Supporting information for article:

Building inorganic supramolecular architectures using principles adopted from the organic solid state

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S1. Experimental

S1.1. Methods

CHN analyses were performed with a Perkin-Elmer 2400 Series II CHNS analyzer in the Analytical Services Laboratories of the Ruđer Bošković Institute, Zagreb, Croatia.

IR analyses were performed on a PerkinElmer Spectrum Two spectrometer equipped with Diamond UATR accessory. FT-IR spectra were measured in ATR mode in the range 4000−450 cm\(^{-1}\) with resolution 2 cm\(^{-1}\).

Thermogravimetric measurements were performed using a simultaneous TGA-DTA analyzer (Mettler-Toledo TGA/SDTA 851e). The samples were placed in aluminum pans (40 μL), heated in flowing nitrogen (120 mL min\(^{-1}\)) from room temperature up to 600 °C at a rate of 10 °C min\(^{-1}\). Data collection and analysis were performed using the program package STARe Software 9.01 (MettlerToledo GmbH, 2006.).

X-Ray powder diffraction experiments were performed on a Philips PW 1850 diffractometer, CuKα radiation, voltage 40 kV, and current 40 mA. The patterns were collected in the angle region between 4° and 50° (2θ) with a step size of 0.02°.

S1.2. Synthesis

\([\text{CdCl}_2(2\text{-pyz})_2]\), 1. Used: CdCl\(_2\) (18.3 mg, 0.1 mmol) and 2(1\(H\))-pyrazinone (2-pyz) (19.2 mg, 0.2 mmol). Yield: 73 % (27.4 mg). Microanalysis. Calc. for C\(_8\)H\(_8\)N\(_4\)O\(_2\)CdCl\(_2\) (Mr = 375.49): C, 25.59; H, 2.15; N, 14.92. Found: C, 25.16; H, 1.97; N, 14.72 %. ATR-FTIR (cm\(^{-1}\)): 1722 w, 1680 vs (ν(C=O)), 1608 vs (C=N and C=C in plane ring vibration). Thermal analysis: decomposition occurs in three steps, the first one between 164 and 294 °C (endothermic DTA peak at 276 °C); the second one between 295 and 449 °C (endothermic DTA peak at 355 °C); further decomposition is observed between 450 and 600 °C (endothermic DTA peak at 473 °C); after heating up to 600 °C 51 % of initial mass remains.

The powder diffraction pattern (bulk sample) was consistent with the pattern calculated from single crystal data (Fig. S4).

Mechanochemical synthesis. Used: CdCl\(_2\) (73.3 mg; 0.4 mmol) and 2(1\(H\))-pyrazinone (2pyz) (76.9 mg; 0.8 mmol). Microanalysis. Calc. for C\(_8\)H\(_8\)N\(_4\)O\(_2\)CdCl\(_2\) (Mr = 375.49): C, 25.59; H, 2.15; N, 14.92. Found: C, 25.21; H, 2.01; N, 14.11%. The powder diffraction pattern matched with that of 1 prepared by the solution method (Fig. S4).
[CdBr₂(2-pyz)]ₙ, 2. Used: CdBr₂·4H₂O (34.4 mg, 0.1 mmol) and 2(1H)-pyrazinone (2-pyz) (19.2 mg, 0.2 mmol). Yield: 80 % (37.2 mg). Microanalysis. Calc. for C₅H₆N₂O₂CdBr₂ (Mr = 464.40): C, 20.69; H, 1.74; N, 12.07. Found: C, 20.54; H, 1.34; N, 11.97 %. ATR-FTIR (cm⁻¹): 1721 w, 1674 vs (ν(C=O)), 1603 s (C=N and C=C in plane ring vibration). Thermal analysis: decomposition occurs in three steps, the first one between 219 and 282 °C (endothermic DTA peak at 276 °C); the second one between 283 and 314 °C (endothermic DTA peak at 303 °C); further decomposition is observed between 424 and 600 °C (endothermic DTA peak at 563 °C); after heating up to 600 °C 14 % of initial mass remains.

The powder diffraction pattern (bulk sample) was consistent with the pattern calculated from single crystal data (Fig. S5).

Mechanochemical synthesis. Used: CdBr₂·4H₂O (137.7 mg; 0.4 mmol) and 2(1H)-pyrazinone (2-pyz) (76.9 mg; 0.8 mmol). Microanalysis. Calc. for C₅H₆N₂O₂CdBr₂ (Mr = 464.40): C, 20.69; H, 1.74; N, 12.07. Found: C, 20.09; H, 1.26; N, 11.89 %. The powder diffraction pattern matched with that of 2 prepared by the solution method (Fig. S5).

[CdI₂(2-pyz)]ₙ, 3. Used: CdI₂ (36.6 mg, 0.1 mmol) and 2(1H)-pyrazinone (2-pyz) (19.2 mg, 0.2 mmol). Yield: 78 % (43.6 mg). Microanalysis. Calc. for C₅H₆N₂O₂CdI₂ (Mr = 558.40): C, 17.21; H, 1.44; N, 10.03. Found: C, 16.88; H, 1.26; N, 10.13 %. ATR-FTIR (cm⁻¹): 1715 w, 1675 s (ν(C=O)), 1599 s (C=N and C=C in plane ring vibration). Thermal analysis: decomposition occurs in two steps, the first one between 160 and 223 °C (endothermic DTA peak at 208 °C); further decomposition is observed between 224 and 600 °C; after heating up to 600 °C 48 % of initial mass remains.

The powder diffraction pattern (bulk sample) was consistent with the pattern calculated from single crystal data (Fig. S6).

Mechanochemical synthesis. Used: CdI₂ (146.5 mg; 0.4 mmol) and 2(1H)-pyrazinone (2-pyz) (76.9 mg; 0.8 mmol). Calc. for C₅H₆N₂O₂CdI₂ (Mr = 558.40): C, 17.21; H, 1.44; N, 10.03. Found: C, 17.37; H, 1.12; N, 9.83 %. The powder diffraction pattern matched with that of 3 prepared by the solution method (Fig. S6).

[CdCl₂(4-pym)]ₙ, 4. Used: CdCl₂ (18.3 mg, 0.1 mmol) and 4(3H)-pyrimidinone (4-pym) (19.2 mg, 0.2 mmol). Yield: 84 % (31.5 mg). Microanalysis. Calc. for C₅H₆N₂O₂CdCl₂ (Mr = 375.49): C, 25.59; H, 2.15; N, 14.92. Found: C, 25.40; H, 1.27; N, 14.81 %. ATR-FTIR (cm⁻¹): 1728 s, 1702 s (ν(C=O)), 1600 vs (C=N and C=C in plane ring vibration). Thermal analysis: decomposition occurs in three steps, the first one between 175 and 288 °C (endothermic DTA peak at 279 °C); the second one between 289 and 395 °C (endothermic DTA peak at 336 °C); further decomposition is observed
between 426 and 600 °C (endothermic DTA peak at 483 °C); after heating up to 600 °C 51 % of initial mass remains.

The powder diffraction pattern (bulk sample) was consistent with the pattern calculated from single crystal data (Fig. S8).

**Mechanochemical synthesis.** Used: CdCl$_2$ (73.3 mg; 0.4 mmol) and 4(3$H$)-pyrimidinone (4-pym) (76.9 mg; 0.8 mmol). **Microanalysis.** Calc. for C$_8$H$_8$N$_4$O$_2$CdCl$_2$ ($M_r = 375.49$): C, 25.59; H, 2.15; N, 14.92. Found: C, 25.79; H, 2.07; N, 14.63%. The powder diffraction pattern matched with that of 4 prepared by the solution method (Fig. S8).

[$\text{CdBr}_2(4\text{-pym})_2$]$_n$, 5. Used: CdBr$_2$·4H$_2$O (34.4 mg, 0.1 mmol) and 4(3$H$)-pyrimidinone (4-pym) (19.2 mg, 0.2 mmol). Yield: 77 % (35.8 mg). **Microanalysis.** Calc. for C$_8$H$_8$N$_4$O$_2$CdBr$_2$ ($M_r = 464.40$): C, 20.69; H, 1.74; N, 12.07. Found: C, 19.69; H, 1.07; N, 11.38%. **ATR-FTIR (cm$^{-1}$):** 1721 m, 1699 m (ν(C=O)), 1597 s (C=N and C=C in plane ring vibration). **Thermal analysis:** decomposition occurs in three steps, the first one between 245 and 312 °C (endothermic DTA peak at 303 °C); the second one between 313 and 359 °C (endothermic DTA peak at 321 °C); further decomposition is observed between 360 and 600 °C; after heating up to 600 °C 56 % of initial mass remains.

The powder diffraction pattern (bulk sample) was consistent with the pattern calculated from single crystal data (Fig. S9).

**Mechanochemical synthesis.** Used: CdBr$_2$·4H$_2$O (137.7 mg; 0.4 mmol) and 4(3$H$)-pyrimidinone (4-pym) (76.9 mg; 0.8 mmol). **Microanalysis.** Calc. for C$_8$H$_8$N$_4$O$_2$CdBr$_2$ ($M_r = 464.40$): C, 20.69; H, 1.74; N, 12.07. Found: C, 20.23; H, 1.65; N, 11.96 %. The powder diffraction pattern matched with that of 5 prepared by the solution method (Fig. S9).

[$\text{CdI}_2(4\text{-pym})_2$]$_n$, 6. Used: CdI$_2$ (36.6 mg, 0.1 mmol) and 4(3$H$)-pyrimidinone (4-pym) (19.2 mg, 0.2 mmol). Yield: 81 % (45.3 mg). **Microanalysis.** Calc. for C$_8$H$_8$N$_4$O$_2$CdI$_2$ ($M_r = 558.40$): C, 17.21; H, 1.44; N, 10.03. Found: C, 17.04; H, 1.26; N, 9.73 %. **ATR-FTIR (cm$^{-1}$):** 1722 m, 1693 s (ν(C=O)), 1599 s (C=N and C=C in plane ring vibration). **Thermal analysis:** endothermic DTA peak due to the melting of the compound is observed at 187 °C; decomposition occurs in two steps, the first one between 220 and 320 °C (endothermic DTA peak at 280 °C); further decomposition is observed between 321 and 600 °C; after heating up to 600 °C 38 % of initial mass remains.

The powder diffraction pattern (bulk sample) was consistent with the pattern calculated from single crystal data (Figs. S10).
Mechanochemical synthesis. Used: CdI$_2$ (146.5 mg; 0.4 mmol) and 4(3$H$)-pyrimidinone (4-pym) (76.9 mg; 0.8 mmol). Calc. for C$_8$H$_8$N$_4$O$_2$CdI$_2$ ($M_r$ = 558.40): C, 17.21; H, 1.44; N, 10.03. Found: C, 17.13; H, 1.31; N, 9.76 %. The powder diffraction pattern matched with that of 6 prepared by the solution method (Fig. S10).

[CdCl$_2$(4-quz)$_2$]$_n$, 7. Mechanochemical synthesis. Used: CdCl$_2$ (73.3 mg; 0.4 mmol) and 4(3$H$)-quinazolinone (4-quz) (116.9 mg; 0.8 mmol). Microanalysis. Calc. for C$_8$H$_8$N$_4$O$_2$CdCl$_2$ ($M_r$ = 375.49): C, 25.59; H, 2.15; N, 14.92. Found: C, 25.22; H, 1.81; N, 14.51 %. The powder diffraction pattern matched with that of 7 prepared by the solution method and with the pattern calculated from single crystal data (Fig. S12).

[CdBr$_2$(4-quz)$_2$]$_n$, 8. Used: CdBr$_2$·4H$_2$O (34.4 mg, 0.1 mmol) and 4(3$H$)-quinazolinone (4-quz) (29.2 mg, 0.2 mmol). Yield: 84% (47.4 mg). Microanalysis. Calc. for C$_8$H$_8$N$_4$O$_2$CdBr$_2$ ($M_r$ = 564.52): C, 34.04; H, 2.14; N, 9.93. Found: C, 33.89; H, 1.38; N, 9.86 %. ATR-FTIR (cm$^{-1}$): 1690 vs ($\nu$(C=O)), 1618 m (C=N and C=C in plane ring vibration). Thermal analysis: endothermic DTA peak due to the melting of the compound is observed at 241 °C; decomposition occurs in two steps, the first one between 243 and 367 °C (endothermic DTA peak at 346 °C); further decomposition is observed between 368 and 600 °C (endothermic DTA peak at 450 °C); after heating up to 600 °C 58 % of initial mass remains.

The powder diffraction pattern (bulk sample) was consistent with the pattern calculated from single crystal data (Fig. S13).

Mechanochemical synthesis. Used: CdBr$_2$·4H$_2$O (137.7 mg; 0.4 mmol) and 4(3$H$)-quinazolinone (4-quz) (116.9 mg; 0.8 mmol). Microanalysis. Calc. for C$_8$H$_8$N$_4$O$_2$CdBr$_2$ ($M_r$ = 464.40): C, 20.69; H, 1.74; N, 12.07. Found: C, 20.49; H, 1.56; N, 11.97 %. The powder diffraction pattern matched with that of 7 prepared by the solution method (Fig. S13).

[CdI$_2$(4-quz)$_2$]$_n$, 9. Used: CdI$_2$ (36.6 mg, 0.1 mmol) and 4(3$H$)-quinazolinone (4-quz) (29.2 mg, 0.2 mmol). Yield: 77 % (50.7 mg). Microanalysis. Calc. for C$_8$H$_8$N$_4$O$_2$CdI$_2$ ($M_r$ = 658.51): C, 29.18; H, 1.84; N, 8.51. Found: C, 29.06; H, 1.70; N, 8.50 %. ATR-FTIR (cm$^{-1}$): 1690 vs ($\nu$(C=O)), 1571 m (C=N and C=C in plane ring vibration). Thermal analysis: endothermic DTA peak due to the melting of the compound is observed at 227 °C; decomposition occurs in two steps, the first one between 230 and 500 °C (exothermic DTA peak at 336 °C); further decomposition is observed between 501 and 600 °C (endothermic DTA peak at 543 °C); after heating up to 600 °C 52 % of initial mass remains.
The powder diffraction pattern (bulk sample) was consistent with the pattern calculated from single crystal data (Fig. S14).

**Mechanochemical synthesis.** Used: CdI$_2$ (146.5 mg; 0.4 mmol) and 4(3H)-quinazolinone (4-quz) (116.9 mg; 0.8 mmol). Calc. for C$_{16}$H$_{12}$N$_4$O$_2$CdI$_2$ (Mr = 658.51): C, 29.18; H, 1.84; N, 8.51. Found: C, 28.98; H, 1.36; N, 8.42 %.

The powder diffraction pattern matched with that of 8 prepared by the solution method (Fig. S14).

**S2. Single crystal X-ray crystallography**

**Table S1** Crystal data and details of the structure determination for 1–3, 5–6, 8–9.

| Compound | 1 | 2 | 3 | 4 | 5 |
|----------|---|---|---|---|---|
| Formula  | C$_8$H$_8$CdCl$_2$N$_4$O$_2$ | C$_8$H$_8$CdBr$_2$N$_4$O$_2$ | C$_8$H$_8$CdI$_2$N$_4$O$_2$ | C$_8$H$_8$CdBr$_2$N$_4$O$_2$ | |
| $M_r$    | 375.48 | 464.40 | 558.38 | 464.40 | |
| Colour and habit | colourless, prism | colourless, prism | colourless, prism | colourless, prism | |
| Crystal system, space group | monoclinic, $P2_1/c$ (No. 14) | monoclinic, $P2_1/c$ (No. 14) | monoclinic, $P2_1/c$ (No. 14) | monoclinic, $P2_1/n$ (No. 14) | |
| Crystal dimensions (mm$^3$) | 0.82 $\times$ 0.14 $\times$ 0.10 | 0.34 $\times$ 0.24 $\times$ 0.16 | 0.60 $\times$ 0.18 $\times$ 0.14 | 0.80 $\times$ 0.10 $\times$ 0.06 | |
| $a$ (Å) | 3.7833(3) | 3.9043(2) | 4.1497(2) | 3.8840(3) | |
| $b$ (Å) | 7.6139(7) | 7.7180(5) | 7.8783(4) | 23.164(2) | |
| $c$ (Å) | 20.1473(18) | 20.6142(14) | 21.0091(14) | 7.0359(8) | |
| $\alpha$ (°) | 90 | 90 | 90 | 90 | |
| $\beta$ (°) | 92.131(7) | 92.442(5) | 92.551(4) | 93.712(9) | |
| $\gamma$ (°) | 90 | 90 | 90 | 90 | |
| $V$ (Å$^3$) | 579.96(9) | 620.61(7) | 686.16(7) | 631.67(10) | |
| $Z$ | 2 | 2 | 2 | 2 | |
| $D_{calc}$ (g cm$^{-3}$) | 2.150 | 2.485 | 2.703 | 2.442 | |
| $\mu$ (mm$^{-1}$) | 2.337 | 8.192 | 6.086 | 8.049 | |
| $F$(000) | 364 | 436 | 508 | 436 | |
| $\theta$ range for data collection (°) | 4.86–24.99 | 4.76–25.00 | 4.67–24.99 | 4.56–24.99 | |
| $h,k,l$ range | -3:4, -9:9, -23:23 | -4:4, -8:9, -24:24 | -4:4, -5:9, -24:24 | -4:4, -14:27, -24:24 |
|---|---|---|---|---|
| Scan type | $\omega$ | $\omega$ | $\omega$ | $\omega$ |
| No. measured reflections | 4107 | 3352 | 2305 | 1940 |
| No. independent reflections ($R_{int}$) | 1020 (0.0357) | 1092 (0.0189) | 1198 (0.0167) | 1108 (0.0284) |
| No. observed reflections, $I \geq 2\sigma(I)$ | 961 | 1037 | 1121 | 944 |
| No. refined parameters | 82 | 83 | 82 | 82 |
| $R$, $wR$ [$I \geq 2\sigma(I)$] | 0.0470, 0.1074 | 0.0384, 0.0989 | 0.0254, 0.0574 | 0.0445, 0.0962 |
| $R$, $wR$ [all data] | 0.0492, 0.1080 | 0.0397, 0.0993 | 0.0275, 0.0584 | 0.0550, 0.1012 |
| Goodness of fit on $F^2$, $S$ | 1.531 | 1.376 | 1.187 | 1.147 |
| Max., min. electron density (e Å$^{-3}$) | 1.55, -0.74 | 1.76, -0.87 | 0.73, -0.62 | 1.67, -0.79 |
| CCDC number | 1559137 | 1559138 | 1559139 | 1559140 |
| Compound | 6 | 8 | 9 |
|----------|---|---|---|
| Formula  | C$_8$H$_8$CdI$_2$N$_4$O$_2$ | C$_{16}$H$_{12}$CdBr$_2$N$_4$O$_2$ | C$_{16}$H$_{12}$CdI$_2$N$_4$O$_2$ |
| $M_r$    | 558.38 | 564.52 | 658.50 |
| Colour and habit | colourless, prism | colourless, prism | colourless, prism |
| Crystal system, space group | monoclinic, $P2_1/c$ (No. 14) | monoclinic, $I2/a$ (No. 15) | monoclinic, $I2/a$ (No. 15) |
| Crystal dimensions (mm$^3$) | $0.42 \times 0.14 \times 0.06$ | $0.76 \times 0.07 \times 0.06$ | $0.30 \times 0.19 \times 0.14$ |
| $a$ (Å) | 4.0953(3) | 18.2590(12) | 19.7099(5) |
| $b$ (Å) | 7.8089(6) | 3.8670(2) | 6.8535(2) |
| $c$ (Å) | 21.7078(13) | 24.2737(18) | 13.6310(4) |
| $\alpha$ (%) | 90 | 90 | 90 |
| $\beta$ (%) | 92.307(6) | 95.491(6) | 98.052(3) |
| $\gamma$ (%) | 90 | 90 | 90 |
| $V$ (Å$^3$) | 693.65(8) | 1706.04(19) | 1823.15(9) |
| $Z$ | 2 | 4 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 2.673 | 2.198 | 2.399 |
| $\mu$ (mm$^{-1}$) | 6.020 | 5.982 | 4.602 |
| $F(000)$ | 508 | 1080 | 1224 |
| $\theta$ range for data collection (˚) | 4.58–26.97 | 4.23–26.99 | 4.18–25.00 |
| $h,k,l$ range | -5:4, -4:9, | -23:22, -4:4, | -23:23, -8:4, |
| | -13:27 | -30:27 | -16:16 |
| Scan type | $\omega$ | $\omega$ | $\omega$ |
| No. measured reflections | 2578 | 7204 | 5658 |
| No. independent reflections ($R_{int}$) | 1480 (0.0260) | 1841 (0.0488) | 1596 (0.0294) |
| No. observed reflections, $I \geq 2\sigma(I)$ | 1368 | 1446 | 1439 |
| $I \geq 2\sigma(I)$ | 83 | 115 | 117 |
| $R$, $wR \left[ I \geq 2\sigma(I) \right]$ | 0.0501, 0.1437 | 0.0551, 0.1629 | 0.0382, 0.0936 |
|          |           |           |           |
|----------|-----------|-----------|-----------|
| $R$, $wR$ [all data] | 0.0556, 0.1491 | 0.0690, 0.1769 | 0.0431, 0.0980 |
| Goodness-of-fit on $F^2$, $S$ | 1.171 | 1.076 | 1.086 |
| Max., min. electron density (e Å$^{-3}$) | 3.59, -1.38 | 3.64, -0.76 | 3.46, -0.65 |
| CCDC number | 1559141 | 1559142 | 1559143 |
Table S2  Selected bond distances (Å) and angles (°) for 1–3, 5–6, 8–9.

| Bond distances             | 1  | 2  | 5  |
|----------------------------|----|----|----|
| Cd1–N1                     | 2.411(6) | Cd1–N1 | 2.455(7) | Cd1–N1 | 2.404(6) |
| Cd1–Cl1                    | 2.600(2) | Cd1–Br1 | 2.7098(9) | Cd1–Br1 | 2.7498(7) |
| Cd1–Cl1iv                  | 2.617(2) | Cd1–Br1iv | 2.7585(9) | Cd1–Br1iv | 2.7507(8) |

| Bond angles                |     |     |     |
|----------------------------|----|----|----|
| N1–Cd1–Cl1                 | 86.6(2) | N1–Cd1–Br1 | 93.1(2) | N1–Cd1–Br1 | 89.5(1) |
| N1–Cd1–Cl1ii               | 93.5(2) | N1–Cd1–Br1ii | 86.9(2) | N1–Cd1–Br1vi | 90.5(1) |
| N1–Cd1–Cl1i                | 90.8(2) | N1–Cd1–Br1iv | 89.2(2) | N1–Cd1–Br1vi | 88.9(1) |
| Cl1–Cd1–Cl1i               | 92.96(6) | Br1–Cd1–Br1iv | 91.12(3) | Br1–Cd1–Br1iv | 89.84(2) |
| N1–Cd1–Cl1iii              | 89.2(2) | N1–Cd1–Br1v | 90.8(2) | N1–Cd1–Br1vii | 91.2(1) |
| Cl1–Cd1–Cl1iii             | 87.04(6) | Br1–Cd1–Br1v | 88.88(3) | Br1–Cd1–Br1vii | 90.16(2) |

Symmetry codes (i): x+1, y, z; (ii): -x+1, -y+1, -z+1; (iii): -x, -y+1, -z+1; (iv): x-1, y, z; (v): -x+2, -y+1, -z+1; (vi): -x+1, -y, -z+1; (vii): -x+2, -y, -z+1

| Bond distances             | 3  | 6  |
|----------------------------|----|----|
| Cd1–N1                     | 2.506(4) | 2.429(9) |
| Cd1–Ii                     | 2.8729(3) | 2.8916(7) |
| Cd1–Iiiv                   | 2.9957(3) | 3.0046(7) |

| Bond angles                |     |     |
|----------------------------|----|----|
| N1–Cd1–Ii                  | 93.46(9) | 87.2(3) |
| N1–Cd1–Iiiv                | 86.54(9) | 92.8(3) |
| N1–Cd1–Iiiv                | 89.39(9) | 90.2(2) |
| Ii–Cd1–Iiiv                | 89.975(9) | 87.96(2) |
| N1–Cd1–Iiv                 | 90.61(9) | 89.8(2) |
| Ii–Cd1–Iiv                 | 90.03(1) | 92.04(2) |

Symmetry codes (ii): -x+1, -y+1, -z+1; (iv): x-1, y, z; (v): -x+2, -y+1, -z+1
### Bond distances

| Bond          | Distance (Å)  |
|---------------|---------------|
| Cd1–N1        | 2.482(6)      |
| Cd1–Br1       | 2.7474(8)     |
| Cd1–Br1<sup>viii</sup> | 2.7040(8)    |
| Cd1–N1<sup>vii</sup> | 2.305(4)     |
| Cd1–I1        | 2.7207(5)     |
| Cd1–Br1<sup>viii</sup> | 2.7040(8)    |

### Bond angles

| Bond          | Angle (°)  |
|---------------|------------|
| N1–Cd1–N1<sup>ix</sup> | 175.6(3) |
| N1–Cd1–Br1<sup>viii</sup> | 94.6(2)  |
| N1–Cd1–Br1<sup>x</sup> | 88.5(2)   |
| Br1<sup>viii</sup>–Cd1–Br1<sup>x</sup> | 90.54(4) |
| N1–Cd1–Br1<sup>x</sup> | 85.4(2)   |
| N1–Cd1–Br1<sup>i</sup> | 91.4(2)   |
| Br1<sup>vii</sup>–Cd1–Br1<sup>x</sup> | 90.36(2) |
| Br1<sup>x</sup>–Cd1–Br1 | 179.09(3) |
| Br1<sup>i</sup>–Cd1–Br1 | 88.73(3)  |

Symmetry code (viii): x, y+1, z; (ix): -x+3/2, y, -z+1; (x): -x+3/2, y+1, -z+1; (xi): -x+1/2, y, -z+1
Table S3  Hydrogen bond geometry for 1−3, 5−6, 8−9.

| D–H⋯A   | d(D−H)/Å | d(H⋯A)/Å | d(D⋯A)/Å | \(\angle(D–H\cdots A)/^\circ\) | Symmetry code on A                      |
|---------|----------|----------|----------|-------------------------------|----------------------------------------|
| 1       |          |          |          |                               |                                        |
| N2−H21⋯O1 | 0.88(2)  | 1.87(4)  | 2.712(8) | 160(8)                        | -x, y+1/2, -z+1/2                      |
| C1−H1⋯Cl1 | 0.95     | 2.83     | 3.446(8) | 123.1                         | -x, -y+1, -z+1                         |
| C3−H3⋯Cl1 | 0.95     | 2.72     | 3.512(7) | 141.5                         | -x+1, -y+2, -z+1                       |
| C4−H4⋯Cl1 | 0.95     | 2.81     | 3.500(8) | 130.2                         | x+1, y, z                              |
| 2       |          |          |          |                               |                                        |
| N2−H21⋯O1 | 0.86(2)  | 1.92(5)  | 2.72(1)  | 155(10)                       | -x, y-1/2, -z+1/2                      |
| C1−H1⋯Br1 | 0.93     | 2.92     | 3.542(9) | 125.9                         | x-1, y, z                              |
| C3−H3⋯Br1 | 0.93     | 2.92     | 3.659(9) | 137.8                         | x, y-1, z                              |
| C4−H4⋯Br1 | 0.93     | 2.90     | 3.596(9) | 132.6                         | -x+2, -y+1, -z+1                       |
| 3       |          |          |          |                               |                                        |
| N2−H21⋯O1 | 0.86(2)  | 1.89(3)  | 2.714(6) | 161(5)                        | -x, y-1/2, -z+1/2                      |
| C1−H1⋯I1  | 0.93     | 3.05     | 3.703(5) | 128.2                         | x-1, y, z                              |
| C4−H4⋯I1  | 0.93     | 3.06     | 3.789(5) | 136.0                         | -x+2, -y+1, -z+1                       |
| C3−H3⋯I1  | 0.93     | 3.19     | 3.896(5) | 133.8                         | x, y-1, z                              |
| 5       |          |          |          |                               |                                        |
| N2−H21⋯O1 | 0.85(2)  | 1.96(4)  | 2.750(8) | 154(7)                        | x+1/2, -y+1/2, z-1/2                   |
| C1−H1⋯Br1 | 0.93     | 2.81     | 3.521(7) | 133.8                         | x, y, z                                |
| C3−H3⋯Br1 | 0.93     | 3.24     | 3.824(7) | 122.9                         | x-1, y, z+1                            |
| 6       |          |          |          |                               |                                        |
| N2−H21⋯O1 | 0.88(2)  | 1.89(5)  | 2.74(2)  | 163(14)                       | -x+2, y+1/2, -z+3/2                    |
| C1−H1⋯I1  | 0.95     | 3.02     | 3.66(1)  | 125.6                         | -x+2, -y+1, -z+1                       |
| C3−H3⋯I1  | 0.95     | 3.47     | 4.10(1)  | 126.1                         | -x+1, -y, -z+1                         |
| 8       |          |          |          |                               |                                        |
| N2−H21⋯O1 | 0.88     | 1.88     | 2.76(1)  | 175.5                         | -x+3/2, -y+1/2, -z+3/2                 |
| C1−H1⋯Br1 | 0.95     | 2.88     | 3.571(7) | 130.8                         | -x+3/2, y+1, -z+1                      |
|          | 9                  | 10                   | 11                | 12               | 13           |
|----------|--------------------|----------------------|-------------------|------------------|--------------|
| C5—H5—O1| 0.95               | 3.08                 | 3.57(1)           | 114.0            | -x+2, y+1/2, -z+3/2 |
| N2—H21—O1| 0.85(2)            | 2.08(2)              | 2.930(6)          | 173(6)           | x, y+1, z    |
**Figure S1** ORTEP-style plot of $[\text{CdBr}_2(2\text{-pyz})_2]_n$ (2), with a labelling scheme of the asymmetric unit. Thermal ellipsoids are drawn at 50% probability level at 296(2) K.

**Figure S2** ORTEP-style plot of $[\text{CdI}_2(2\text{-pyz})_2]_n$ (3), with a labelling scheme of the asymmetric unit. Thermal ellipsoids are drawn at 50% probability level at 296(2) K.
Figure S3  ORTEP-style plot of [CdI$_2$(4-pym)$_2$]$_n$ (6), with a labelling scheme of the asymmetric unit. Thermal ellipsoids are drawn at 50% probability level at 200(2) K.
S3. Powder X-ray crystallography

Figure S4 Experimental (solution – black; mechanochemical – red) and simulated (blue) PXRD traces of [CdCl$_2$(2-pyz)$_2$)$_n$ (1)

Figure S5 Experimental (solution – black; mechanochemical – red) and simulated (blue) PXRD traces of [CdBr$_2$(2-pyz)$_2$)$_n$ (2)
Figure S6  Experimental (solution – black; mechanochemical – red) and simulated (blue) PXRD traces of [CdI₂(2-pyz)₂]ₙ (3)

Figure S7  Overlay of experimental PXRD traces for [CdCl₂(2-pyz)₂]ₙ (1) (green), [CdBr₂(2-pyz)₂]ₙ (2) (brown) and [CdI₂(2-pyz)₂]ₙ (3) (violet).
**Figure S8** Experimental, solution (black) and mechanochemical (red) PXRD traces of \([\text{CdCl}_2(4\text{-pym})_2]_n\) (4).

**Figure S9** Experimental (solution – black; mechanochemical – red) and simulated (blue) PXRD traces of \([\text{CdBr}_2(4\text{-pym})_2]_n\) (5)
**Figure S10** Experimental (solution – black; mechanochemical – red) and simulated (blue) PXRD traces of [CdI$_2$(4-pym)$_2$]$_n$ (6)

**Figure S11** Overlay of experimental PXRD traces for [CdCl$_2$(4-pym)$_2$]$_n$ (4) (green), [CdBr$_2$(4-pym)$_2$]$_n$ (5) (brown) and [CdI$_2$(4-pym)$_2$]$_n$ (6) (violet).
**Figure S12**  Experimental (solution – black; mechanochemical – red) and simulated (blue) PXRD traces of [CdCl$_2$(4-quz)$_2$]$_n$ (7)

**Figure S13**  Experimental (solution – black; mechanochemical – red) and simulated (blue) PXRD traces of [CdBr$_2$(4-quz)$_2$]$_n$ (8)
Figure S14  Experimental (solution – black; mechanochemical – red) and simulated (blue) PXRD traces of [CdI₂(4-quz)₂]ₙ (9)

Figure S15  Overlay of experimental PXRD traces for [CdCl₂(4-quz)₂]ₙ (7) (green), [CdBr₂(4-quz)₂]ₙ (8) (brown) and [CdI₂(4-quz)₂]ₙ (9) (violet).
S4. QTAIM analysis

Figure S16 QTAIM analysis of 1.
**Figure S17** QTAIM analysis of 3.
Figure S18 QTAIM analysis of 6.
Figure S19 QTAIM analysis of NALFEN.