Exploring the diversity of elastic responses of crystalline cadmium(II) coordination polymers: From elastic towards plastic and brittle

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Supplementary information

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1. Synthesis
Crystal growth

Crystals (**1**–**3**) were grown in test tubes by layering an aqueous solution of cadmium(II) salt with pure ethanol (1 mL) and then with an ethanol solution of the corresponding ligand.

$[CdCl_2(3\text{-Clpy})_2]_n$, (**1**, **IPAYED**). Used: $CdCl_2$ aqueous solution (1 mL, 0.048 mol dm^{-3}), 3-Clpy ethanol solution (2 mL, 0.050 mol dm^{-3}).

$[CdCl_2(3\text{-Brpy})_2]_n$, (**2**, **IPAYUT**). Used: $CdCl_2$ aqueous solution (1 mL, 0.051 mol dm^{-3}), 3-Brpy ethanol solution (2 mL, 0.049 mol dm^{-3}).

$[CdBr_2(3\text{-Brpy})_2]_n$, (**3**, **IPAZAA**). Used: $CdBr_2$ aqueous solution (1 mL, 0.053 mol dm^{-3}), 3-Brpy ethanol solution (2 mL, 0.049 mol dm^{-3}).

2. Intermolecular interactions

Table S1. Details on hydrogen bond geometry (Å, ˚) for **1**−**3**.

D—H···A	d(H···A) / Å	d(D···A) / Å	$\angle$ (D—H···A) / °	R_{HX}[a]
1(IPAYED)				
C3—H2···Cl2[i]	2,98	3.830(6)	145.0	1.01
C4—H3···Cl1[ii]	2.87	3.646(6)	136.0	0.97
C5—H4···Cl2[iii]	3.04	3.910(5)	149.0	1.03
2(IPAYUT)				
C3—H2···Br1[i]	3.05	3.903(4)	146.0	0.99
C4—H3···Cl1[ii]	2.95	3.736(4)	138.0	1.00
C5—H4···Br1[iii]	3.00	3.875(4)	150.0	0.98
3 (IPAZAA)				
C3—H2···Br2[i]	3.14	4.003(3)	148.0	1.03
C4—H3···Br1[ii]	3.01	3.777(4)	136.0	0.98
C5—H4···Br2[iii]	3.17	4.027(3)	147.0	1.04

[a] The normalized distance, R, defined according to Lommerse *et al.*[1] R_{HX} = d(H···A) / (r_H + r_A), where r_H and r_A are the Bondi van der Waals radii of the respective hydrogen-bond donor and acceptor atoms (H 1.20, Cl 1.75 or Br 1.86 Å) in the C—H···X hydrogen bond.
Symmetry codes (*i*): −x, -y+1, −z; (*ii*) −x-1, y+1/2, −z−1/2; (*iii*): −x+1/2, y+1/2, −z+1/2

**Table S2.** Details on halogen bond geometry (Å, ˚) for **1**−**3**.

D—X1···X2	d(X1···X2) / Å	$\angle$ (D—X···A) / °	R_{X1X2}[a]
1 (IPAYIH)			
C2—Cl2···Cl1[i]	3.617(2)	164.01(18)	1.033
2 (IPAYON)			
C2—Br1···Cl1[i]	3.5704(12)	164.58(11)	0.989
3 (IPAZEE)			
C2—Br2···Br1[i]	3.6260(14)	166.37(10)	0.975

[a] The normalized distance, R, defined according to Lommerse *et al*[1] R_{X1X2} = d(X1···X2) / ($r1$ + $r2$), where $r1$ and $r2$ are the Bondi van der Waals radii of the respective halogen atoms (Cl 1.75 or Br 1.86 Å) in the D—X1···X2 halogen bond.
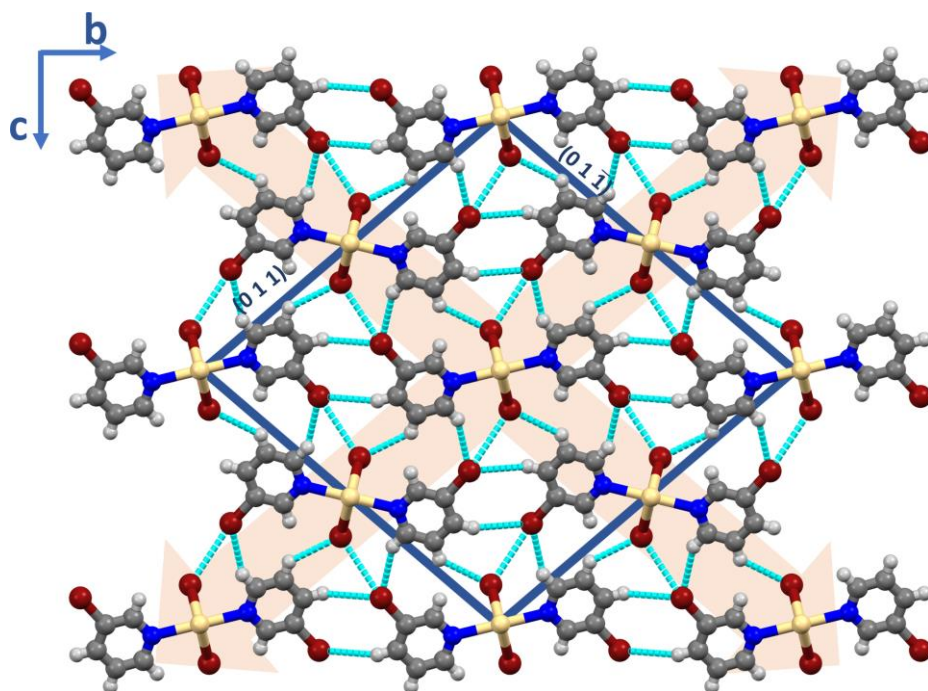Symmetry code: (*i*): 1+x,1/2-y,1/2+z
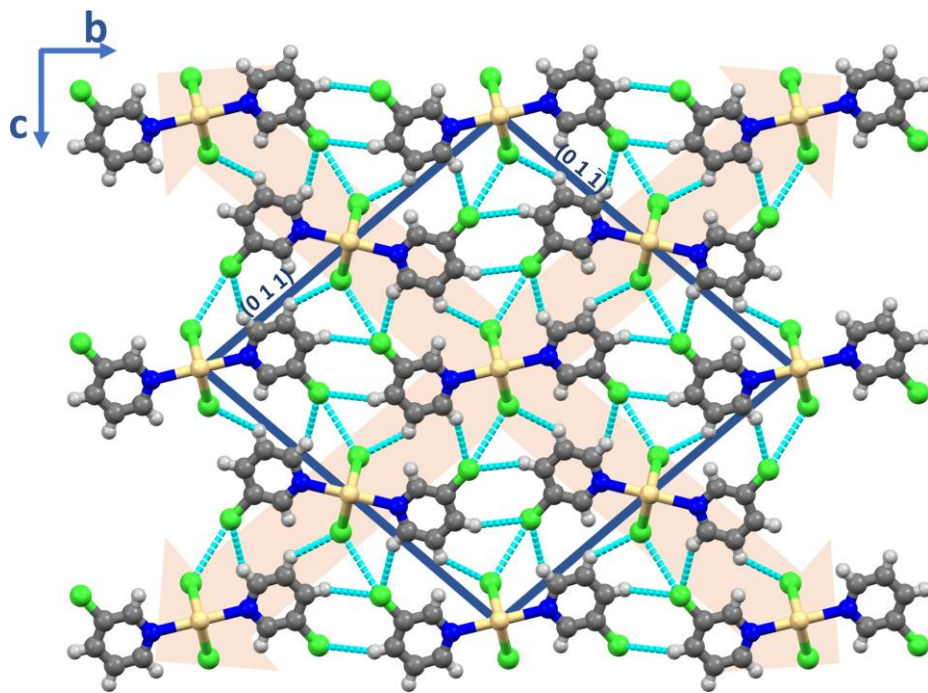
[CdCl$_2$(3-Clpy)$_2$]$_n$ (**1**)
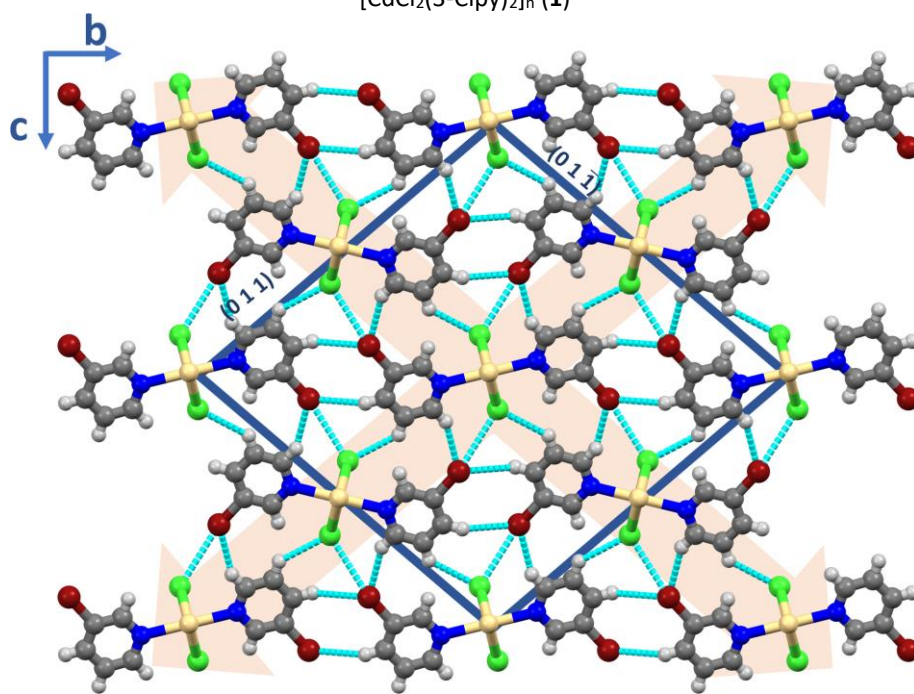
[CdCl$_2$(3-Brpy)$_2$]$_n$ (**2**)

[CdBr$_2$(3-Brpy)$_2$]$_n$ (**3**)

Figure S1. The relative orientation of adjacent polymeric chains (a view down the *a* axis) in the crystal structures of **1**–**3**, linked via halogen and hydrogen bonds listed in tables S1 and S2, shown as blue dotted lines, forming a 2-D network in the directions orthogonal to the elongation of the crystal. Crystal faces (011)/(0$\bar{1}\bar{1}$) and (0$\bar{1}$1)/(01$\bar{1}$) are indicated by blue lines. Directions along which the mechanical force is applied are indicated by pale orange arrows.

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3. Crystal bending experiments

The extent of elastic response of the crystals **1**–**3** was quantified using Euler-Bernoulli equation.[2] For that purpose, thickness (t) of the crystals, together with the distance between the tips of metal tweezers holding the bent crystal (L) and maximal displacement (h_{max}) at a point of maximal curvature, i.e. just before the breakage of a crystal, were measured (Figure S2). The radius of circle describing curvature of bent crystal was calculated using geometrical construction presented in Figure S2 [1, 2]:

$$R^2 = \left(\frac{L}{2}\right)^2 + (R - h_{max})^2 \qquad [1]$$

$$R = \frac{\left(\frac{L}{2}\right)^2 + h_{max}^{\;2}}{2h_{max}} \qquad [2]$$

The bending strain was calculated from Euler-Bernoulli equation [3][2] (considering pure bending without shear component):

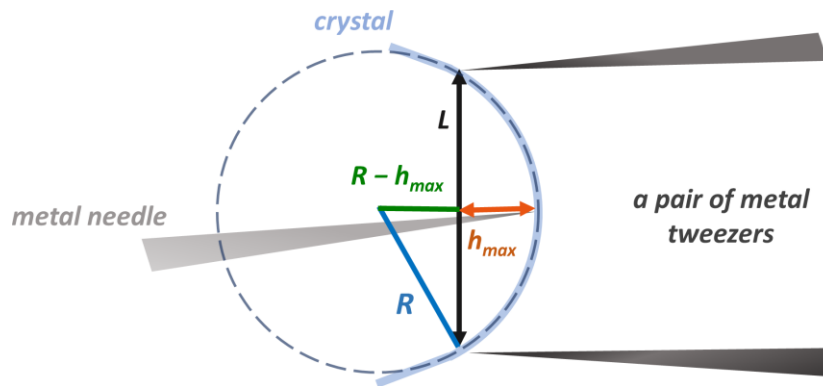$$\varepsilon\,(\%) = \frac{\frac{t}{2}}{R} \cdot 100 \qquad [3]$$

Figure S2. Schematic representation of three-point bending experiment highlighting measured (black arrow, distance between tips of metal tweezers, L; orange arrow, maximal displacement, h_{max}) and calculated (blue line, radius of the circle approximating the curvature of the bent crystal, R) geometrical parameters needed for determining bending strain (ε).
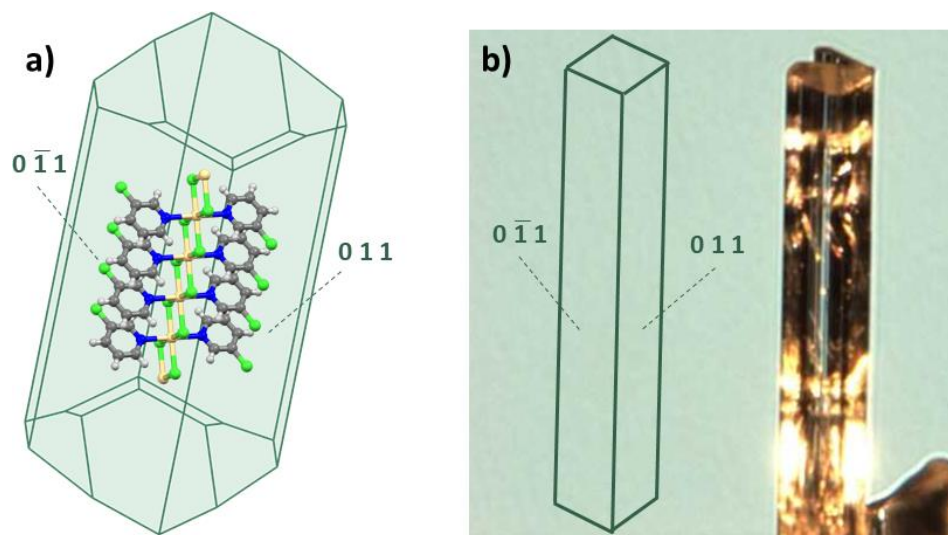
Figure S3. Face indexing (a) and calculated BFDH morphology (using Mercury 4.3.1)[3] (b) for $[CdCl_2(3\text{-}Clpy)_2]_n$ (**1**).

Table S3. Geometrical parameters used to calculate bending strain (ε). The mean value of the bending strain (shown in red) was determined on the basis of measurements of ten different crystals for the compound **1** (from several different batches) by applying mechanical force on the $(011)/(0\overline{1}\overline{1})$ or $(0\overline{1}1)/(01\overline{1})$ pair of crystal faces. Thickness (t) of the selected crystals was measured before bending, while length (L) and maximal displacement (h_{max}) were measured at the point of maximal curvature (see Figure S4 below).

Sample	$\bar{t}$ / mm	L / mm	h_{max} / mm	R / mm	ε / mm
1-1	0.016	2.277	0.573	1.418	**0.58**
1-2	0.008	0.933	0. 412	0.470	**0.85**
1-3	0.015	1.999	0.553	1.180	**0.65**
1-4	0.022	2.368	0.498	1.656	**0.66**
1-5	0.028	2.255	0.261	2.566	**0.55**
1-6	0.031	1.850	0.223	2.030	**0.76**
1-7	0.015	1.837	0.606	0.999	**0.73**
1-8	0.017	1.596	0.418	0.971	**0.88**
1-9	0.021	2.211	0.706	1.219	**0.86**
1-10	0.028	2.387	0.345	2.237	**0.62**
				average	**0.71 ± 0.12**

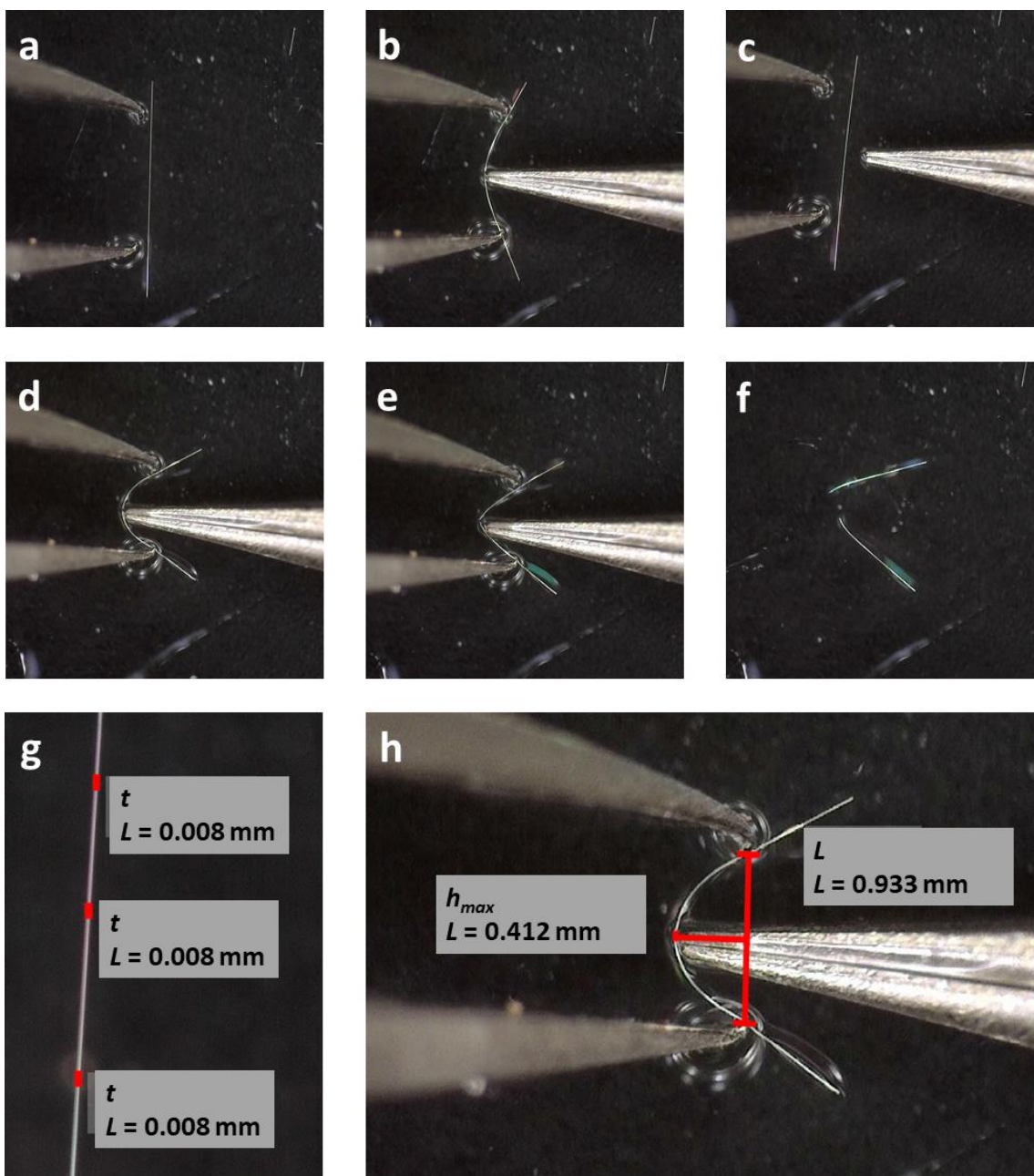**Figure S4.** Bending experiment with $[CdCl_2(3\text{-}Clpy)_2]_n$ (**1**, sample **1-2**; images a–f, h magnified 50 times; image g magnified 200 times), $\varepsilon = 0.85$ %. Slight elastic bending of the crystal followed by relaxation (a–c); the crystal fractures once bent over the critical radius (d–f) with plastically deformed ends of the broken crystal (f). Geometrical parameters: (g) thickness, t, (h) length, L, and maximal displacement, h.
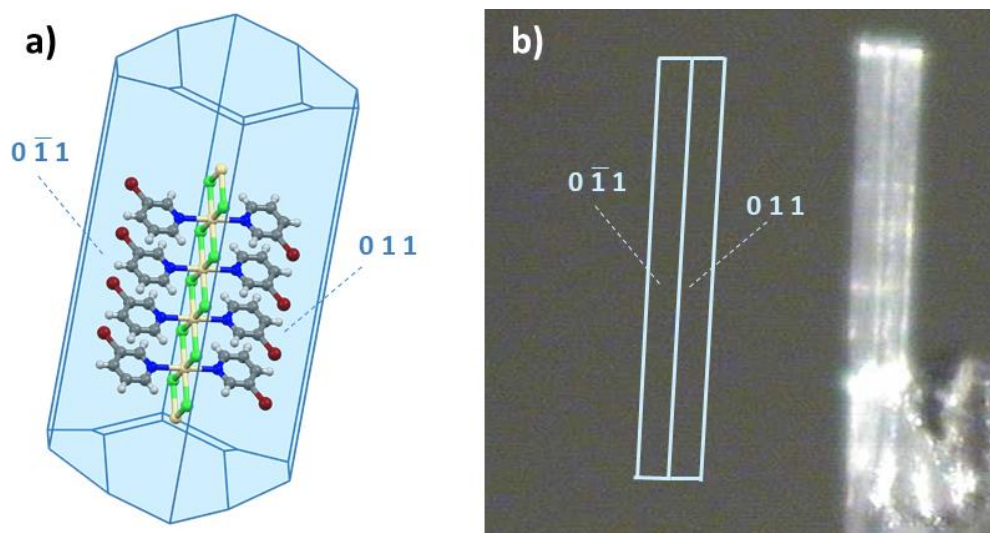
Figure S5. Face indexing (a) and calculated BFDH morphology (using Mercury 4.3.1)[3] (b) for $[CdCl_2(3\text{-}Brpy)_2]_n$ (**2**).

Table S4. Geometrical parameters used to calculate bending strain (ε). The mean value of the bending strain (shown in red) was determined on the basis of measurements of ten different crystals for the compound **2** (from several different batches) by applying mechanical force on the $(011)/(0\bar{1}\bar{1})$ or $(0\bar{1}1)/(01\bar{1})$ pair of crystal faces. Thickness (t) of the selected crystals was measured before bending, length (L) and maximal displacement (h_{max}) were measured at the point of maximal curvature (see Figure S6 below).

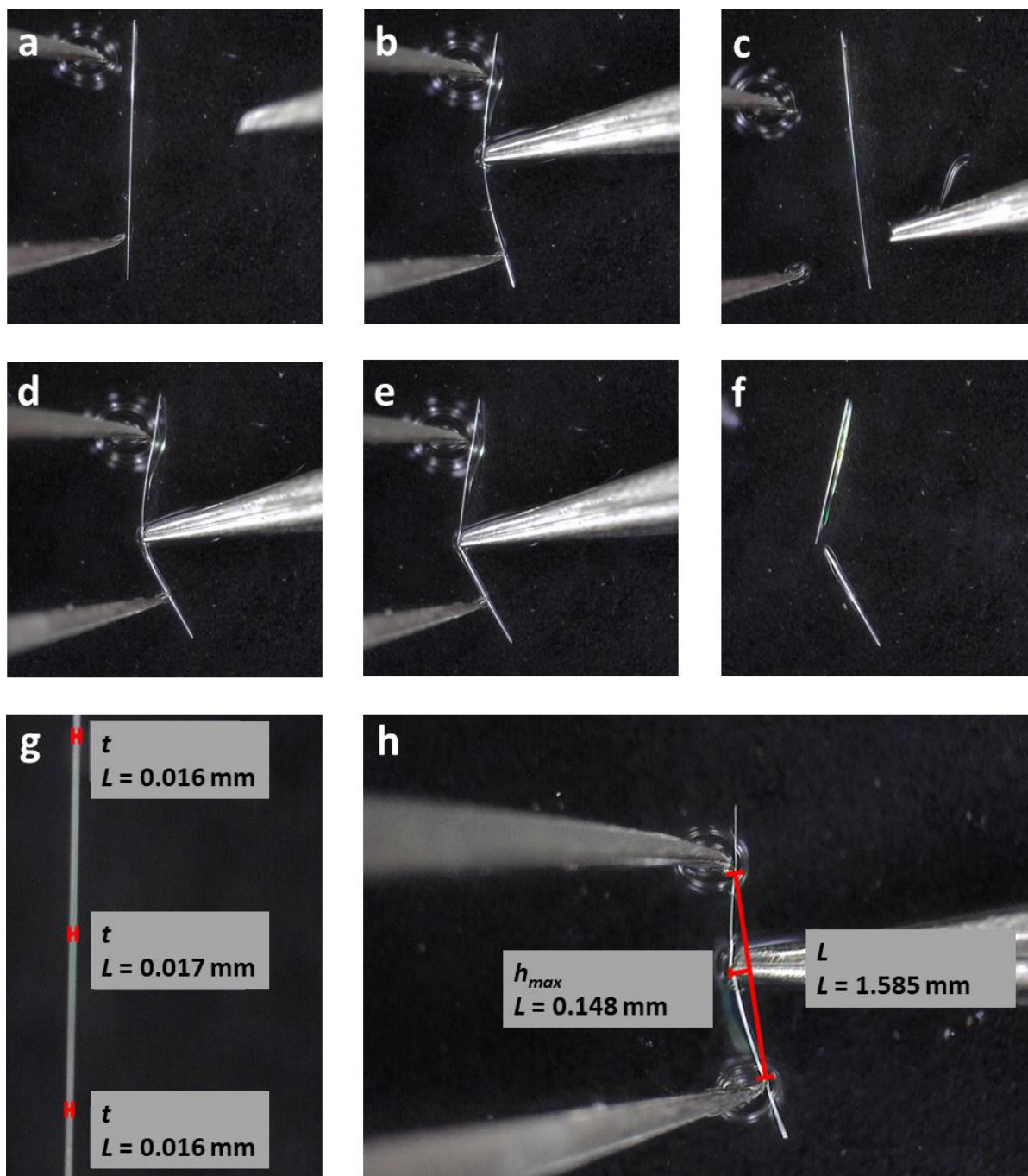| Sample	$\bar{t}$ / mm	L / mm	h_{max} / mm	R / mm	ε / mm
2-1	0.016	1.624	0.198	1.764	**0.46**
2-2	0.019	2.023	0.248	2.187	**0.44**
2-3	0.023	1.415	0.125	2.065	**0.56**
2-4	0.030	1.982	0.150	3.349	**0.45**
2-5	0.026	1.236	0.094	2.079	**0.63**
2-6	0.019	1.478	0.115	2.432	**0.40**
2-7	0.032	1.366	0.061	3.854	**0.41**
2-8	0.031	2.333	0.229	3.086	**0.50**
2-9	0.022	1.561	0.128	2.444	**0.45**
2-10	0.014	1.061	0.081	1.778	**0.38**
				average	**0.47 ± 0.08**

Figure S6. Bending experiment with $[CdCl_2(3\text{-}Brpy)_2]_n$ (**2**, sample **2-1**; images a-f, h magnified 50 times; image g magnified 200 times), ε = 0.46 %. Slight elastic bending of the crystal followed by relaxation (a–c); crystal fractures once bent over the critical radius (d–f). Geometrical parameters: (g) thickness t, (h) length L and maximal displacement h
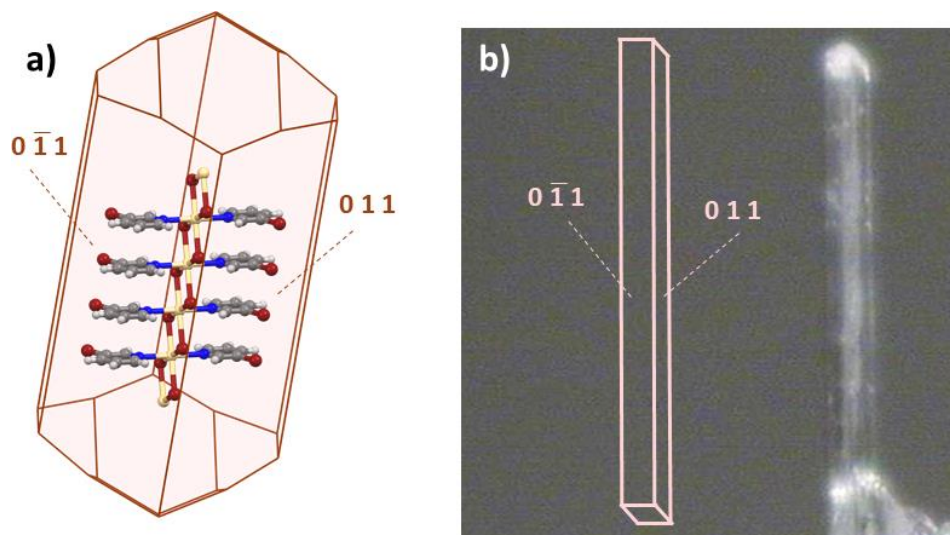
Figure S7. Face indexing (a) and calculated BFDH morphology (using Mercury 4.3.1)[3] (b) for crystals of $[CdBr_2(3\text{-}Brpy)_2]_n$ **(3).**

Table S5. Geometrical parameters used to calculate bending strain (ε). The mean value of the bending strain (shown in red) was determined on the basis of measurements of ten different crystals for the compound **3** (from several different batches) by applying mechanical force on the $(011)/(0\bar{1}\bar{1})$ or $(0\bar{1}1)/(01\bar{1})$ pair of crystal faces. Thickness (t) of the selected crystals was measured before bending, length (L) and maximal displacement (h_{max}) were measured at the point of maximal curvature (see Figure S8 below).

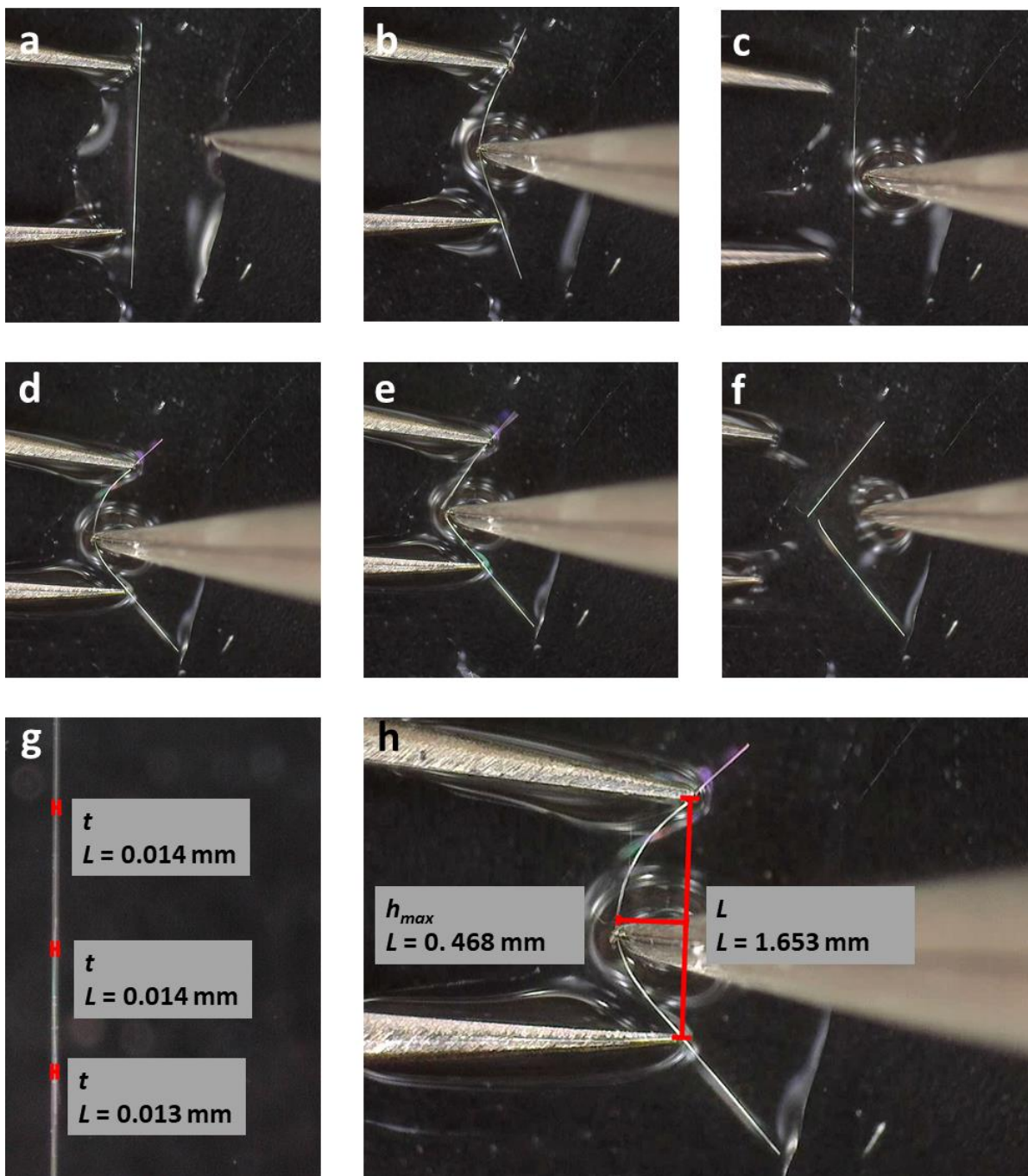| Sample	$\bar{t}$ / mm	L / mm	h_{max} / mm	R / mm	ε / mm
3-1	0.021	1.965	0.303	1.744	**0.60**
3-2	0.011	1.720	0.314	1.335	**0.41**
3-3	0.027	1.708	0.141	2.657	**0.51**
3-4	0.013	1.658	0.450	0.989	**0.66**
3-5	0.034	2.032	0.219	2.466	**0.69**
3-6	0.025	2.160	0.265	2.333	**0.54**
3-7	0.021	1.977	0.307	1.745	**0.60**
3-8	0.026	2.202	0.307	2.128	**0.62**
3-9	0.020	1.604	0.184	1.840	**0.53**
3-10	0.014	1.653	0.468	0.964	**0.71**
				average	**0.59 ± 0.09**

Figure S8. Bending experiment with $[CdBr_2(3\text{-}Brpy)_2]_n$ (**3**, sample **3-10**; images a-f, h magnified 50 times; image g magnified 200 times), ε = 0.71 %. Slight elastic bending of the crystal followed by relaxation (a–c); crystal fractures once bent over the critical radius (d–f) with slightly plastically deformed ends of broken crystal (f). Geometrical parameters: (g) thickness t, (h) length L and maximal displacement h.

4. Atomic force microscopy

The Young's moduli of straight crystals **1**–**3** shown in Table S6 are averaged values of Young's moduli acquired from fitting force-separation curves (at least 1500 data points were collected) for each compound.

Table S6. Young's moduli obtained on straight crystals of **1**–**3**.

Compound	E/ GPa
$[CdCl_2(3\text{-}Clpy)_2]_n$ **(1)**	3.58 ± 1.02
$[CdCl_2(3\text{-}Brpy)_2]_n$ **(2)**	9.50 ± 2.15
$[CdBr_2(3\text{-}Brpy)_2]_n$ **(3)**	4.55 ± 0.85
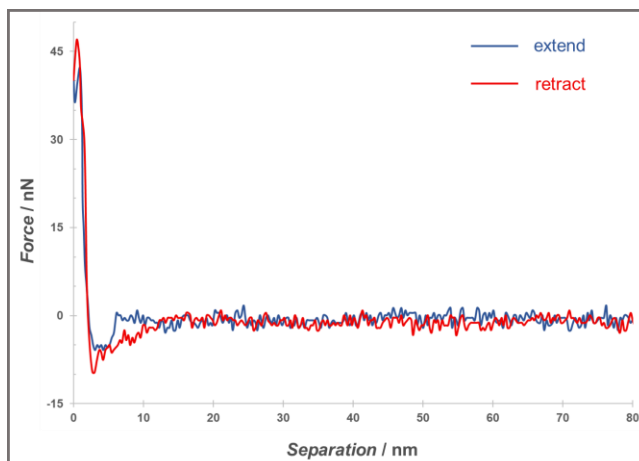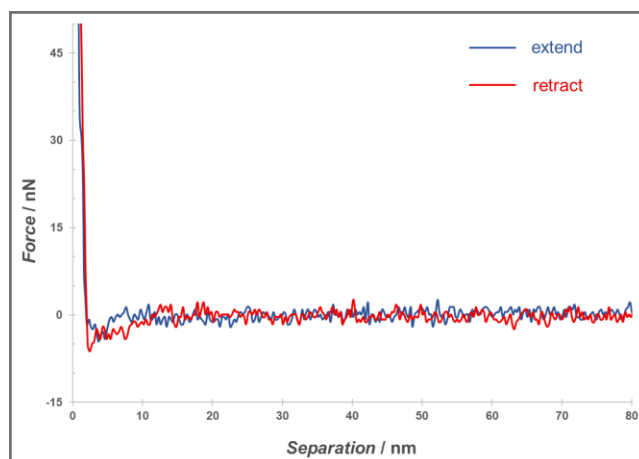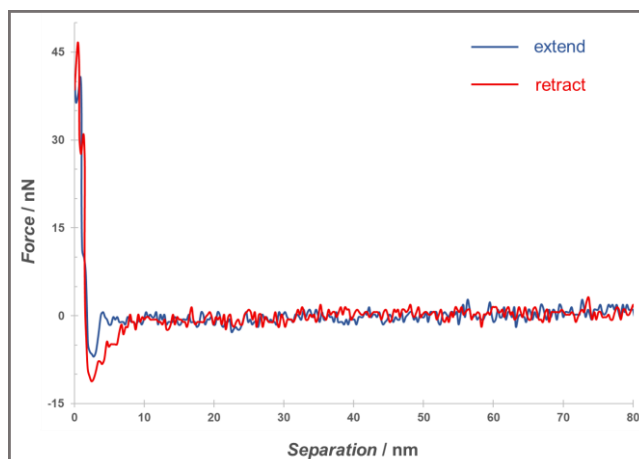
Figure S9. Force distance curves for [CdCl$_2$(3-Clpy)$_2$]$_n$ (**1**) (top), [CdCl$_2$(3-Brpy)$_2$]$_n$ (**2**) (middle) and [CdBr$_2$(3-Brpy)$_2$]$_n$ (**3**) (bottom).

5. Computational study

The interactions between 1-D coordination polymers were calculated in the way that each adjacent 1-D coordination polymer was truncated from the crystal structure as an electroneutral chain made of three metal centres to obtain more representative results in comparison with only one metal centre. In **model I**, terminal metal centres were not octahedrally coordinated, but two halides were left out from the structure to retain electroneutrality. Very similar trends (see ΔE_{int} values in Tables S7 and S8) were obtained for **models II** and **III** in which negative charge on the terminal octahedrally coordinated metal centres were neutralized via capping by cationic species (like H^+ and Na^+). Due to almost the same ΔE_{int} values in all three models, we have opted to pursue the structurally simpler **model I**.

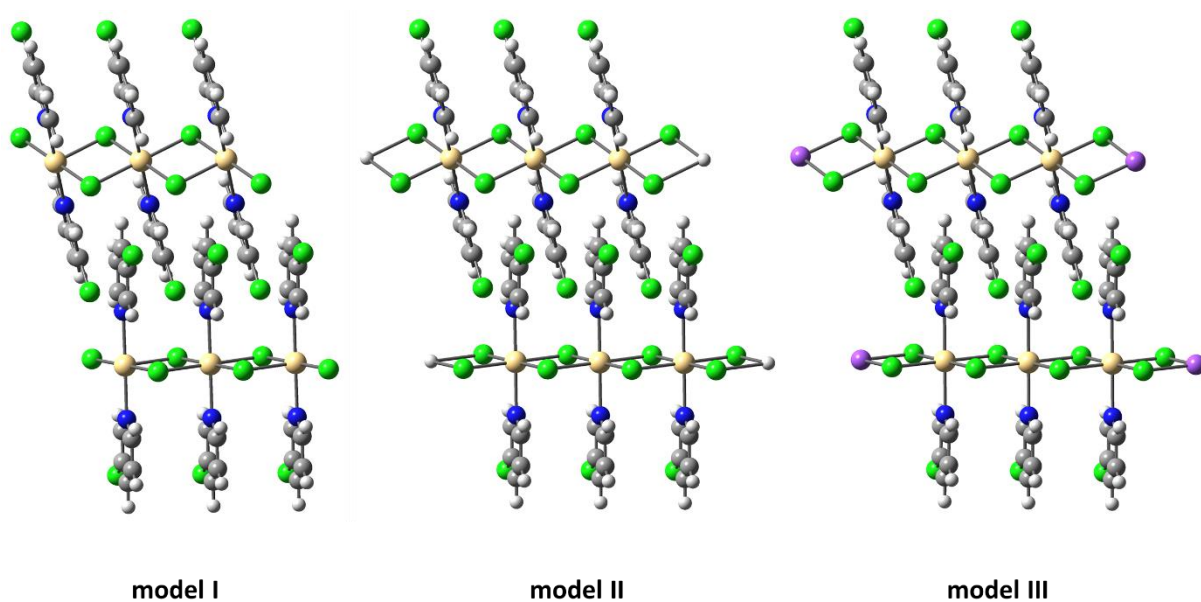| model I | model II | model III |

Figure S10. Three models used for calculation of interaction energies between single pairs of the truncated 1-D coordination polymers (trimeric units) of compounds **1** and **3**. All three models included electroneutral chains. In **model I** two terminal halides were left out, while **model II** and **model III** involved trimeric units terminally capped by two cations, H^+ or Na^+, respectively.
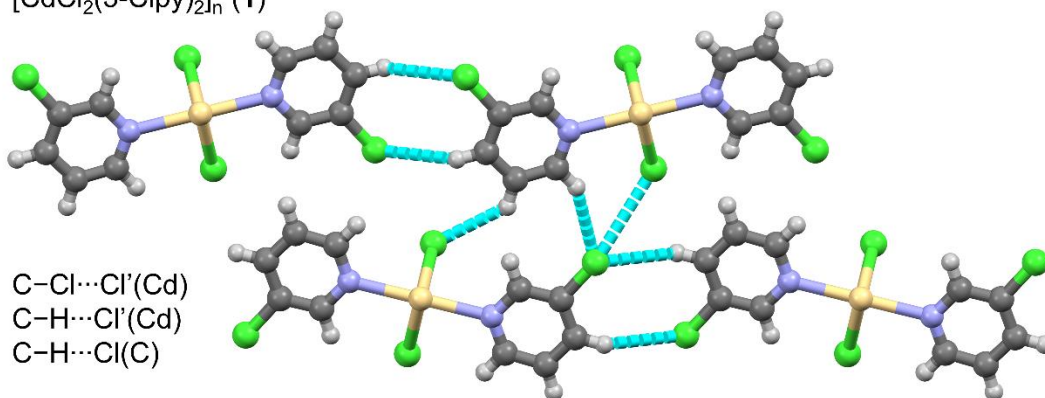
Table S7. Interaction energies (describing **A** type, Figure 5) and energy differences between the single pairs of the truncated 1-D coordination polymers of compounds **1** and **3**.

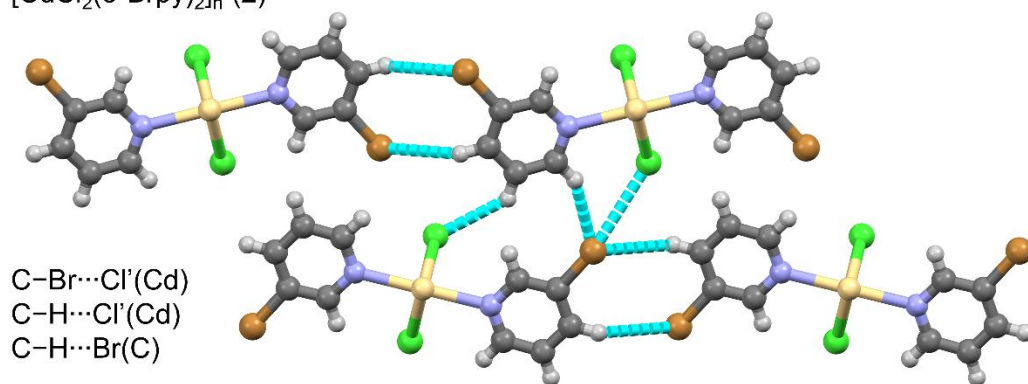| model	E_{int} / kJ mol^{-1} compound 1	E_{int} / kJ mol^{-1} compound 3	ΔE_{int} / kJ mol^{-1}
I	−30.68	−35.31	4.63
II	−25.93	−30.21	4.28
III	−27.87	−32.77	4.90

Table S8. Interaction energies (describing **B** type, Figure 5) and energy differences between the single pairs of the truncated 1-D coordination polymers of compounds **1** and **3**.

model	E_{int} / kJ mol^{-1} compound 1	E_{int} / kJ mol^{-1} compound 3	ΔE_{int} / kJ mol^{-1}
I	−8.67	−7.20	−1.47
II	−9.34	−7.84	−1.49
III	−9.89	−8.47	−1.42

[CdCl$_2$(3-Clpy)$_2$]$_n$ (**1**)

C−Cl···Cl'(Cd)
C−H···Cl'(Cd)
C−H···Cl(C)

[CdCl$_2$(3-Brpy)$_2$]$_n$ (**2**)

C−Br···Cl'(Cd)
C−H···Cl'(Cd)
C−H···Br(C)

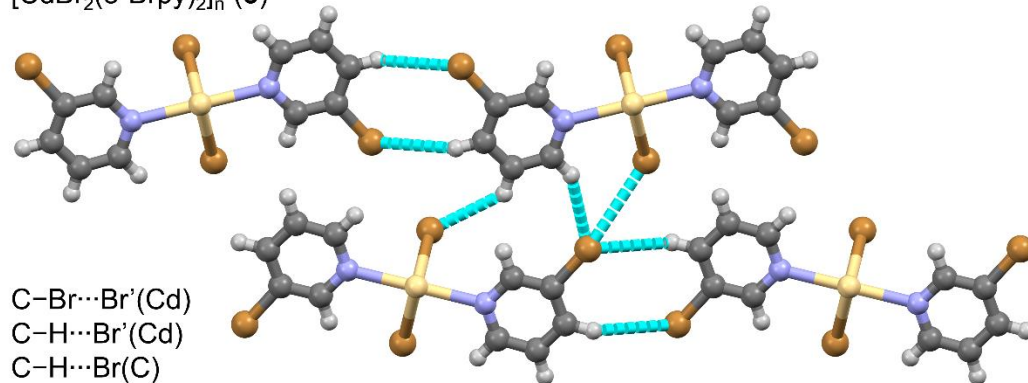[CdBr$_2$(3-Brpy)$_2$]$_n$ (**3**)

C−Br···Br'(Cd)
C−H···Br'(Cd)
C−H···Br(C)

Figure S11. Intermolecular interactions (model **C**, Figure 5) between double pairs of truncated 1-D coordination polymers in compounds **1**–**3**.

[CdCl$_2$(3-Clpy)$_2$]$_n$ (**1**)

C−Cl⋯Cl'(Cd)
C−H⋯Cl'(Cd)
C−H⋯Cl(C)

[CdCl$_2$(3-Brpy)$_2$]$_n$ (**2**)

C−Br⋯Cl'(Cd)
C−H⋯Cl'(Cd)
C−H⋯Br(C)

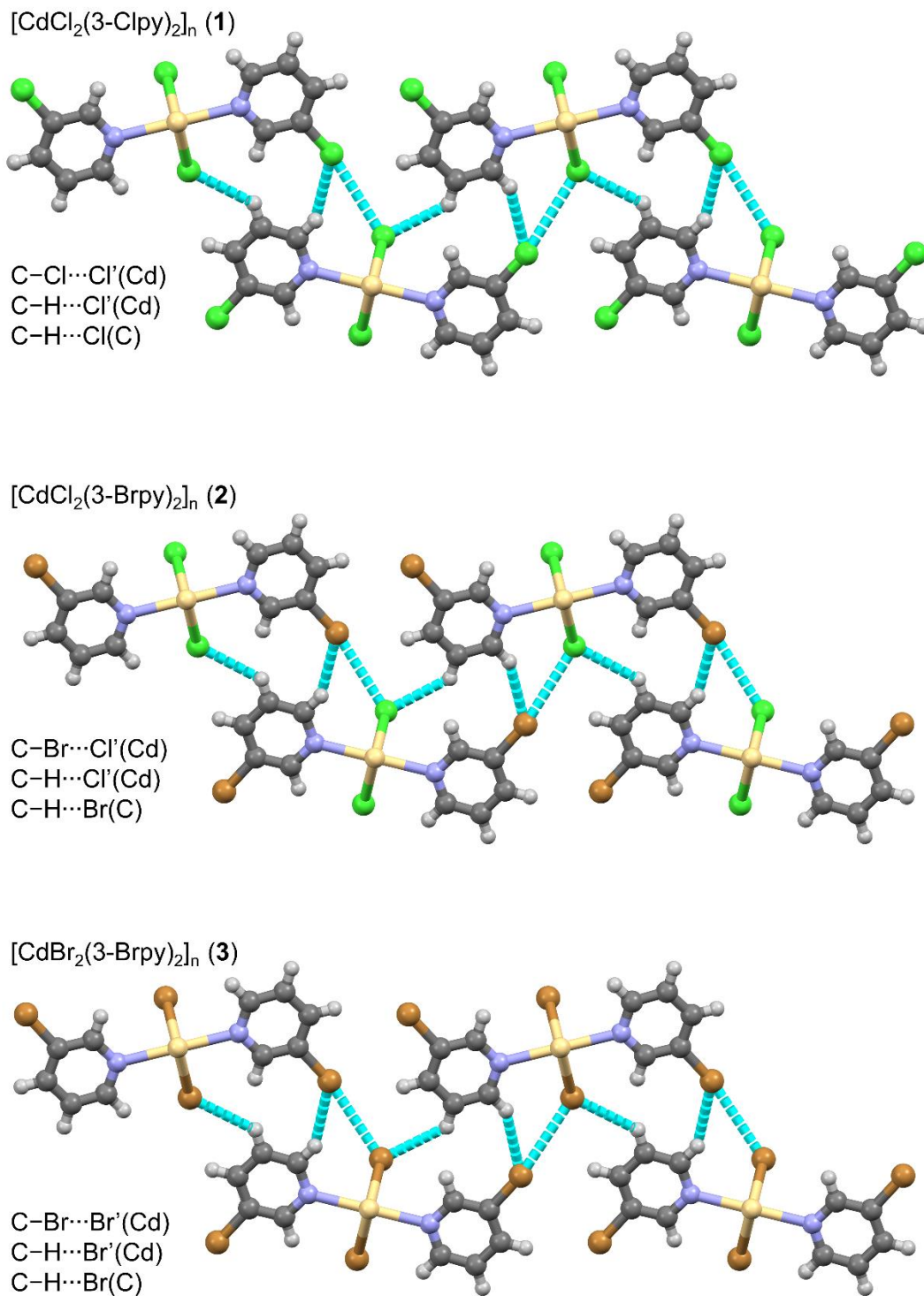[CdBr$_2$(3-Brpy)$_2$]$_n$ (**3**)

C−Br⋯Br'(Cd)
C−H⋯Br'(Cd)
C−H⋯Br(C)

Figure S12. Intermolecular interactions (model **D**, Figure 5) between double pairs of truncated 1-D coordination polymers in compounds **1–3**.

6. References

[1] Lommerse, J. P. M.; Stone, A. J.; Taylor, R.; Allen, F. H., *J. Am. Chem. Soc.*, 1996, **118**, 3108.

[2] Timoshenko, S. Strength of materials, D. Van Nostrand Company, New York, 1940.

[3] C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler, P. A. Wood, *J. Appl. Cryst.,* 2020, **53**, 226.