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Conformational Preferences of Diimide-Based Dicarboxylate Species and their Coordination Polymers

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Supporting Information

Table S1. Summary of coordination polymers discussed in this work.

Compound #	Formula	Dimensionality	Reference
1Mn	$[Mn(GlyPmDI)(DMF)_2]_n$	2D	Y. Gong, T. J. Prior and C. Redshaw, *Inorg. Chim. Acta*, 2024, **561**, 121871
2Mn	$\{[Mn_2(GlyPmDI)_2(DMF)_3]\cdot 1.5H_2O\}_n$	2D	This work
1Zn	$[Zn(GlyPmDI)(DMF)_2]_n$	2D	This work
2Zn	$[Zn_2(GlyPmDI)_2(DMF)_3]_n$	2D	S. Zhang, X. Liu, P. Hao, G. Li, J. Shen and Y. Fu, *Inorg. Chem.*, 2023, **62**, 14912–14921
1Co	$[Co(GlyPmDI)(DMF)_2]_n$	2D	Y. Gong, T. J. Prior and C. Redshaw, *Inorg. Chim. Acta*, 2024, **561**, 121871
2Co	$[Co_2(GlyPmDI)_2(DMF)_3]_n$	2D	This work
3Ca	$[Ca(GlyPmDI)(DMF)_2]_n$	2D	This work
1Cd	$[Cd(GlyPmDI)(DMF)_2]_n$	2D	This work
N/A	$[Cd(GlyPmDI)(OH_2)_2]_n$	2D	Z. Zhang, L. Zhao, H.-Y. Yu and H.-T. Zhang, *Acta Crystallographica Section C*, 2024, **80**, 633–647
N/A	$[Cd(GlyPmDI)(OH_2)_2]_n$	3D	H. Rong, Z. Liu, G. Gao, L. Su, X. Chen, H. Huang, W. Liu and Q. Liu, *Journal of Alloys and Compounds*, 2025, **1010**, 177894
4Cd	$[Cd(GlyPmDI)(DMF)]_n$	3D	This work
5Co	$[Co(AlaPmDI)(DMF)]_n$	3D	This work
5Zn	$[Zn(AlaPmDI)(DMF)]_n$	3D	B. Joarder, S. Mukherjee, A. K. Chaudhari, A. V. Desai, B. Manna and S. K. Ghosh, *Chem. Eur. J.*, 2014, **20**, 15303–15308
N/A	$\{[Cu(GlyPmDI)(DMA)(OH_2)]\cdot DMA\}_n$	1D	H. Rong, G. Gao, X. Liu, X. Chen, Q. Jiang, X. Song, D. Shen, W. Liu and Q. Liu, *Cryst. Growth Des.*, 2023, **23**, 5437–5445

Table S2. Crystallographic and refinement parameters for the structures of the three diacids.

Compound	**H_2GlyPmDI**	**H_2AlaPmDI·H_2O**	**H_2ibaPmDI**
Empirical formula	$C_{14}H_8N_2O_8$	$C_{16}H_{14}N_2O_9$	$C_{18}H_{16}N_2O_8$
Formula weight	332.22	378.29	388.33
Temperature/K	100(2)	122.99(11)	122.99(10)
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$C2$	$P\bar{1}$
a/Å	5.0740(10)	20.7529(5)	5.7316(2)
b/Å	5.2610(11)	5.63890(10)	6.1988(3)
c/Å	12.385(3)	16.0661(3)	12.4730(5)
α/°	90.10(3)	90	85.726(3)
β/°	97.94(3)	118.704(2)	80.660(3)
γ/°	95.82(3)	90	81.607(3)
Volume/Å^3	325.71(12)	1649.07(6)	432.01(3)
Z	1	4	1
ρ_{calc}g/cm^3	1.694	1.524	1.493
μ/mm^1	0.143	1.099	1.02
F(000)	170	784	202
Crystal size/mm^3	0.03 × 0.02 × 0.01	0.45 × 0.09 × 0.04	0.30 × 0.30 × 0.10
Radiation	Synchrotron (λ = 0.7108)	CuKα (λ = 1.54178)	CuKα (λ = 1.54184)
Collected using	Australian Synchrotron, MX1	Rigaku SynergyS	Rigaku SynergyS
2Θ range for data collection/°	3.322 to 63.366	6.272 to 154.032	7.192 to 153.958
Index ranges	-7 ≤ h ≤ 7, -7 ≤ k ≤ 7, -17 ≤ l ≤ 17	-26 ≤ h ≤ 26, -6 ≤ k ≤ 6, -19 ≤ l ≤ 20	-5 ≤ h ≤ 7, -7 ≤ k ≤ 7, -13 ≤ l ≤ 15
Reflections collected	11748	16340	4416
Independent reflections	1857 [R_{int} = 0.0509, R_{sigma} = 0.0296]	3312 [R_{int} = 0.0817, R_{sigma} = 0.0427]	1726 [R_{int} = 0.0333, R_{sigma} = 0.0364]
Data/restraints/parameters	1857/1/112	3312/6/268	1726/1/133
Goodness-of-fit on F^2	1.027	1.107	1.194
Final R indexes [I>=2σ (I)]	R_1 = 0.0551, wR_2 = 0.1392	R_1 = 0.0465, wR_2 = 0.1268	R_1 = 0.0445, wR_2 = 0.1134
Final R indexes [all data]	R_1 = 0.0712, wR_2 = 0.1512	R_1 = 0.0482, wR_2 = 0.1286	R_1 = 0.0568, wR_2 = 0.1599
Largest peak/hole / e Å^{-3}	0.329/-0.336	0.214/-0.268	0.384/-0.377
Flack parameter	-	0.01(14)	-
CCDC No.	2486232	2486233	2486234

Table S3. Crystallographic and refinement parameters for the structures of the Mn-, Zn- and Co-based coordination polymers containing $GlyPMDI^{2-}$.

Compound	**1Mn**	**2Mn**	**2Zn**	**1Co**
Empirical formula	$C_{20}H_{20}MnN_4O_{10}$	$C_{18.33}H_{19.09}MnN_{3.44}O_{10.94}$	$C_{18.45}H_{19.38}N_{3.48}O_{10.98}Zn$	$C_{20}H_{20}CoN_4O_{10}$
Formula weight	531.34	517.56	531.00	535.33
Temperature/K	100	100	100	123
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$C2/c$	$C2/c$	$P\bar{1}$
a/Å	9.880(2)	31.934(6)	32.040(6)	9.6362(5)
b/Å	10.140(2)	4.7500(9)	4.7400(9)	10.1021(7)
c/Å	13.570(3)	29.072(6)	29.170(6)	13.5166(6)
α/°	84.31(3)	90	90	84.244(4)
β/°	71.44(3)	99.72(3)	99.52(3)	71.817(4)
γ/°	63.63(3)	90	90	63.400(6)
Volume/$Å^3$	1153.3(5)	4346.6(15)	4369.0(15)	1116.56(12)
Z	2	8	8	2
$\rho_{calc}g/cm^3$	1.530	1.582	1.615	1.592
μ/mm^{-1}	0.636	0.675	1.192	6.617
F(000)	546	2005	2179	550
Crystal size/mm^3	0.05 × 0.01 × 0.01	0.3 × 0.1 × 0.1	0.1 × 0.1 x 0.05	0.4 × 0.05 × 0.05
Radiation	Synchrotron (λ = 0.71076)	Synchrotron (λ = 0.71080)	Synchrotron (λ = 0.71076)	CuKα (λ = 1.54184)
Collected using	Australian Synchrotron, MX2	Australian Synchrotron, MX1	Australian Synchrotron, MX2	Rigaku SynergyS
2Θ range for data collection/°	4.836 to 63.538	2.588 to 63.424	2.578 to 64.224	9.802 to 157.264
Index ranges	$-13 \le h \le 13$, $-13 \le k \le 15$, $-20 \le l \le 20$	$-44 \le h \le 44$, $-6 \le k \le 6$, $-36 \le l \le 42$	$-46 \le h \le 46$, $-6 \le k \le 6$, $-43 \le l \le 43$	$-12 \le h \le 10$, $-12 \le k \le 12$, $-17 \le l \le 15$
Reflections collected	20472	17719	36573	22192
Independent reflections	6226 [R_{int} = 0.0918, R_{sigma} = 0.1191]	5848 [R_{int} = 0.0956, R_{sigma} = 0.1086]	6345 [R_{int} = 0.0625, R_{sigma} = 0.0512]	4614 [R_{int} = 0.0892, R_{sigma} = 0.0520]
Data/restraints/parameters	6226/0/323	5848/48/377	6345/0/377	4614/0/323
Goodness-of-fit on F^2	1.148	1.063	1.162	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0880, wR_2 = 0.2614	R_1 = 0.0980, wR_2 = 0.2783	R_1 = 0.0565, wR_2 = 0.1702	R_1 = 0.0751, wR_2 = 0.2171
Final R indexes [all data]	R_1 = 0.0962, wR_2 = 0.2727	R_1 = 0.1431, wR_2 = 0.3254	R_1 = 0.0602, wR_2 = 0.1745	R_1 = 0.0919, wR_2 = 0.2322
Largest diff. peak/hole / e $Å^{-3}$	2.688/-1.493	1.029/-0.749	1.146/-1.051	1.106/-0.804
CCDC No.	2486235	2486236	2486237	2486238

Table S4. Crystallographic and refinement parameters for the structures of the Ca- and Cd-based coordination polymers containing $GlyPMDI^{2-}$ and of **5Co**.

Compound	**3Ca**	**1Cd**	**4Cd**	**5Co**
Empirical formula	$C_{20}H_{20}CaN_4O_{10}$	$C_{20}H_{20}CdN_4O_{10}$	$C_{17}H_{13}Cd_1N_3O_9$	$C_{38}H_{34}Co_2N_6O_{18}$
Formula weight	516.48	588.80	515.70	980.57
Temperature/K	100	123	100	100
Crystal system	monoclinic	triclinic	orthorhombic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P2_1$
a/Å	13.425(3)	4.97300(10)	4.7900(10)	8.6250(17)
b/Å	17.687(4)	9.0826(4)	15.013(3)	20.581(4)
c/Å	9.6290(19)	12.8166(4)	25.310(5)	12.070(2)
α/°	90	91.128(3)	90	90
β/°	91.03(3)	92.195(2)	90	101.80(3)
γ/°	90	94.386(2)	90	90
Volume/$Å^3$	2286.0(8)	576.63(3)	1820.1(6)	2099.7(8)
Z	4	1	4	2
$\rho_{calc}g/cm^3$	1.501	1.696	1.882	1.551
μ/mm^{-1}	0.339	1.010	1.260	0.874
F(000)	1072	296	1024	1004
Crystal size/mm^3	0.05 × 0.01 × 0.01	0.42 × 0.05 × 0.03	0.3 × 0.1 × 0.1	0.06 x 0.02 x 0.01
Radiation	Synchrotron (λ = 0.71092)	MoKα (λ = 0.71073)	Synchrotron (λ = 0.71090)	Synchrotron (λ = 0.71080)
Collected using	Australian Synchrotron, MX2	Rigaku SynergyS	Australian Synchrotron, MX1	Australian Synchrotron, MX1
2Θ range for data collection/°	3.034 to 54.998	5.452 to 49.984	3.154 to 54.998	3.44 – 57.00
Index ranges	$-17 \le h \le 17$, $-22 \le k \le 22$, $-12 \le l \le 12$	$-5 \le h \le 5$, $-10 \le k \le 10$, $-15 \le l \le 15$	$-6 \le h \le 6$, $-14 \le k \le 19$, $-32 \le l \le 25$	$-11 \le h \le 11$, $-27 \le k \le 27$, $-15 \le l \le 16$
Reflections collected	30533	34715	8379	56343
Independent reflections	5201 [R_{int} = 0.1666, R_{sigma} = 0.1027]	2019 [R_{int} = 0.1281, R_{sigma} = 0.0360]	4053 [R_{int} = 0.1694, R_{sigma} = 0.1635]	10548 [R_{int} = 0.0.0923, R_{sigma} = 0.0.0515]
Data/restraints/parameters	5201/0/320	2019/0/192	4053/28/143	10548/199/775
Goodness-of-fit on F^2	1.092	1.062	1.201	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.1531, wR_2 = 0.3902	R_1 = 0.0236, wR_2 = 0.0556	R_1 = 0.1419, wR_2 = 0.3587	R_1 = 0.0634, wR_2 = 0.1744
Final R indexes [all data]	R_1 = 0.2235, wR_2 = 0.4302	R_1 = 0.0240, wR_2 = 0.0558	R_1 = 0.2473, wR_2 = 0.4283	R_1 = 0.0770, wR_2 = 0.1879
Largest diff. peak/hole / e $Å^{-3}$	1.029/-0.617	0.370/-0.447	3.910/-1.499	0.747/-0.454
Flack parameter	N/A	N/A	0.5(2)	0.06(2)
CCDC No.	2486239	2486240	2486241	2486242

Additional Crystallographic Refinement Details

H_2AlaPmDI·H_2O

One oxygen atom was disordered over two positions with occupancies refined against each other (66:34).

$[Mn(GlyPmDI)(DMF)_2]_n$ (**1Mn**)

Electron density within voids that could not be sensibly modelled had its contribution to the diffraction data accounted for using the BYPASS routine within Olex2. This corresponded to 45 $Å^3$ and 5 electrons per asymmetric unit, insufficient to assign any sensible solvent model.

$\{[Mn_2(GlyPmDI)_2(DMF)_3]·1.5H_2O\}_n$ (**2Mn**)

The metal was modelled as disordered over two positions, Mn1 and Mn2, with the occupancies of refined freely to a 44:56 ratio. Mn1 has two axial DMF ligands, Mn2 has one DMF ligand. All DMF ligands were refined using the same free variable for occupancy as the metal to which they are coordinated. Two of the DMF positions are overlapping and are modelled using some isotropic restraints (SHELX ISOR). The structure contains small voids in which no sensible model could be generated (50 $Å^3$ per ASU containing 16 e^-); this was tentatively attributed to 1.5 H_2O molecules per ASU and is incorporated into the molecular formula.

$\{[Zn_2(GlyPmDI)_2(DMF)_3]·1.5H_2O\}_n$ (**2Zn**)

Isostructural to **2Mn** (above) with the Zn1 and Zn2 occupancies, and those of their attached DMF ligands, freely refined to 48:52. The structure contains small voids in which no sensible model could be generated (50 $Å^3$ per ASU containing 14 e^-); this was tentatively attributed to 1.5 H_2O molecules per ASU and is incorporated into the molecular formula.

$[Ca(GlyPmDI)(DMF)_2]_n$ (**3Ca**)

The data is of very low quality (evidenced by high R_{int} and consequently high wR_2 values). This is the best data that could be obtained, using synchrotron radiation, despite many attempts. However, the structure was able to be refined without restraints.

$[Cd(GlyPmDI)(DMF)]_n$ (**4Cd**)

The data is of very low quality (evidenced by high R_{int} and consequently high wR_2 values). This is the best data that could be obtained, using synchrotron radiation, despite many attempts,

yet is sufficient for unambiguous connectivity to be established and it is presented in this context only.

Only the metal ion was modelled anisotropically, with all other atoms modelled isotropically. SHELXL distance restraints (DFIX and DANG) were utilised to make several bond lengths and angles more chemically sensible. The coordinated DMF is disordered over two positions (fixed occupancies of 50:50) and restraints (SHELX FLAT, DFIX, DANG) were used to model the DMF. The structure was refined as a racemic twin.

$[Co(AlaPmDI)(DMF)]_n$ (**5Co**)

One of the $AlaPmDI^{2-}$ ligands is almost entirely disordered over two positions; only one N-$CH(CH_3)$-CO_2 fragment and the carboxylate oxygen atoms of the opposing end are shared between the two positions. The two positions were refined at fixed 50:50 occupancies as this is geometrically required to avoid clashes between the two components. A number of SHELX DFIX/DANG restraints were employed to fix the geometry of the two components, alongside ISOR restraints to control the displacement ellipsoids. One of the DMF ligands is also disordered over two positions (50:50 as the orientations are related to those of the disordered ligand).

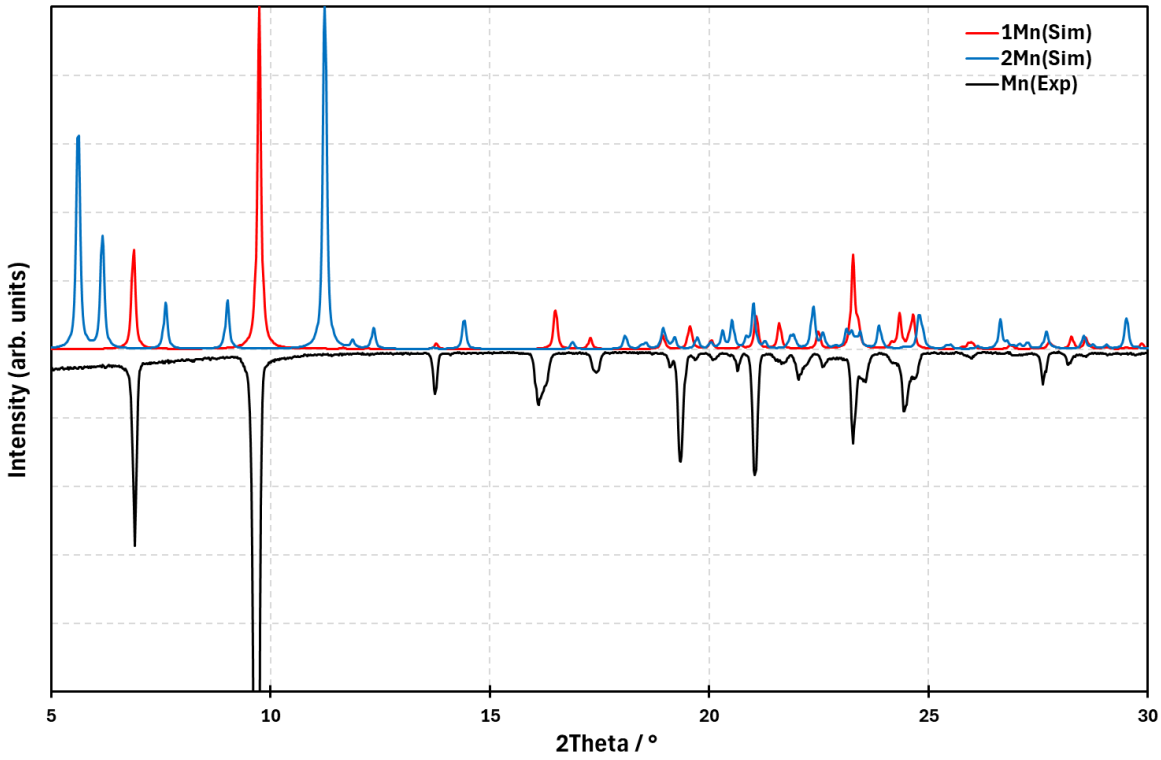

Figure S1. Comparison of the experimental PXRD pattern (at room temperature) from reaction of H_2GlyPmDI and $Mn(NO_3)_2$ that isolated the single crystal structure **1Mn** and the calculated PXRD patterns from the SCXRD structures of **1Mn** and **2Mn** collected at 100 K. The bulk sample is purely **1Mn** with no indication of the less solvated **2Mn**.

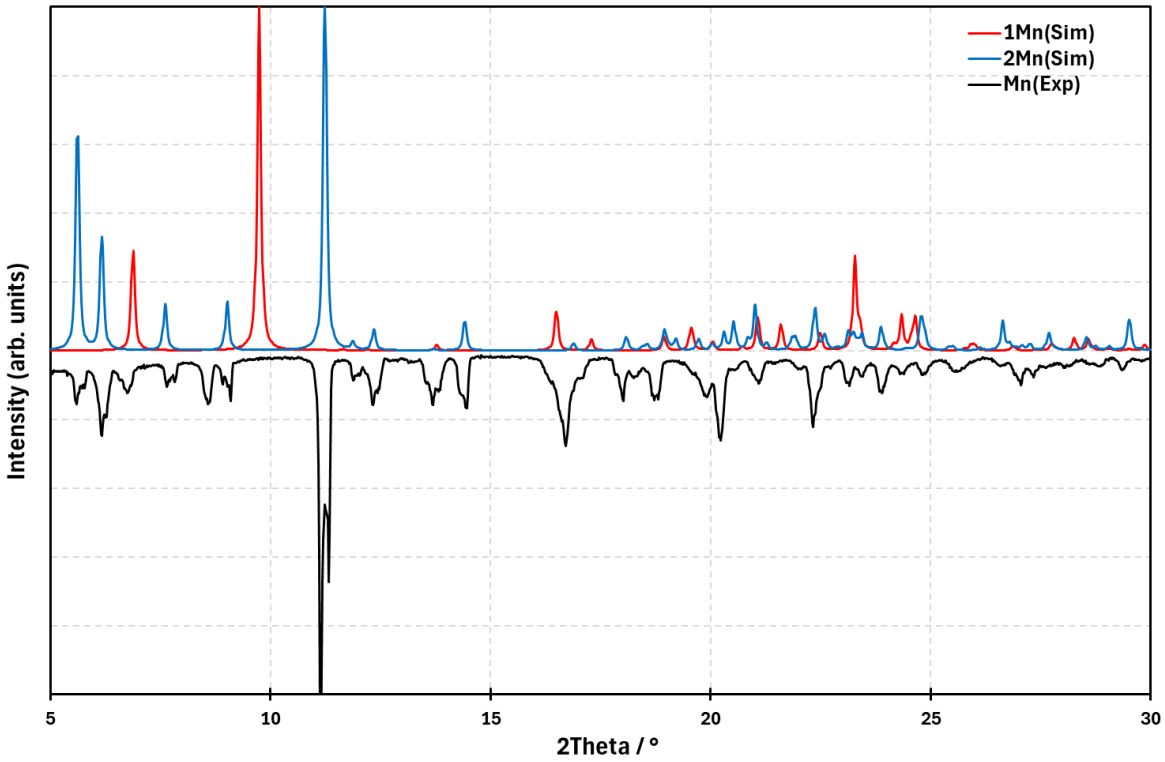

Figure S2. Comparison of the experimental PXRD pattern (at room temperature) from reaction of H_2GlyPmDI and $Mn(NO_3)_2$ that isolated the single crystal structure **2Mn** and the calculated PXRD patterns from the SCXRD structures of **1Mn** and **2Mn** collected at 100 K. The bulk sample contains both **1Mn** and **2Mn**.

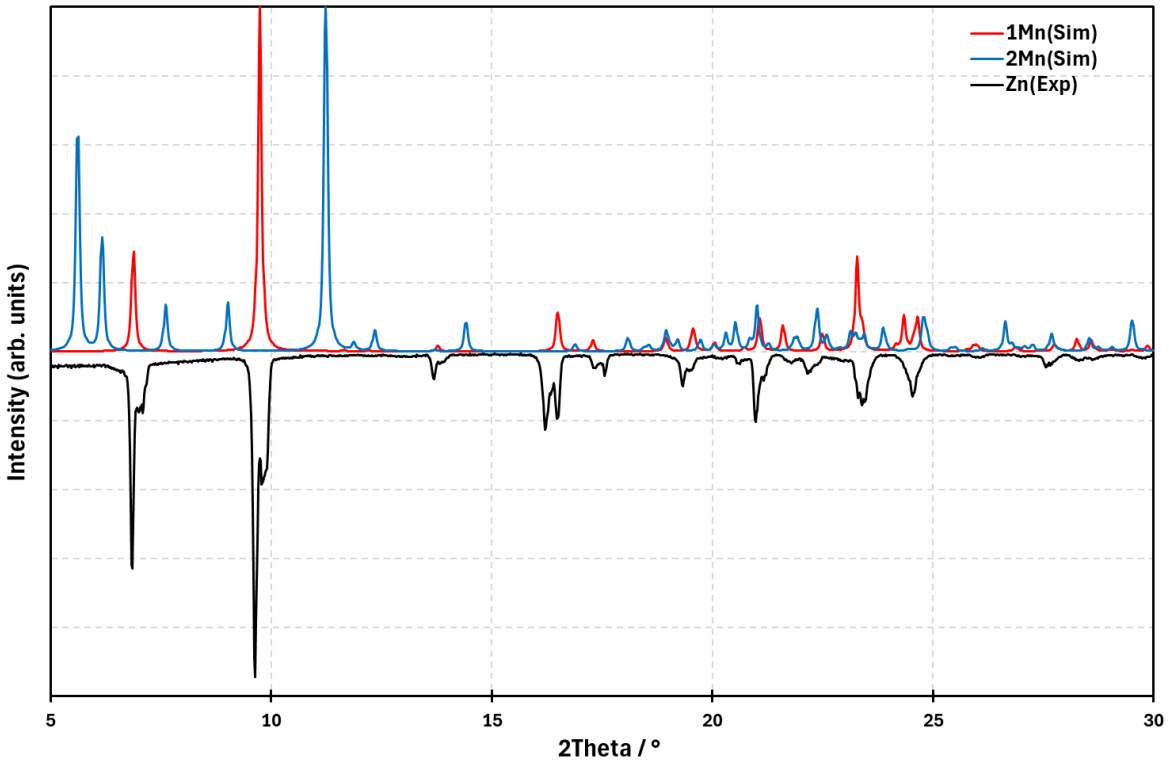

Figure S3. Comparison of the experimental PXRD pattern (at room temperature) from reaction of H_2GlyPmDI and $Zn(NO_3)_2$ and the calculated PXRD patterns from the SCXRD structures of **1Mn** and **2Mn** collected at 100 K. Although the SCXRD structure of **2Zn** was obtained from this reaction, the bulk material is isostructural with **1Mn**.

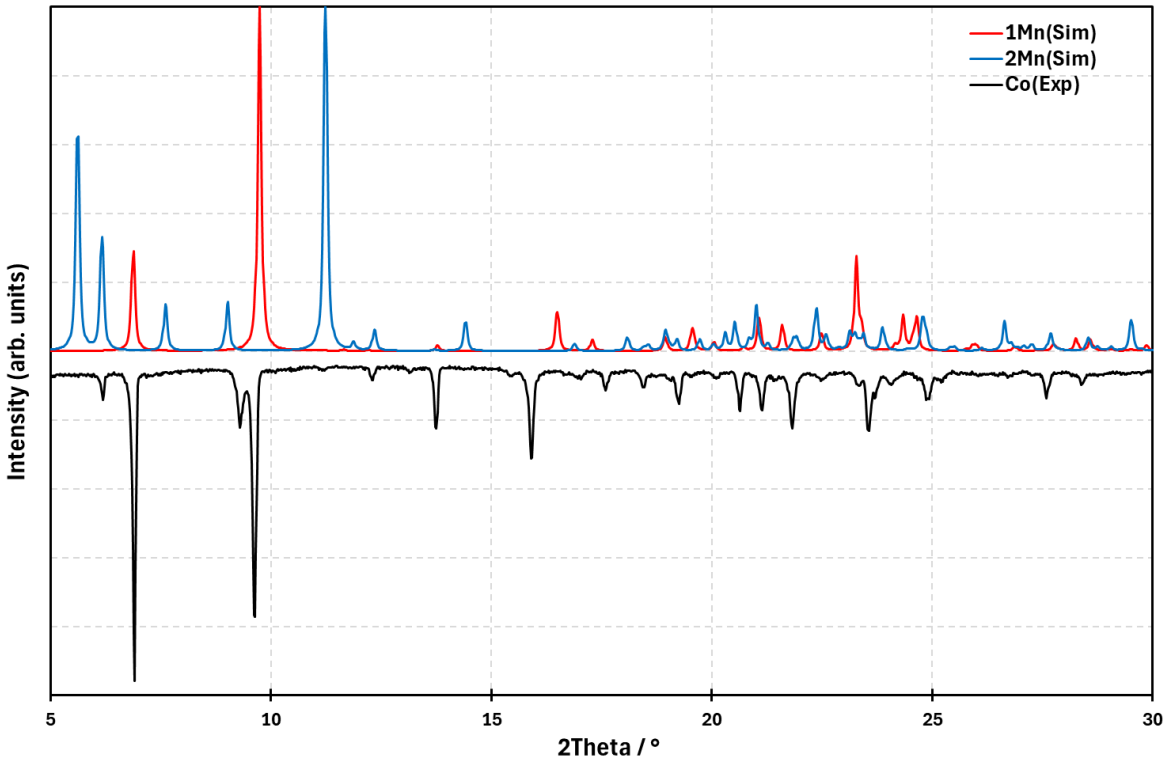

Figure S4. Comparison of the experimental PXRD pattern (at room temperature) from reaction of H_2GlyPmDI and $Co(NO_3)_2$ and the calculated PXRD patterns from the SCXRD structures of **1Mn** and **2Mn** collected at 100 K.

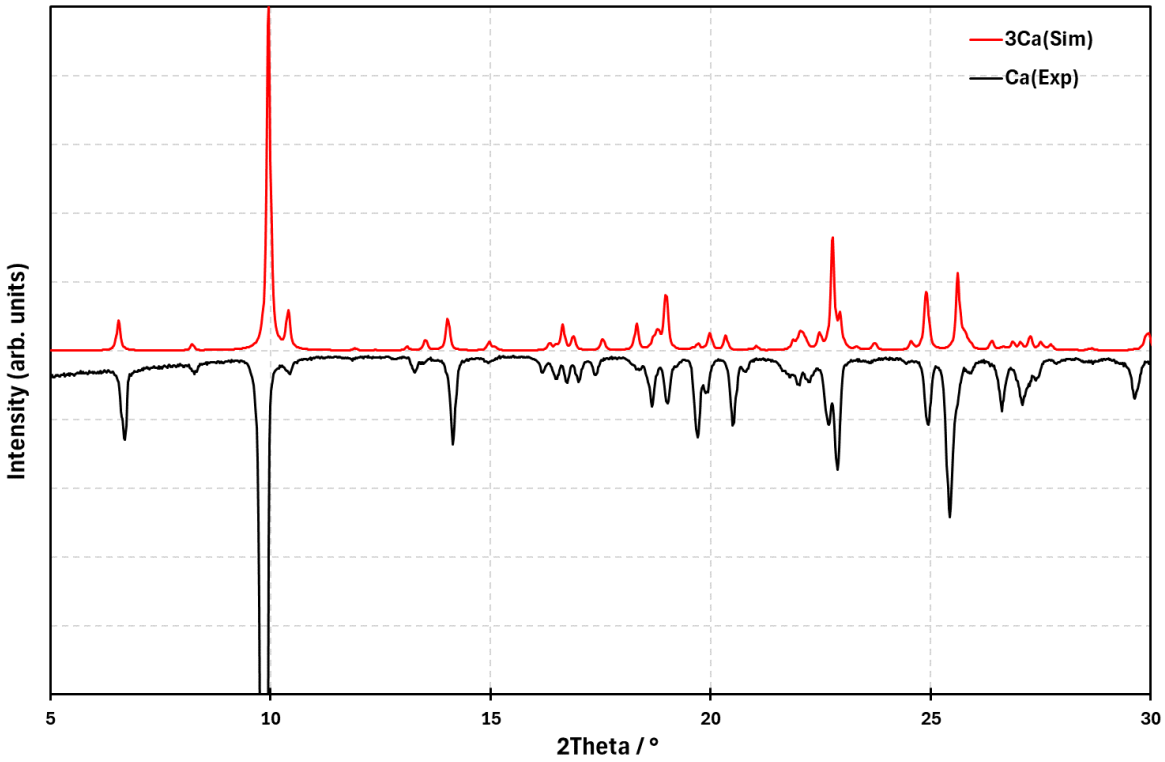

Figure S5. Comparison of the experimental PXRD pattern (at room temperature) from reaction of H_2GlyPmDI and $Ca(NO_3)_2$ and the calculated PXRD patterns from the SCXRD structure of **3Ca** collected at 100 K.

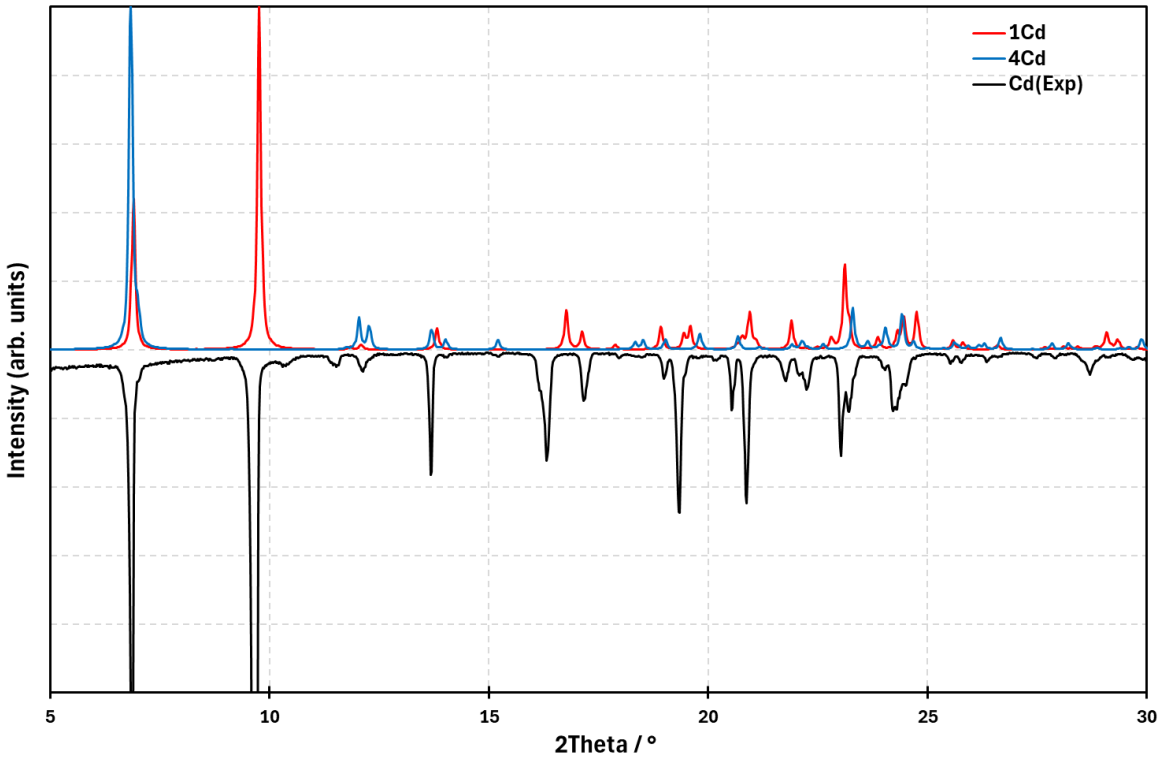

Figure S6. Comparison of the experimental PXRD pattern (at room temperature) from reaction of H_2GlyPmDI and $Cd(NO_3)_2$ at 70 °C and the calculated PXRD patterns from the SCXRD structure of **1Cd** and **4Cd** collected at 100 K.

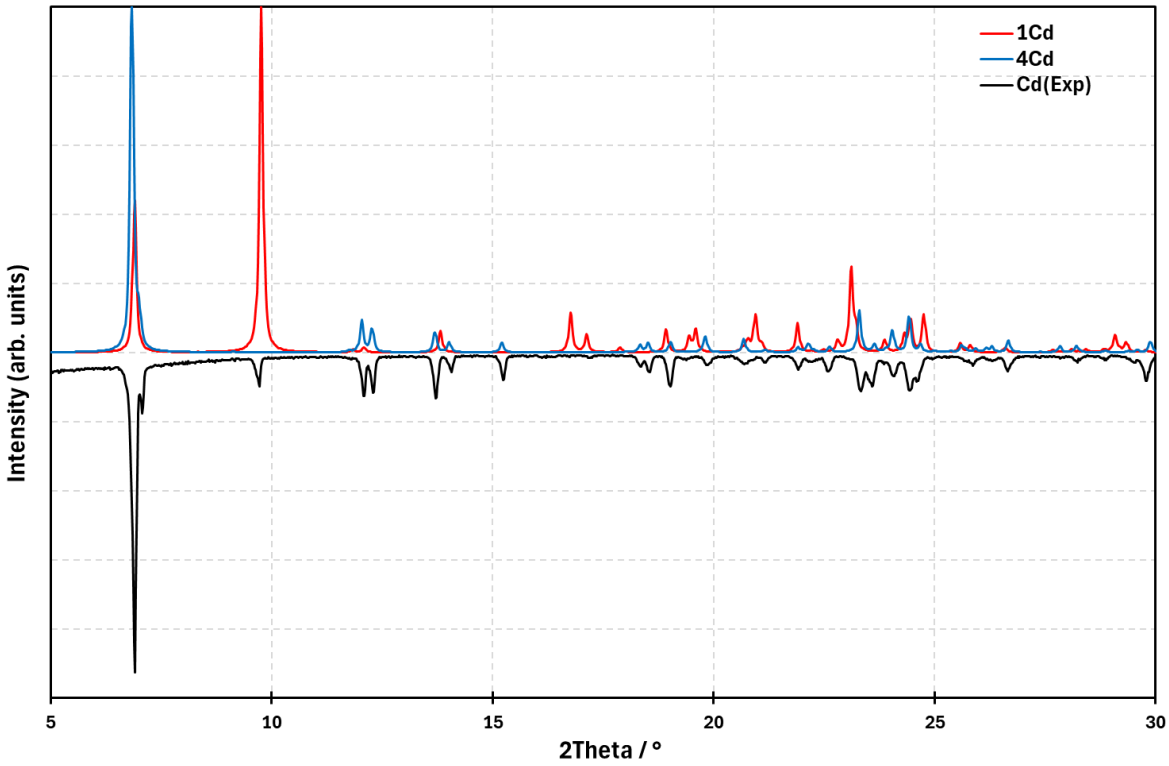

Figure S7. Comparison of the experimental PXRD pattern (at room temperature) from reaction of H_2GlyPmDI and $Cd(NO_3)_2$ at 70 °C and the calculated PXRD patterns from the SCXRD structure of **1Cd** and **4Cd** collected at 100 K.

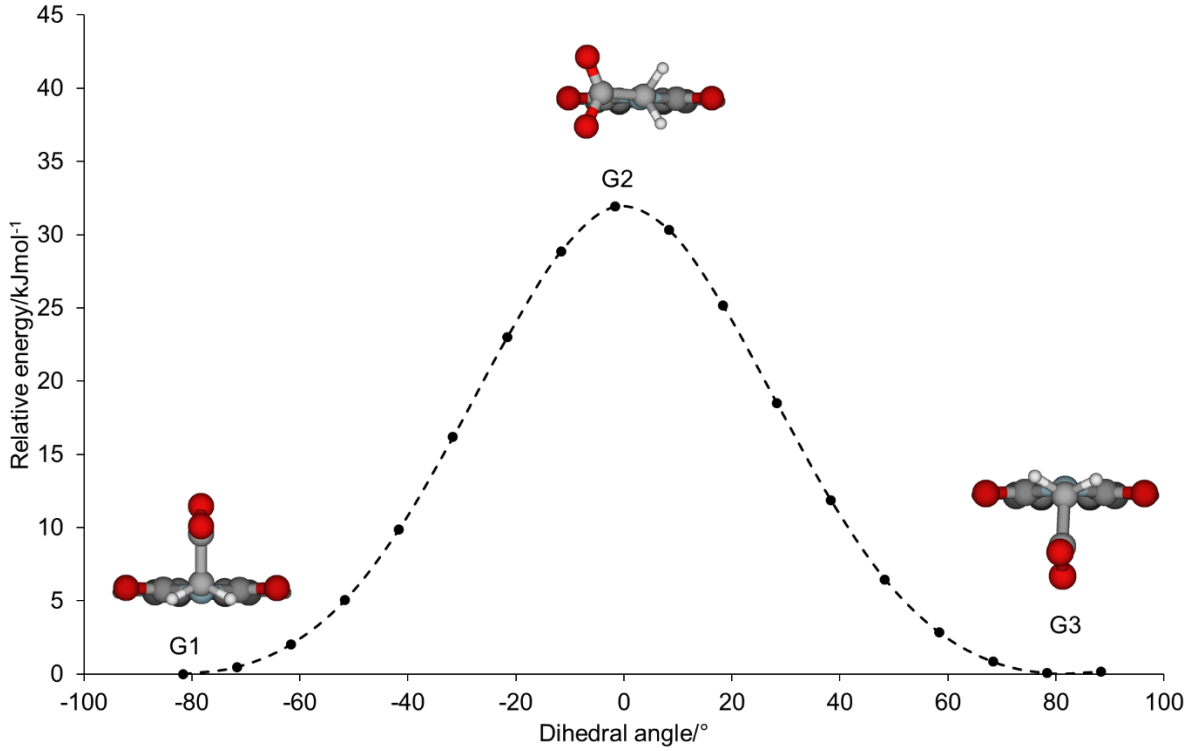

Figure S8. Energy profile for a relaxed rotational scan around the imide N-αC bond for glycine-phthalimide, highlighting the structures of the minima/maxima.

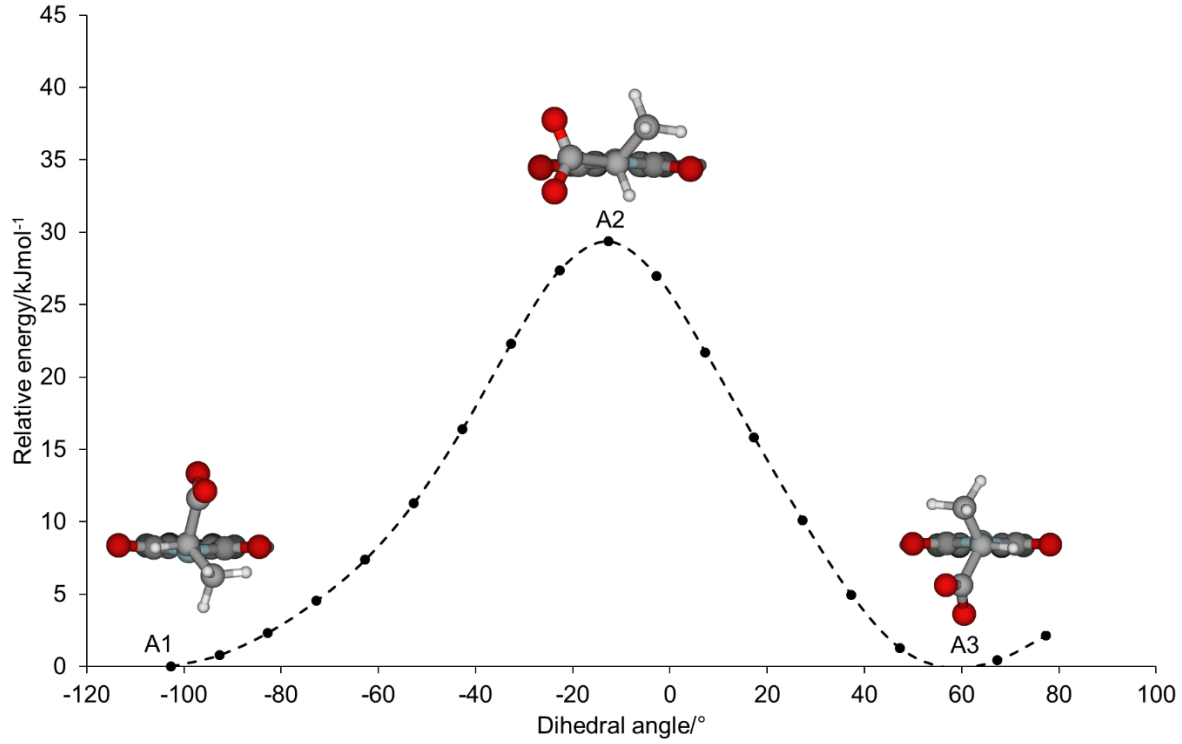

Figure S9. Energy profile for a relaxed rotational scan around the imide N-αC bond for alanine-phthalimide, highlighting the structures of the minima/maxima.

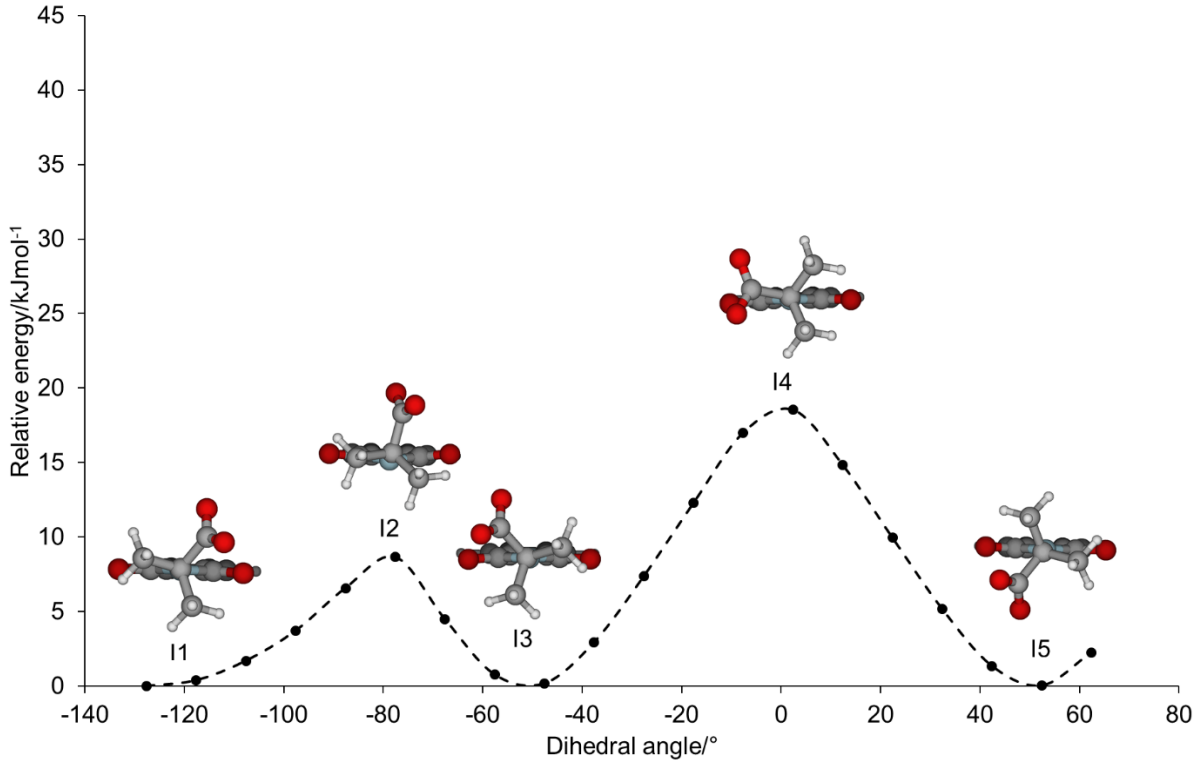

Figure S10. Energy profile for a relaxed rotational scan around the imide N-αC bond for isobutyrate-phthalimide, highlighting the structures of the minima/maxima.

References

1. A. Spek, *Acta Crystallographica Section C*, 2015, **71**, 9-18.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Journal of Applied Crystallography*, 2009, **42**, 339-341.