Supporting Information

Title: Facile synthesis and supramolecular chemistry of hydrogen bond/halogen bond-driven multi-tasking tectons

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Table of contents

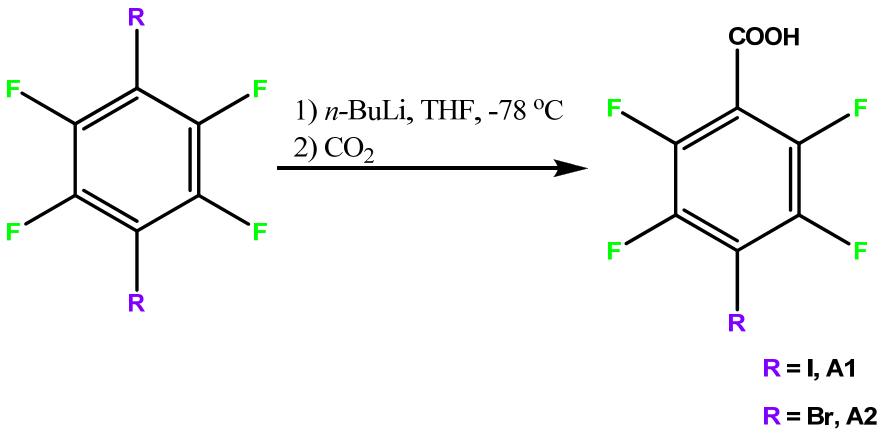
General Experimental Details

^{1}H NMR spectra were recorded on a Varian Unity plus 400 MHz spectrometer spectrometer in $CDCl_3$. Data is expressed in parts per million (ppm) downfield shift from tetramethylsilane or residual protiosolvent as internal reference and are reported as position (in ppm), multiplicity (s

= singlet, d = doublet, t = triplet, m = multiplet), coupling constant (*J* in Hz) and integration (number of protons). Melting points were recorded on Fisher-Johns melting point apparatus and are uncorrected. Infrared spectroscopy (IR) was done on a Nicolet 380 FT-IR. 1,4-diiodo-2,3,5,6-tetrafluorobenzene and 1,4-dibromo-2,3,5,6-tetrafluorobenzene were purchased from Sigma Aldrich and Matrix Scientific respectively. All the other chemicals were purchased from Aldrich and Fisher and used without further purification, unless otherwise noted. Solvents and reagents were purified according to the procedures outlined by Perrin and Armarego. [Purification of Laboratory Chemicals; D. D. Perrin, W.L.F. Armarego; 3rd Ed., Pergamon Press, 1988].

Experimental Procedures and Product Characterization Data

Synthesis of A1 and A2

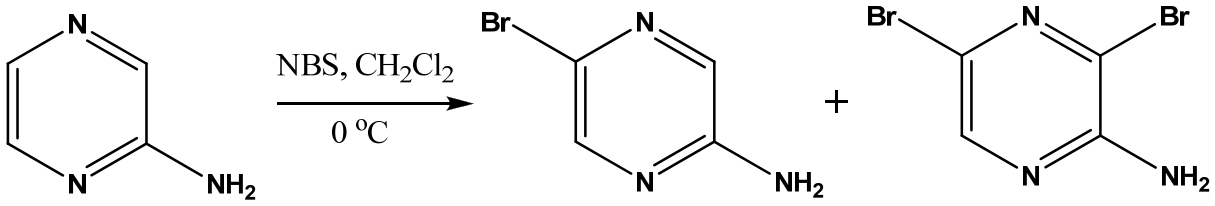


Synthesis of A1 : To oven dried one-necked round-bottomed flask with stir bar added 1,4-diiodo-2,3,5,6-tetrafluorobenzene (1g, 2.5 mmol) under stream of Ar and sealed the flask with rubber septum. To this flask was added dry, freshly distilled THF (70ml) via canula. This solution was cooled down to -78 °C by immersing into dry ice –acetone bath for 5-7 mins. To this solution was then slowly added *n*-butyllithium (1.6 M solutions in hexanes, 1.65 ml, 2.6

mmol). After 20 minutes, carbon dioxide gas was purged into reaction mixture for 15 mins followed by addition of excess solid dry ice to reaction mixture. The reaction mixture was slowly warmed to 0 ^{o}C and quenched with 2M HCl carefully. The solvent was removed on rotary evaporator and product was extracted in methylene chloride. The organic phase was washed with saturated sodium thiosulfate solution, brine solution and dried using anhydrous magnesium sulfate. The solvent was removed on rotary evaporator to yield crude product which was triturated with cold hexane and filtered off to yield pure **A1** (0.414g, 52% yield). Dec. 140 ºC and all other characterization data matches with previously reported data.[1]

Synthesis of A2 : Prepared according to procedure used to synthesize **A1** starting with 1,4-dibromo-2,3,5,6-tetrafluorobenzene, the only difference was after aqueous work up directly got pure **A2** (0.764g, 86% yield). M.p. 128-130 ºC and all other characterization data matches with previously reported data.[1]

Synthesis of B1 and B2



B1 **B2** **B3**

A solution of N-bromosuccinimide (2.4 g, 13.4 mmol) in methylene chloride was added dropwise to 2-aminopyrazine (1.0 g, 10.6 mmol) dissolved in methylene chloride cooled at 0 ºC. The reaction mixture was stirred at 0-5ºC for 2 hr. The reaction was monitored closely by TLC and upon completion, was quenched with 10% sodium bicarbonate and 10% sodium sulfite solution. The mixture was filtered and the precipitate washed with water. The filtrate was extracted with methylene chloride and dried over anhydrous magnesium sulfate. The solvent was

removed on a rotary evaporator and the residue was chromatographed on silica with hexane: ethyl acetate (10:0→4:6) mixture as eluant. The product **B2** was isolated as a yellowish-white powder(Eluant- Hexane: Ethyl acetate 10:0→10:2) and the product **B3** as a white powder (Eluant- Hexane: Ethyl acetate 10:3→10:5). The products were recrystallized from ethyl acetate:hexane.

Product **B2** (2-amino-5-bromopyrazine), (2.70 g, 62%). M. P. 105-107 ºC (Reported M. P. 105-110 ºC [2]); ^{1}H NMR (δ_H; 200 MHz, $CDCl_3$): 8.09 (s, 1H), 7.78 (s, 1H), 4.64 (br, 2H).

Product **B3** (2-amino-3,5-dibromopyrazine), (0.76 g, 12%). M. P. 111-113 ^{o}C (Reported M. P. 109-110 ºC[3]); ^{1}H NMR (δ_H; 200 MHz, $CDCl_3$): 8.05 (s, 1H), 5.05 (br, 2H).

Synthesis and characterization of A1·B1 – A2·B3

All the co-crystals or salts were synthesized via slow evaporation in clear 2 dram borosilicate vial via mixing required acid (15mg) and base in 1:1 ratio in following solvents (Table S1). All crystals were first analysed by IR spectroscopy for presence of broad OH···N hydrogen bonding stretches in 1800 and 2500 cm^{-1} region prior to XRD analysis.

Table S1. Synthesis and IR data for **A1·B1** - **A2·B3**

	Co-crystal or Salt	Solvent/s (ratios)	IR bands(cm^{-1})		Melting Point (^{o}C)
			~1800	~2500	
A1·B1	Salt	Methanol	1952	2688	184-186
A2·B1	Salt	Ethanol:water (9:1)	2024	2707	dec. 135
A1·B2	Co-crystal	CH_2Cl_2:EtOAc:Hexane (1:1:1)	1887	2406	Dec. 150
A2·B2	Co-crystal	Ethanol:water (9:1)	1891	2435	120-124
A1·B3	Co-crystal	Ethanol:water (9:1)	1878	2461	139-141
A2·B3	Co-crystal	Ethanol:water (1:1)	1862	2369	106-107

Table S2. Summary showing interactions of *anti* NH proton in crystal structures

	anti NH···O (of COOH)	*d*(N···O) Å
A1·B1	N221-H22B1...O122#1	2.779(2)
	N222-H22B2...O111#2	2.893(2)
A2·B1	N221-H22B1...O122#1	2.846(3)
	N222-H22B2...O121#1	2.903(3)
	N223-H22B3...O124#2	2.864(3)
	N224-H22B4...O123#2	2.887(3)
A1·B2	N(12)-H(12B)...O(22)#1	2.904(2)
A2·B2	N(15)-H(15B)...O(22)#1	2.973(4)
A1·B3	N(12)-H(12B)...O(22)#1	3.196(2)
A2·B3	None	None

Crystallographic Experimental Details[4]

X-ray data were collected on a Bruker Kappa APEX II CCD diffractometer at 120 K using, a fine-focus molybdenum Kα tube. Data were collected using APEX2 software. Initial cell constants were found by small widely separated "matrix" runs. Scan speed and scan width were chosen based on scattering power and peak rocking curves.

Unit cell constants and orientation matrix were improved by least-squares refinement of reflections thresholded from the entire dataset. Integration was performed with SAINT, using this improved unit cell as a starting point. Precise unit cell constants were calculated in SAINT from the final merged dataset. Lorenz and polarization corrections were applied. Laué symmetry, space group, and unit cell contents were found with XPREP.

Data were reduced with SHELXTL. The structures were solved in all cases by direct methods without incident. Except where indicated, hydrogens were assigned to idealized positions and were allowed to ride. Heavy atoms were refined with anisotropic thermal parameters. Absorption correction was carried out on all datasets.

A1.B1 Two acid / base pairs are contained in the asymmetric unit. For each pair, proton transfer from acid to pyridine nitrogen was observed. The coordinates of the amino and pyridinium protons were allowed to refine.

A2.B1 Four acid / base pairs are contained in the asymmetric unit. For all four pairs, proton transfer from acid to pyridine nitrogen atom was observed. The coordinates of the pyridinium protons were allowed to refine. The amino protons were assigned to idealized positions and were allowed to ride.

A1.B2 The coordinates of the amino and carboxylic acid protons were allowed to refine.

A2.B2 All hydrogen atoms were assigned to idealized positions and were allowed to ride.

A1.B3 Coordinates for the amine and carboxylic acid protons were allowed to refine.

A2.B3 Four acid / base pairs are contained in the asymmetric unit. Anisotropic thermal parameters for each amine and for each acid were tied using the EADP command. The FLAT command was used to enforce planarity for aromatic rings and the carboxylic acid. All hydrogen atoms were assigned to idealized positions and were allowed to ride.

Table S3. Summary of X-ray data

	A1.B1 (CG0902)	**A2.B1 (PC0806)**	**A1.B2 (PC1006)**	**A2.B2 (PC0808)**	**A1.B3 (PC0803)**	**A2.B3 (PC1020)**
Systematic name	2-aminopyrazine, 2,3,5,6-tetrafluoro-4-iodobenzoic acid	2-aminopyrazine, 2,3,5,6-tetrafluoro-4-bromobenzoic acid	2-amino-5-bromopyrazine, 2,3,5,6-tetrafluoro-4-iodobenzoic acid	2-amino-5-bromopyrazine, 2,3,5,6-tetrafluoro-4-bromobenzoic acid	2-amino-3,5-dibromopyrazine, 2,3,5,6-tetrafluoro-4-iodobenzoic acid	2-amino-3,5-dibromopyrazine, 2,3,5,6-tetrafluoro-4-bromobenzoic acid
Formula moiety	($C_4H_5N_3$) ($C_7HF_4O_2I$)	($C_4H_5N_3$) ($C_7HBrF_4O_2$)	($C_4H_4N_3Br$) ($C_7HO_2F_4I$)	($C_7HBrO_2F_4$) ($C_4H_4BrN_3$)	($C_4H_3N_3Br_2$) ($C_7HO_2F_4I$)	($C_4H_3N_3Br_2$) ($C_7HBrF_4O_2$)
Empirical formula	$C_{11}H_6F_4IN_3O_2$	$C_{11}H_6BrF_4N_3O_2$	$C_{11}H_5BrF_4IN_3O_2$	$C_{11}H_5Br_2F_4N_3O_2$	$C_{11}H_4Br_2F_4IN_3O_2$	$C_{11}H_4Br_3F_4N_3O_2$
Molecular weight	415.09	368.10	493.99	447.00	572.89	525.90
Color, Habit	orange prism	orange prism	orange prism	colourless plate	colourless prism	colourless rod
Crystal size, mm^3	0.26 x 0.20 x 0.14	0.20 x 0.20 x 0.15	0.26 x 0.20 x 0.12	0.18 x 0.16 x 0.10	0.25 x 0.20 x 0.15	0.28 x 0.14 x 0.10
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group, Z	P2/n, 8	P-1, 8	P2(1)/c, 4	P-1, 2	P2(1)/c, 4	P2(1)/n, 12
a, Å	15.2832(8)	10.6236(4)	14.3341(10)	7.1539(4)	10.4824(4)	15.2443(14)
b, Å	11.5421(6)	10.6899(4)	14.1571(10)	9.6066(5)	5.7580(3)	13.9577(16)
c, Å	15.3499(8)	22.3295(9)	6.8919(5)	10.2884(6)	25.7816(11)	21.995(3)
α, °	90.00	84.593(2)	90.00	89.546(4)	90.00	90.00
β, °	107.171(2)	76.279(2)	96.564(3)	73.888(3)	98.9360(10)	109.743(6)
γ, °	90.00	90.002(2)	90.00	83.695(3)	90.00	90.00
Volume, $Å^3$	2587.0(2)	2451.87(16)	1389.40(17)	675.00(6)	1537.23(12)	4405.0(8)
Density, g/cm^3	2.131	1.994	2.362	2.199	2.475	2.379
Temperature, K	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
X-ray wavelength	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	2.533	3.413	5.237	6.062	7.335	8.298
θ_{min}, °	1.76	1.91	2.03	2.93	2.33	1.76
θ_{max}, °	33.14	33.19	33.14	32.03	32.48	29.57
Reflections						
collected	41424	54908	24833	9855	17435	45126
independent	9835	54908	5302	3975	5467	12261
R_{int}	0.0441	0.0000	0.0505	0.0210	0.0228	0.1747
observed	8674	42573	4470	3084	4867	6482
Threshold expression	>2σ(I)	>2σ(I)	>2σ(I)	>2σ(I)	>2σ(I)	>2σ(I)
Absorption corr	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Trans min/max	0.5589 / 0.7181	0.5485 / 0.6285	0.3430 / 0.5722	0.4083 / 0.5824	0.2614 / 0.4058	0.2047 / 0.4908
R_1 (observed)	0.0274	0.0436	0.0290	0.0379	0.0227	0.1678
wR_2 (all)	0.0678	0.1041	0.0705	0.1015	0.0559	0.3995
Δρ max / min	1.319 / -1.014	1.188 / -0.933	1.485 / -0.874	2.207 / -1.296	1.367 / -0.850	9.959 / -3.595

To test the homogenity of the bulk sample we have carried out Powder X-ray Diffraction on all six samples (**A1·B1 – A2·B3)**. Figures S1-S12 shows comparison of PXRD pattern calculated from crystal structure and experimental.

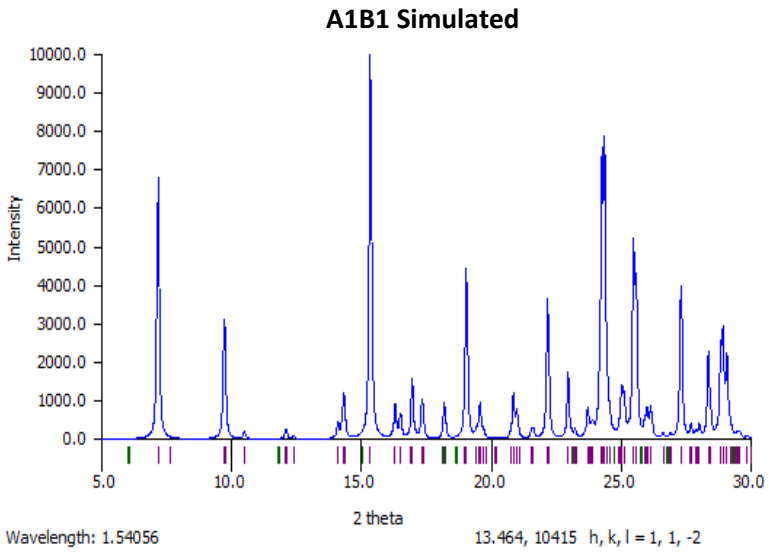


Figure S1. Simulated PXRD pattern of A1B1.

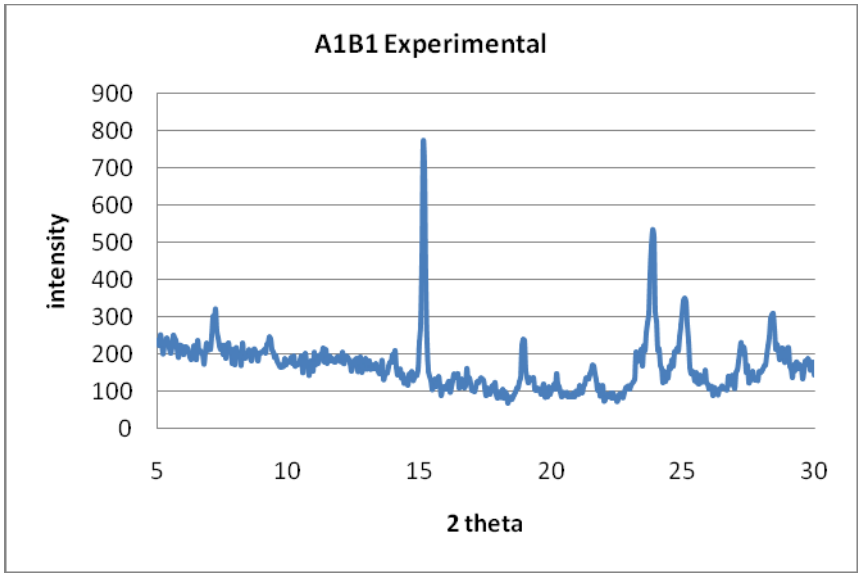


Figure S2. Experimental PXRD pattern of A1B1.

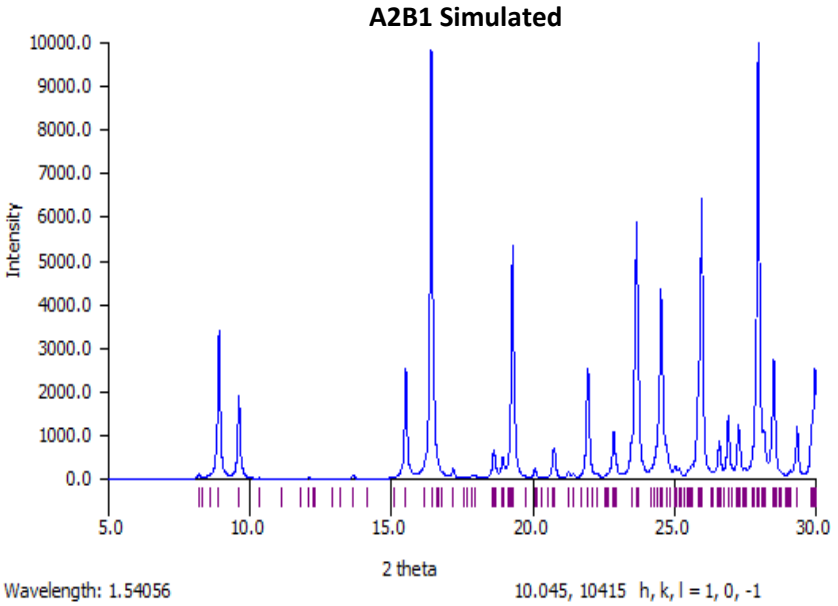


Figure S3. Simulated PXRD pattern of A2B1

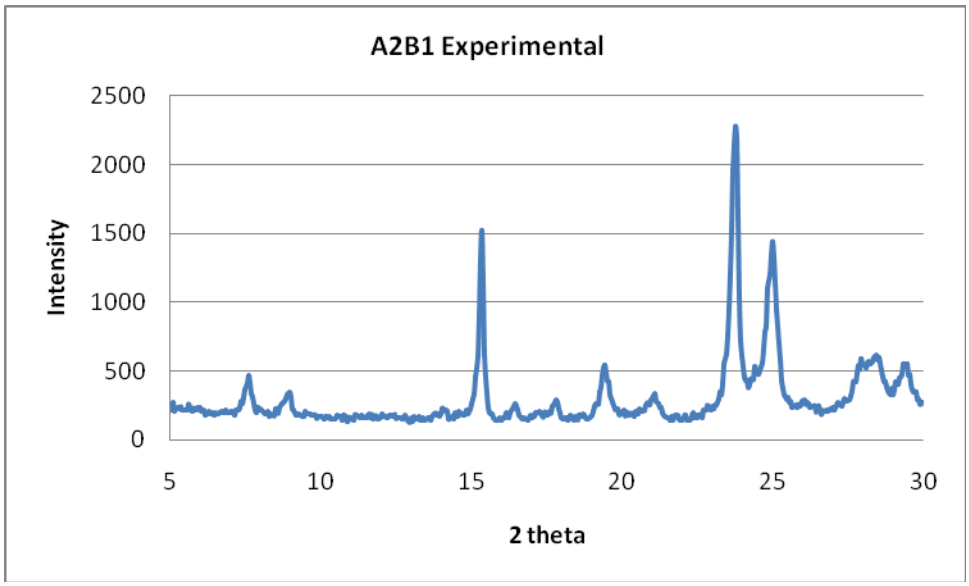


Figure S4. Experimental PXRD pattern of A2B1.

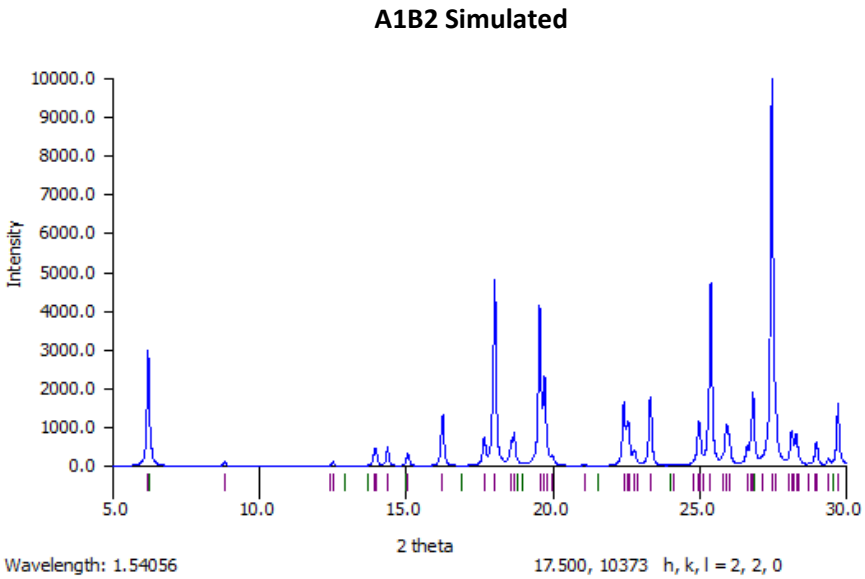


Figure S5. Simulated PXRD pattern of A1B2

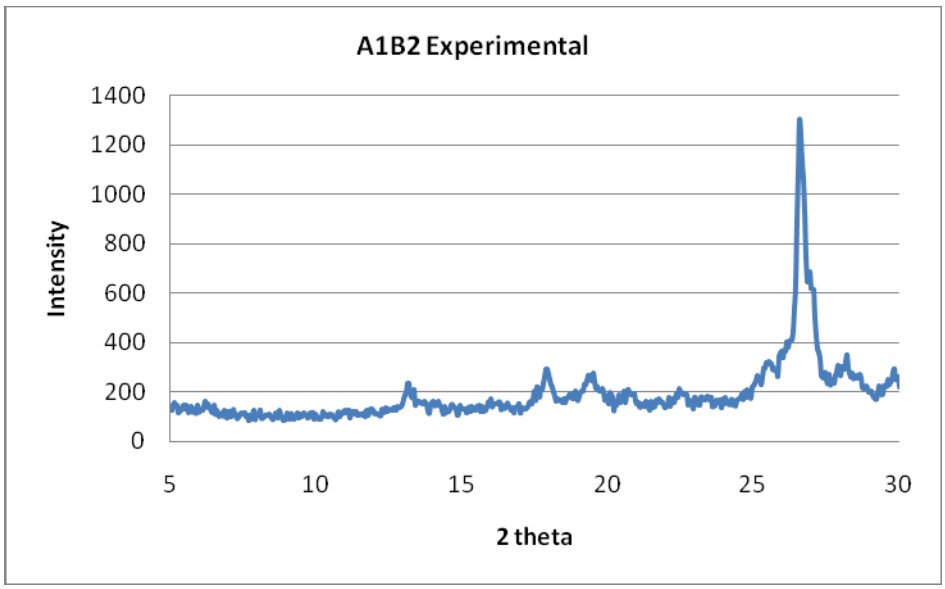


Figure S6. Experimental PXRD pattern of A1B2

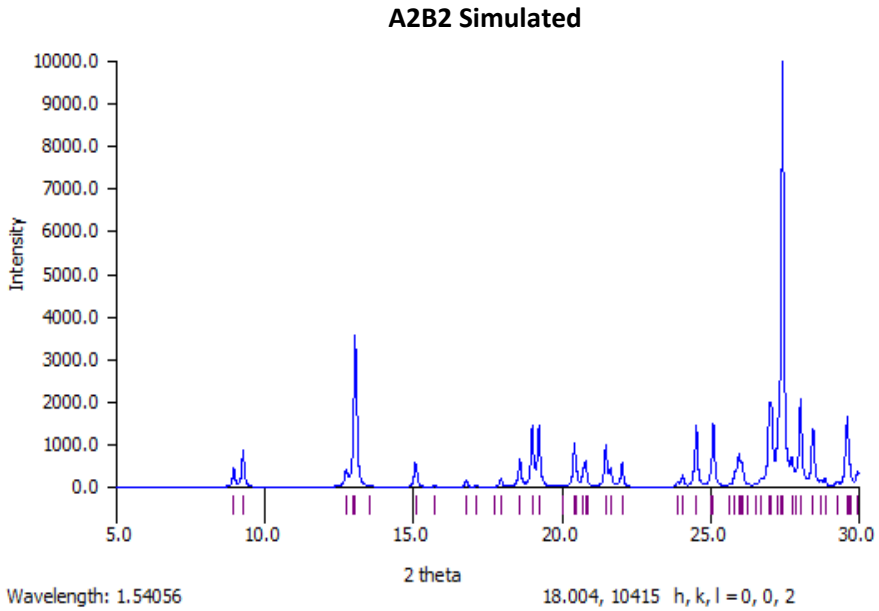


Figure S7. Simulated PXRD pattern of A2B2

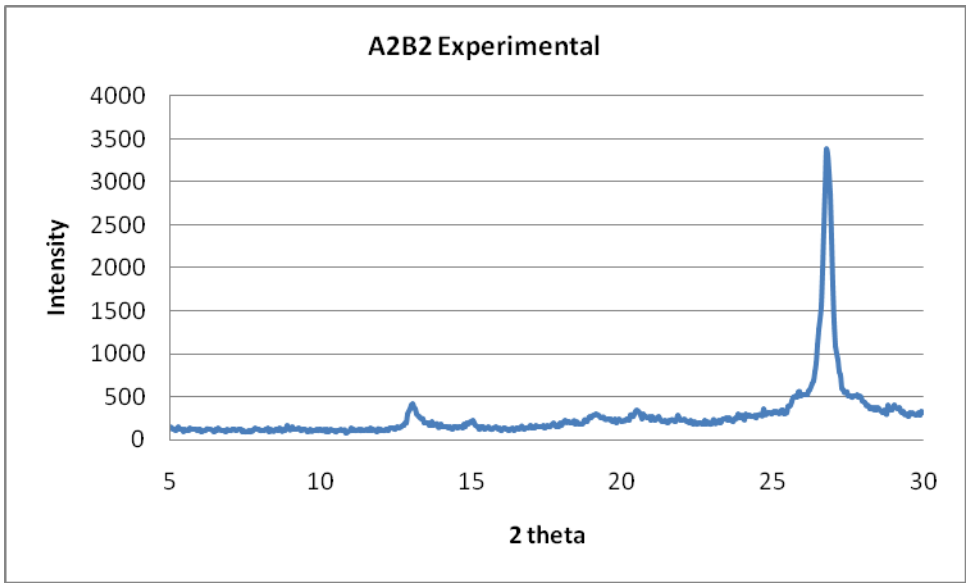


Figure S8. Experimental PXRD pattern of A2B2

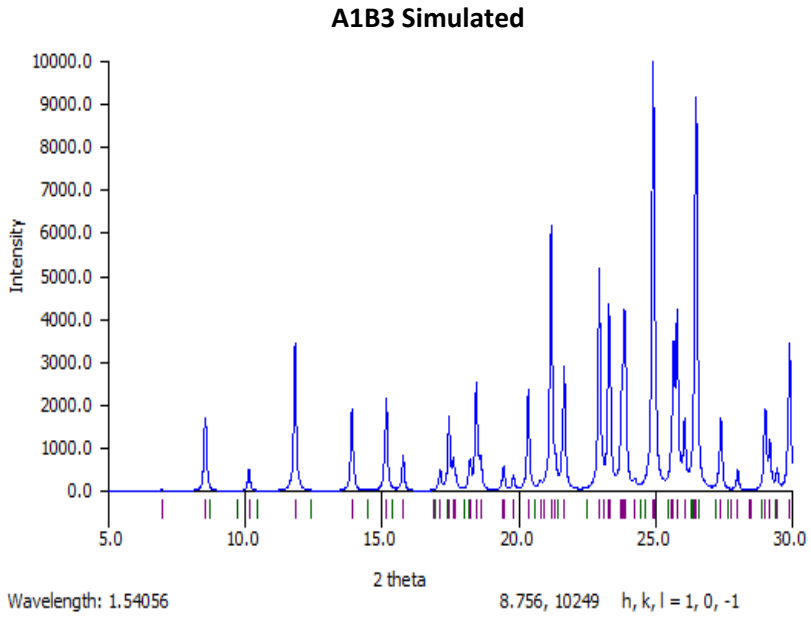


Figure S9. Simulated PXRD pattern of A1B3

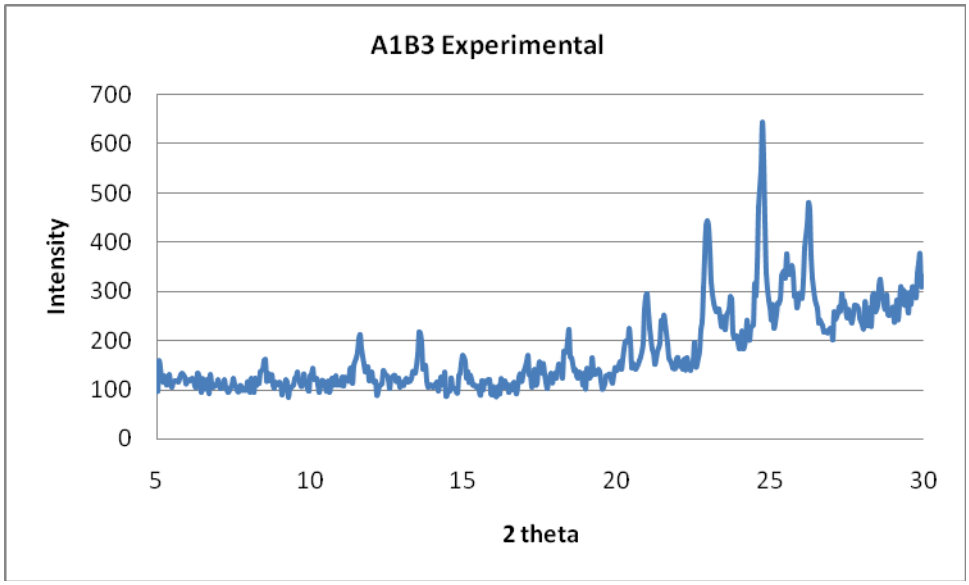


Figure S10. Experimental PXRD pattern of A1B3

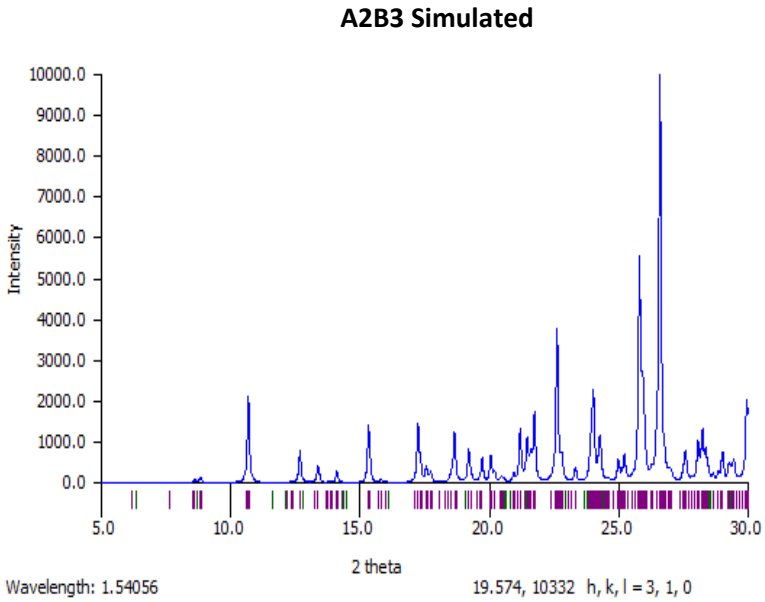


Figure S11. Simulated PXRD pattern of A2B3

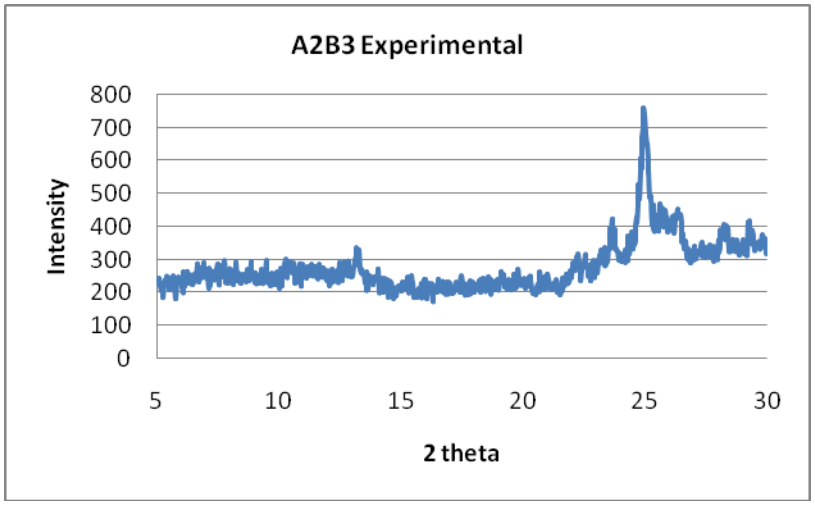


Figure S12. Experimental PXRD pattern of A2B3

References

[1] C. B. Aakeröy, N. C. Schultheiss, A. Rajbanshi, J. Desper, C. Moore, *Cryst. Growth Des.*, 2009, **9**, 432.

[2] R. C. Ellingson, R. L. Henry, *J. Am. Chem. Soc.*, 1949, **71**, 2798.

[3] W. W. Paudler, M. V. Jovanovic, *J. Org. Chem.,* 1983, **48**, 1064.

[4] SMART v5.060, © 1997 - 1999, Bruker Analytical X-ray Systems, Madison, WI; APEX2 v2.2.0 © 2005 - 2007, Bruker AXS, Madison, WI; SAINT v7.46a, © 1997 - 2007, Bruker AXS, Madison, WI; SHELXTL v6.10, © 2001 , Bruker AXS, Madison, WI.