6.29509(3)	6.82628(4)	8.22778(7)	4.883
110.0	223.0	6.29442(3)	6.82634(4)	8.22778(7)	4.856

Table S2 Table S1 continued

		$Cd(CN)_2$	$KMn[Ag(CN)_2]_3$		
T (K)	Radiation (s)	a (Å)	a (Å)	c (Å)	R_{wp} (%)
120.2	11.8	6.31144(4)	6.82993(4)	8.22314(8)	5.233
120.2	22.8	6.31014(4)	6.82990(4)	8.22283(8)	5.276
120.2	33.4	6.30915(4)	6.83000(4)	8.22302(8)	5.234
120.1	43.9	6.30801(4)	6.82997(4)	8.22286(8)	5.200
120.1	55.9	6.30696(4)	6.83005(4)	8.22282(8)	5.186
120.1	67.8	6.30572(4)	6.82998(4)	8.22263(8)	5.201
120.1	78.4	6.30497(4)	6.83015(4)	8.22291(8)	5.141
120.0	88.9	6.30391(4)	6.83005(4)	8.22267(8)	5.176
120.0	100.0	6.30302(4)	6.83007(4)	8.22272(8)	5.190
120.1	112.0	6.30209(4)	6.83007(4)	8.22264(8)	5.161
120.1	122.5	6.30126(4)	6.83011(4)	8.22261(8)	5.151
120.1	133.1	6.30050(4)	6.83009(4)	8.22277(8)	5.140
120.0	143.6	6.29965(4)	6.83008(4)	8.22265(8)	5.176
120.0	153.2	6.29903(4)	6.83017(4)	8.22281(8)	5.081
120.0	164.7	6.29823(4)	6.83017(4)	8.22273(8)	5.092
120.0	175.2	6.29749(4)	6.83011(4)	8.22272(8)	5.127
120.1	186.8	6.29678(4)	6.83016(4)	8.22267(8)	5.139
120.0	198.3	6.29611(4)	6.83015(4)	8.22282(8)	5.124
120.0	208.9	6.29536(4)	6.83019(4)	8.22272(8)	5.127
120.1	218.5	6.29475(4)	6.83019(4)	8.22274(8)	5.130
130.2	11.4	6.31104(3)	6.83359(4)	8.21856(8)	4.612
130.2	22.0	6.31000(3)	6.83374(4)	8.21856(8)	4.602
130.1	32.5	6.30914(3)	6.83389(4)	8.21873(8)	4.594
130.1	44.5	6.30789(3)	6.83379(4)	8.21849(8)	4.558
130.1	55.9	6.30695(3)	6.83388(4)	8.21858(8)	4.531
130.1	67.9	6.30603(3)	6.83396(4)	8.21867(8)	4.548
130.1	78.5	6.30516(3)	6.83406(4)	8.21862(8)	4.512
130.1	90.0	6.30398(3)	6.83388(4)	8.21822(8)	4.523
130.1	101.6	6.30313(3)	6.83393(4)	8.21839(8)	4.506
130.1	112.1	6.30234(3)	6.83393(4)	8.21825(8)	4.504
130.0	122.6	6.30157(3)	6.83392(4)	8.21840(8)	4.466
130.1	133.6	6.30088(3)	6.83413(4)	8.21838(8)	4.469
130.1	145.6	6.30006(3)	6.83411(4)	8.21834(8)	4.426
130.0	157.1	6.29930(3)	6.83409(4)	8.21827(7)	4.432
130.0	168.7	6.29862(3)	6.83406(4)	8.21853(7)	4.448
130.0	179.7	6.29795(3)	6.83415(4)	8.21854(8)	4.422
130.0	191.1	6.29719(3)	6.83415(4)	8.21844(7)	4.430
130.0	202.5	6.29641(3)	6.83408(4)	8.21832(8)	4.433
130.0	213.5	6.29587(3)	6.83409(4)	8.21852(7)	4.411
130.0	224.0	6.29515(3)	6.83405(4)	8.21852(8)	4.454

Table S3 Table S2 continued

		$Cd(CN)_2$	$KMn[Ag(CN)_2]_3$		
T (K)	Radiation (s)	a (Å)	a (Å)	c (Å)	R_{wp} (%)
140.0	11.5	6.31004(3)	6.83787(4)	8.21451(7)	4.069
140.0	22.4	6.30915(3)	6.83809(4)	8.21466(8)	4.048
140.1	32.4	6.30808(3)	6.83797(4)	8.21425(8)	4.003
140.2	43.0	6.30716(3)	6.83800(4)	8.21431(8)	4.029
140.1	54.9	6.30631(3)	6.83814(4)	8.21449(8)	4.017
140.1	64.9	6.30532(3)	6.83810(4)	8.21421(8)	4.031
140.0	75.5	6.30471(3)	6.83826(4)	8.21443(8)	3.992
140.1	87.5	6.30370(3)	6.83820(4)	8.21428(8)	3.992
140.1	99.5	6.30282(3)	6.83804(4)	8.21424(8)	3.951
140.0	111.0	6.30209(3)	6.83821(4)	8.21434(8)	3.950
140.1	122.0	6.30112(3)	6.83803(4)	8.21404(7)	3.933
140.1	133.0	6.30065(3)	6.83841(4)	8.21435(7)	3.941
140.0	145.0	6.29978(3)	6.83824(4)	8.21424(7)	3.927
140.0	154.9	6.29915(3)	6.83838(4)	8.21428(7)	3.905
140.1	165.5	6.29854(3)	6.83830(4)	8.21433(7)	3.903
140.0	178.0	6.29764(3)	6.83815(4)	8.21409(7)	3.904
140.0	189.6	6.29722(3)	6.83848(4)	8.21447(7)	3.891
140.0	201.5	6.29637(3)	6.83828(4)	8.21442(7)	3.895
140.0	213.1	6.29567(3)	6.83829(4)	8.21431(7)	3.911
140.0	224.6	6.29507(3)	6.83831(4)	8.21441(7)	3.882
150.1	11.4	6.31011(3)	6.84231(4)	8.21052(7)	3.747
150.2	22.0	6.30928(3)	6.84248(4)	8.21054(7)	3.720
150.2	32.5	6.30814(3)	6.84226(4)	8.21020(7)	3.729
150.1	43.5	6.30737(3)	6.84254(4)	8.21021(7)	3.656
150.1	53.9	6.30637(3)	6.84250(4)	8.20998(7)	3.683
150.1	64.3	6.30576(3)	6.84261(4)	8.21029(7)	3.659
150.1	76.3	6.30476(3)	6.84262(4)	8.21012(7)	3.679
150.1	86.3	6.30413(3)	6.84284(4)	8.21026(7)	3.650
150.1	96.2	6.30330(3)	6.84279(4)	8.21003(7)	3.666
150.1	106.7	6.30261(3)	6.84282(4)	8.21010(7)	3.667
150.1	118.3	6.30184(3)	6.84277(4)	8.21009(7)	3.642
150.0	128.9	6.30112(3)	6.84280(4)	8.20998(7)	3.625
150.0	139.4	6.30043(3)	6.84271(4)	8.20999(7)	3.606
150.0	151.0	6.29976(3)	6.84273(4)	8.21005(7)	3.644
150.0	163.0	6.29904(3)	6.84283(4)	8.20998(7)	3.622
150.0	173.5	6.29840(3)	6.84279(4)	8.21001(7)	3.634
150.0	184.0	6.29763(3)	6.84268(4)	8.20977(7)	3.681
150.0	196.0	6.29712(3)	6.84280(4)	8.20991(7)	3.627
150.0	206.0	6.29650(3)	6.84285(4)	8.20991(7)	3.657
150.1	216.5	6.29595(3)	6.84283(4)	8.21000(7)	3.602

Table S4 Table S3 continued

		$Cd(CN)_2$	$KMn[Ag(CN)_2]_3$		
T (K)	Radiation (s)	a (Å)	a (Å)	c (Å)	R_{wp} (%)
160.1	10.5	6.30931(3)	6.84645(4)	8.20630(8)	3.405
160.2	21.1	6.30833(3)	6.84635(4)	8.20620(8)	3.365
160.2	31.6	6.30750(3)	6.84640(4)	8.20619(8)	3.344
160.1	43.5	6.30657(3)	6.84649(4)	8.20626(8)	3.359
160.1	54.8	6.30589(3)	6.84677(4)	8.20647(8)	3.346
160.0	65.8	6.30474(3)	6.84649(4)	8.20588(8)	3.359
160.0	76.4	6.30406(3)	6.84677(4)	8.20600(8)	3.336
160.1	88.2	6.30319(3)	6.84678(4)	8.20595(8)	3.343
160.0	100.2	6.30263(3)	6.84696(4)	8.20632(8)	3.333
160.0	111.8	6.30163(3)	6.84670(4)	8.20598(8)	3.332
160.0	124.4	6.30112(3)	6.84700(4)	8.20630(8)	3.294
160.0	135.9	6.30023(3)	6.84696(4)	8.20602(8)	3.330
160.0	146.4	6.29953(3)	6.84693(4)	8.20585(8)	3.312
160.0	158.4	6.29883(3)	6.84683(4)	8.20598(8)	3.305
160.0	168.4	6.29813(3)	6.84679(4)	8.20589(8)	3.315
160.0	178.4	6.29753(3)	6.84680(4)	8.20590(8)	3.325
160.0	190.4	6.29697(3)	6.84684(4)	8.20587(8)	3.300
160.0	202.0	6.29650(3)	6.84700(4)	8.20606(7)	3.276
160.0	213.5	6.29582(3)	6.84702(4)	8.20595(8)	3.298
160.1	224.1	6.29516(3)	6.84694(4)	8.20582(8)	3.308

Table S5 Variation in $Cd(CN)_2$ lattice parameter and volume with temperature as determined *via* Pawley refinements of powder diffraction data. This is shown graphically in Figure 4(a) of the main text.

T (K)	R_{wp} (%)	a (Å)	V (Å^3)
150	10.4363677	6.3182(3)	252.22(3)
210	5.8977919	6.31916(6)	252.336(7)
270	5.2404851	6.30956(6)	251.187(7)
330	5.1719198	6.29567(6)	249.531(7)
390	5.6221029	6.29437(5)	249.377(6)
450	5.322882	6.28693(5)	248.494(6)
510	4.4680513	6.27952(5)	247.616(6)
570	4.1460017	6.27210(5)	246.740(6)
630	4.3596492	6.26498(5)	245.901(6)
690	4.4850049	6.25839(5)	245.126(6)
750	3.6457796	6.25289(5)	244.479(6)

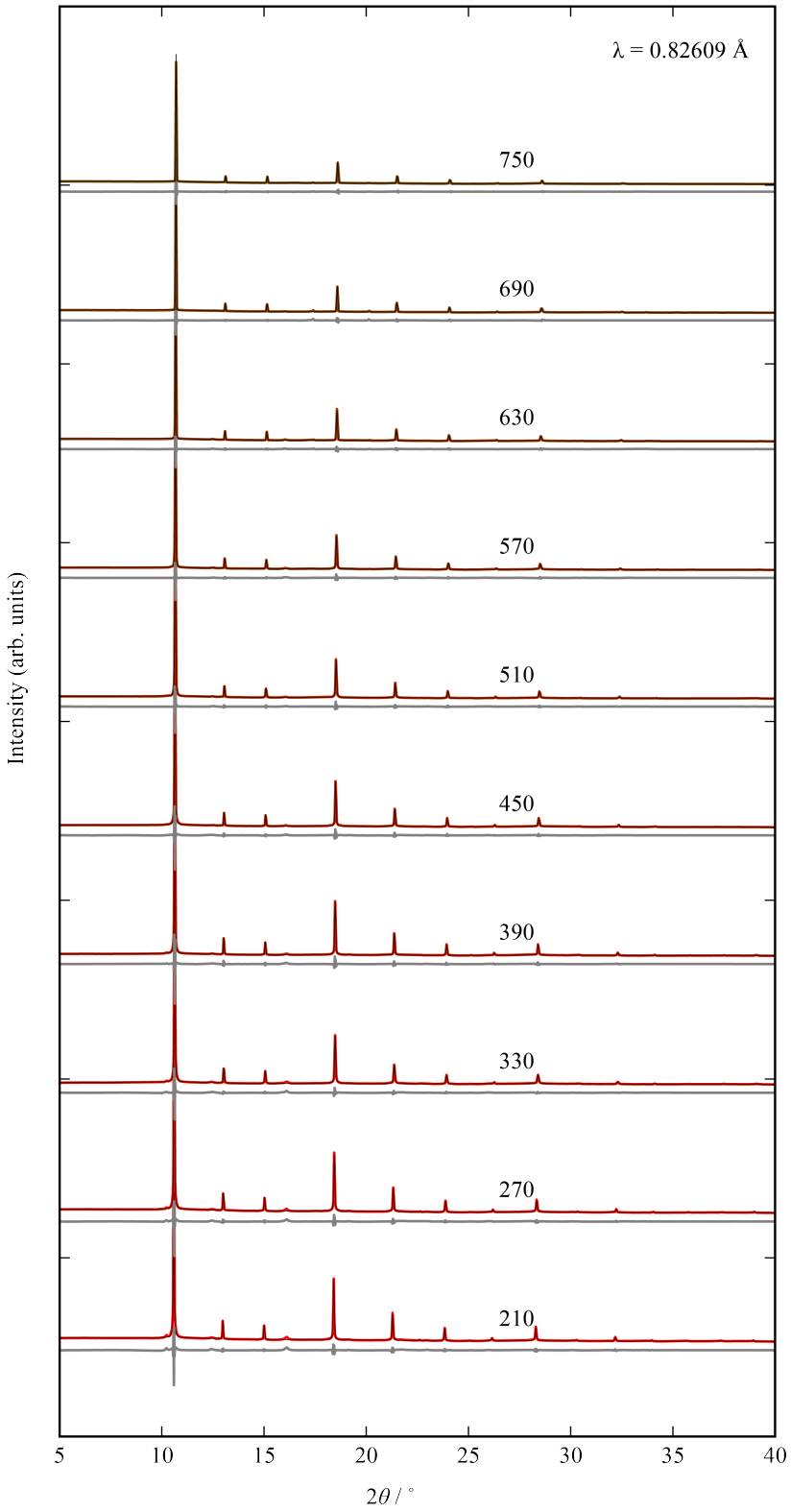

Figure S2 Pawley refinements of variable temperature X-ray data for $Cd(CN)_2$, collected at 60 K intervals between 210 and 750 K. The capillary was translated for each temperature point in order to irradiate pristine $Cd(CN)_2$. Data shown in red, fit in black and difference curve in grey. Space group $Pn\bar{3}m$ with lattice parameter $a \sim 6.3$ Å. $\lambda = 0.82609$ Å. The resulting lattice parameters used for determination of the thermal expansion coefficient are given in the subsequent table.

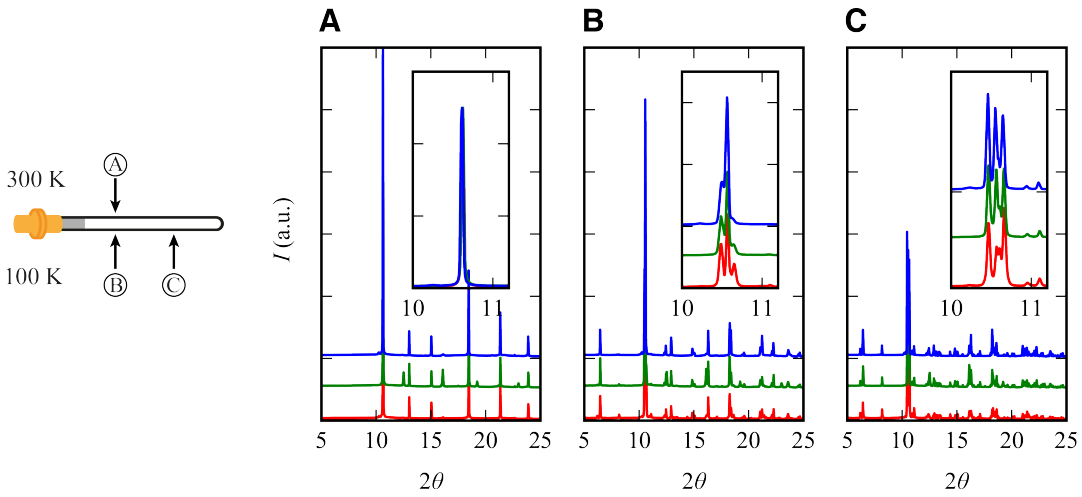

Figure S3 The effect of irradiation with X-rays at room temperature prior to cooling is robust across different samples shown in blue, green and red. Diffraction patterns of samples of $Cd(CN)_2$ collected at (a) room temperature, (b) 100 K in the same position along the capillary and (c) at 100 K having been translated by 2.5 mm in order to measure pristine $Cd(CN)_2$.

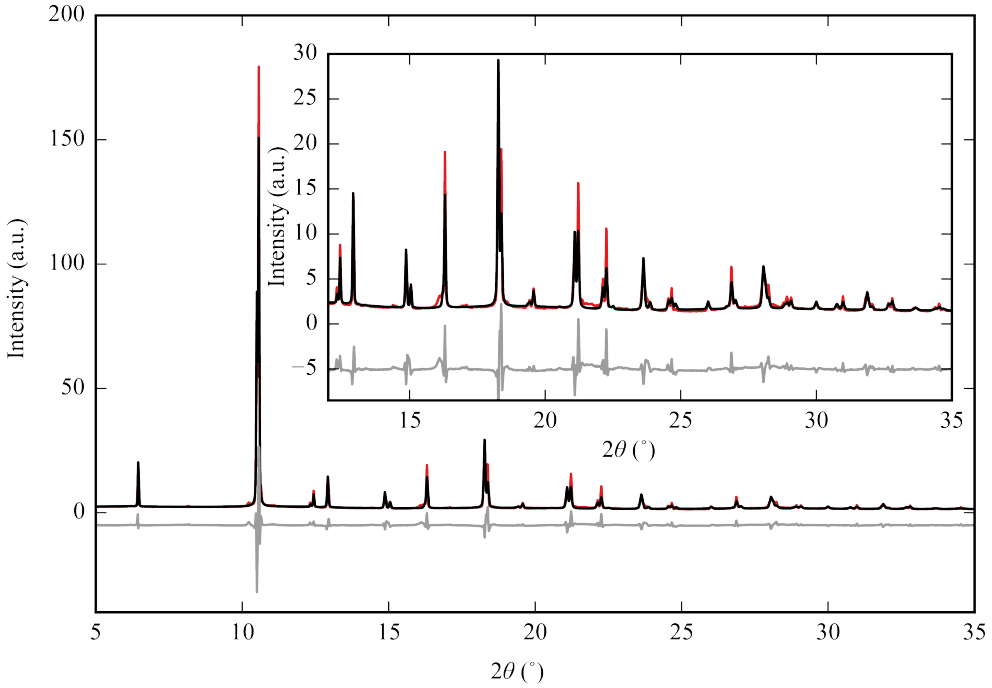

Figure S4 Rietveld refinement of X-ray data for $Cd(CN)_2$, collected at 100 K [Figure 3 in the main text, red pattern] using the $I4_1/amd$ structure at 100 K identified in Ref. 1. The sample was irradiated prior to cooling, resulting in a simpler diffraction pattern compared to pristine $Cd(CN)_2$ at 100 K. This could be refined using the tetragonal low temperature structure determined using neutron diffraction measurements. Data shown in red, fit in black and difference curve in grey. Space group $I4_1/amd$. Lattice parameters $a = 9.0144(15)$ Åand $c = 12.6981(3)$ Å. $\lambda = 0.82484$ Å. $R_{\mathrm{wp}} = 10.571$%. The structure is defined by three atomic positions: Cd (0, 0, $0.72197(11)$) Wyckoff position 8e; C (0, 0.3057(8), 0.4396(6)) Wyckoff position 16h and N (0.2101(9), 0, 0.6242(5)) Wyckoff position 16h. The isotropic thermal displacement parameter B_{iso} was constrained to be the same for C and N. The X-ray data are not sensitive to the C/N occupancies, so the occupancy of each C/N position was fixed at 50% carbon, 50% nitrogen. B_{iso}(Cd) = 7.69(5) Å^2. B_{iso}(C/N) = 1.44(14) Å^2.

Table S6 Input parameters for Raddose-3D used to calculate the dose rate in Gy s^{-1} for $Cd(CN)_2$.[2–4]

	Keyword	Value(s)
Sample	Type	Cylinder
	Dimensions	480 10000
	PixelsPerMicron	0.01
	CoefCalc	SMALLMOLE
	UnitCell	6.3 6.3 6.3
	SmallMoleAtoms	Cd 2 C 4 N 4
	NumMonomers	1
	ContainerMaterialType	mixture
	MaterialMixture	pyrex
	ContainerThickness	10
	ContainerDensity	2.23
Beam	Type	TOPHAT
	Flux	1.7e13
	Energy	15
	Collimation	Rectangular 800 2500
Wedge	Wedge	0 0
	ExposureTime	1

S1 Determining maximum dose and dose rate

The S.I. unit of dose is the Gray (Gy) where 1 Gy=1 J kg^{-1}. Thus to determine the dose experienced by our sample we need to know the energy deposited/absorbed by the crystal which will depend on (i) beam parameters including the flux, X-ray energy, beam size, beam shape and (ii) system-dependent parameters including the absorption coefficient of the crystal, and the crystal volume. Many other factors might also affect the dose including container thickness and composition (in our case the borosilicate capillary); solvent environment (more relevant perhaps in macromolecular crystallography (MX)); particle size for powdered materials. The programme RADDOSE is widely used for MX to help plan optimum data collection strategies by estimating the maximum dose that can be tolerated for a given set of crystal/experimental parameters.[2,3] The programme settings have more recently been adapted to account for the radiation absorbed by samples used for small angle X-ray scattering (SAXS) measurements.[4]

The dose rate determined using RADDOSE (13 407 Gy s^{-1}) is largely consistent with our own estimates of the maximum dose rate ($\sim$ 38 000 Gy S^{-1}), outlined here. The X-ray energy used in these measurements on the I15 beamline at Diamond light source was $E = 15$ keV with a flux of 1.7×10^{13} ph s^{-1}/0.1%BW, where BW is the bandwidth and BW=$\frac{\Delta\lambda}{\lambda}$. The beam has a vertical height of 0.8 mm and a width of 2.5 mm. Thus the total energy provided per second is given by $15 \times 1.602 \times 10^{-16} \times 1.7 \times 10^{13} = 0.040851$ J s^{-1}. The beam profile of I11 can be approximated as a uniform flat-top beam profile.

The mass of $Cd(CN)_2$ can be estimated from the density of $Cd(CN)_2$ and the volume of sample ex-

posed. The volume containing $Cd(CN)_2$ is given by the volume of a 2.5 mm length of a borosilicate capillary of diameter 0.5 mm. Assuming a density of 2.1818 g cm^{-3} and a powder packing density of 50%, results in a mass of irradiated $Cd(CN)_2$ of approximately 0.5 mg. The beam is wider than the sample (0.8 *vs* 0.5 mm) so the maximum energy deposited by the flat-top beam is scaled by $\frac{5}{8}$, resulting in a maximum dose rate of approximately 38 000 Gy s^{-1} (0.038 MGy s^{-1}).The main assumption in the above calculation is that the packing density is 50%. It does not account for absorption either by the sample or the borosilicate capillary.

At 110 K, $Cd(CN)_2$ undergoes a contraction of 0.9% with 225 seconds of X-ray irradiation [see Figure 2 of the main text]. Taking the dose rate as 38,100 Gy s^{-1} suggests a total dose of 8.57 MGy, which allows us to estimate σ_V for $Cd(CN)_2$ at 110 K to be $\sigma_V \sim -1.05$ GGy^{-1}, which is of the same order of magnitude as that of the protein in Ref. 5, only negative. Thus $Cd(CN)_2$ shows a comparable magnitude of response to X-rays as a large, flexible protein only in contraction rather than expansion. $\sigma_V \sim -1.05$ GGy^{-1} is likely to severely underestimate the true X-ray expansion coefficient, since this assumes that the sample absorbs 100% of the available dose, which we know to be false given that diffraction is observed. In protein crystallography an estimated $\sim 98\%$ of the beam passes through the sample without interacting.[5] Whilst we expect a greater degree of absorption here given the higher weight fraction of heavy transition metal elements (Cd) relative to proteins, we can nonetheless assume that the true dose absorbed will be significantly lower than the 8.57 MGy estimated here.

S2 References

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