Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Isolation of unique heterocycles formed from pyridine-thiocarboxamides as diiodine, iodide, or polyiodide salts

Andrew J. Peloquin, Colin D. McMillen,* and William T. Pennington*

Department of Chemistry, Clemson University, Clemson, South Carolina (USA)

*Correspondence e-mail: cmcmill@clemson.edu and billp@clemson.edu

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Table S1. Crystallographic data and selected data collection parameters

Compound	**[1B][I_3]$_2$·(H_2O)$_2$**	**[2B][I]·(MeCN)**	**[2C][I_3]$_2$·(2A)**	**[2B][I]·(CHI_3)**
empirical formula M_r	$C_{12}H_{14}I_6N_4O_2S$	$C_{14}H_{12}IN_5S$	$C_{24}H_{18}I_6N_8S_2$	$C_{26}H_{20}I_8N_8S_2$
crystal system	monoclinic	orthorhombic	monoclinic	triclinic
space group	$P2_1/n$	*Pnma*	$P2_1/n$	*P*-1
a (Å)	7.4815(4)	9.8620(2)	7.7763(6)	8.7340(4)
b (Å)	32.2385(19)	6.3853(2)	25.918(2)	14.0058(6)
c (Å)	10.5446(7)	25.0333(5)	17.0369(13)	16.2738(8)
α (°)	90	90	90	109.150(2)
β (°)	106.562(2)	90	99.309(3)	90.654(2)
γ (°)	90	90	90	96.535(2)
Volume (Å^3)	2437.8(3)	1576.39(7)	3388.5(5)	1865.82(15)
Z	4	4	4	2
D_c (g·cm^{-3})	2.833	1.724	2.438	2.712
transmission coeff.	7.745	2.164	5.653	6.793
No. of ref. total	65198	11018	52923	47569
No. of ref. unique	6891	1756	6943	7641
No. of param.	240	131	405	428
R[a]	0.0311	0.0280	0.0217	0.0161
R_{all}	0.0384	0.0362	0.0253	0.0187
$_wR$[b]	0.0656	0.0529	0.0505	0.0328
$_wR_{all}$	0.0675	0.0578	0.0531	0.0341
GooF	1.127	1.061	1.111	1.074
CCDC #	2182000	2182001	2182002	2182003

[a] $R = \Sigma||F_o| - [F_c||/\Sigma|F_o|$. [b] $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^2]^2\}^{1/2}$

Table S1. Crystallographic data and selected data collection parameters (cont.)

Compound	**[3A][I_5]$_3$·(MeCN)$_2$**	**[3B][I_5]$_4$·(I_2)$_{0.14}$·(MeCN)$_{2.86}$**	**[3C]$_2$[I_5]$_4$[I_3]$_2$·(I_2)$_3$·(H_2O)$_4$**
empirical formula M_r	$C_{22}H_{21}I_{15}N_8$	$C_{41.71}H_{34.57}FeI_{20.29}N_{14.86}$	$C_{60}H_{54}Fe_2I_{32}N_{20}O_6$
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1/c$	*P-1*	*P-1*
a (Å)	7.3464(2)	13.3176(6)	10.36580(10)
b (Å)	26.9370(4)	16.6001(7)	13.9906(2)
c (Å)	24.3715(5)	19.8556(8)	21.5956(3)
α (°)	90	103.605(2)	97.0570(10)
β (°)	94.853(2)	96.773(2)	94.9320(10)
γ (°)	90	111.876(2)	110.7400(10)
Volume (Å^3)	4805.58(18)	3854.9(3)	2878.31(7)
Z	4	2	1
D_c (g·cm^{-3})	3.180	2.907	3.071
transmission coeff.	9.686	8.359	8.882
No. of ref. total	117800	145950	72888
No. of ref. unique	9825	15754	11738
No. of param.	420	759	557
R[a]	0.0260	0.0342	0.0472
R_{all}	0.0341	0.0404	0.0634
$_wR$[b]	0.0454	0.0721	0.1210
$_wR_{all}$	0.0477	0.0771	0.1303
GooF	1.052	1.090	1.090
CCDC #	2182004	2182005	2182006

[a] $R = \Sigma||F_o| - [F_c||/\Sigma|F_o|$. [b] $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^2]^2\}^{1/2}$

Table S1. Crystallographic data and selected data collection parameters (cont.)

Compound	**$[1A]_2[Bi_8I_{28}]\cdot(MeCN)_4$**	**$[1A][1B][Bi_2I_9]\cdot(H_2O)_3$**	**$[2C]_2[Bi_4I_{16}]\cdot(I_2)_2\cdot(MeCN)_2$**
empirical formula M_r	$C_{32}H_{32}Bi_8I_{28}N_{12}S_2$	$C_{24}H_{25}Bi_2I_9N_8O_3S_2$	$C_{28}H_{26}Bi_4I_{20}N_{10}S_2$
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1$	*P-1*
a (Å)	21.2030(12)	8.3663(5)	10.789(2)
b (Å)	11.4331(5)	24.1622(12)	12.598(3)
c (Å)	40.625(2)	12.9374(8)	15.026(3)
α (°)	90	90	107.107(9)
β (°)	90.697(2)	106.602(2)	95.518(8)
γ (°)	90	90	111.229(8)
Volume (Å^3)	9847.4(9)	2506.2(3)	1771.9(7)
Z	4	2	1
D_c (g·cm^{-3})	3.962	2.780	3.693
transmission coeff.	23.093	12.671	18.703
No. of ref. total	199003	77273	85055
No. of ref. unique	24538	13925	8860
No. of param.	792	461	309
R[a]	0.0317	0.0299	0.0275
R_{all}	0.0453	0.0324	0.0307
$_wR$[b]	0.0531	0.0711	0.0605
$_wR_{all}$	0.0570	0.0718	0.0613
GooF	1.058	1.084	1.243
CCDC #	2182007	2182008	2182009

[a] $R = \Sigma||F_o| - [F_c||/\Sigma|F_o|$. [b] $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^2]^2\}^{1/2}$

Table S1. Crystallographic data and selected data collection parameters (cont.)

Compound	**$[2C]_2[Bi_6I_{22}]\cdot(MeOH)_2$**	**$[3A]_3[Bi_6I_{22}]_2[I_7]\cdot(I_2)\cdot(MeCN)_3\cdot(H_2O)_2$**	**$[4A]_4[I_3]_4\cdot(MeCN)_3$**
empirical formula M_r	$C_{26}H_{28}Bi_6I_{22}N_8O_2S_2$	$C_{60}H_{58}Bi_{12}I_{53}N_{21}O_2$	$C_{46}H_{45}I_{12}N_{27}$
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1/c$	*P-1*	*P-1*
a (Å)	14.9488(11)	11.3588(6)	13.5105(5)
b (Å)	10.7020(7)	11.5129(6)	14.6827(7)
c (Å)	25.0852(19)	34.8748(17)	17.4311(8)
α (°)	90	92.184(2)	93.901(2)
β (°)	106.469(3)	93.977(2)	101.189(2)
γ (°)	90	106.355(2)	91.407(2)
Volume (Å^3)	3848.5(5)	4357.7(4)	3381.7(3)
Z	2	1	2
D_c (g·cm^{-3})	3.965	3.940	2.454
transmission coeff.	22.578	21.491	5.550
No. of ref. total	136509	86802	143131
No. of ref. unique	9610	34387	16112
No. of param.	307	1349	817
R[a]	0.0210	0.0458	0.0241
R_{all}	0.0299	0.0610	0.0343
$_wR$[b]	0.0409	0.1029	0.0506
$_wR_{all}$	0.0427	0.1125	0.0567
GooF	1.042	1.014	1.080
CCDC #	2182010	2182011	2182012

[a] $R = \Sigma||F_o| - [F_c||/\Sigma|F_o|$. [b] $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^2]^2\}^{1/2}$

Table S1. Crystallographic data and selected data collection parameters (cont.)

Compound	**[5A]$_4$[Bi$_4$I$_{16}$]·(MeOH)$_4$**	**[5B]$_2$[I$_3$]$_4$·(5)$_2$·(MeCN)**	**[5C][I$_5$]$_2$**	**[6A]$_2$[Bi$_4$I$_{16}$]·(I$_2$)$_2$·(MeCN)$_4$**
empirical formula M_r	$C_{44}H_{52}Bi_4I_{16}N_{24}O_4$	$C_{42}H_{39}I_{12}N_{25}S_2$	$C_{20}H_{16}I_{10}N_{12}$	$C_{64}H_{68}Bi_4I_{20}N_{20}$
crystal system	triclinic	triclinic	monoclinic	triclinic
space group	*P-1*	*P-1*	$P2_1/c$	*P-1*
a (Å)	13.1812(4)	8.0951(4)	25.1259(13)	11.1882(5)
b (Å)	13.8011(4)	12.8879(7)	7.4309(4)	14.4203(6)
c (Å)	14.1644(5)	16.9574(9)	21.0334(9)	17.1240(8)
α (°)	108.4490(10)	78.700(2)	90	109.244(2)
β (°)	99.637(2)	89.492(2)	102.923(2)	91.431(2)
γ (°)	115.4060(10)	77.193(2)	90	97.814(2)
Volume (Å^3)	2065.08(12)	1690.59(15)	3827.6(3)	2576.9(2)
Z	1	1	4	1
D_c (g·cm^{-3})	3.094	2.437	2.939	2.894
transmission coeff.	14.528	5.609	8.128	12.844
No. of ref. total	59364	86268	56327	127858
No. of ref. unique	9485	8055	9664	14514
No. of param.	447	396	391	497
R[a]	0.0320	0.0139	0.0263	0.0308
R_{all}	0.0408	0.0163	0.0357	0.0398
$_wR$[b]	0.0623	0.0277	0.0531	0.0604
$_wR_{all}$	0.0683	0.0286	0.0587	0.0659
GooF	1.241	1.079	1.140	1.122
CCDC #	2182013	2182014	2182015	2182016

[a] $R = \Sigma||F_o| - [F_c||/\Sigma|F_o|$. [b] $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^2]^2\}^{1/2}$

Table SI2. Selected halogen and chalcogen bonding parameters [Å, °]

X–D···A	*D*···A	R_{XB} *or* R_{ChB}	*X–D*···*A*	*D*···*A–Y*
		$[2C][I_3]_2\cdot(2A)$		
C7–S1A···I6	3.492(8)	0.92	160.5(4)	74.17(14)
		$[2B][I]\cdot(CHI_3)$		
C7–S1···I5	3.5915(10)	0.95	173.92(10)	115.02(9)
C25–I2···I4	3.5252(5)	0.89	172.16(7)	
C25–I1···I8	3.5507(4)	0.90	176.13(7)	
C25–I3···I8	3.5715(4)	0.90	161.67(7)	
C26–I5···I4	3.5195(4)	0.89	175.14(8)	
C26–I6···I8	3.4693(4)	0.88	169.04(9)	
C26–I7···I8	3.7225(5)	0.94	171.52(6)	
		$[3A][I_5]_3\cdot(MeCN)_2$		
I7–I6···I3	3.6382(6)	0.92	169.86(2)	101.29(2)
I2–I1···I6	3.9293(7)	0.99	173.63(2)	89.679(15)
I12–I11···I5	3.8776(7)	0.98	178.902(17)	69.197(16)
I4–I5···I8	3.8051(8)	0.96	158.60(2)	92.30(2)
		$[3B][I_5]_4\cdot(I_2)_{0.14}\cdot(MeCN)_{2.86}$		
I11–I10···I7	3.8676(10)	0.98	171.55(3)	135.94(3)
I2–I1···I7	3.6533(10)	0.92	176.74(3)	75.37(2)
I9–I8···I3	3.449(1)	0.87	166.20(3)	93.459(18)
I16–I17···I8	3.6935(10)	0.93	161.20(2)	99.00(2)
I20–I21···I16	3.9186(6)	0.99	159.767(19)	90.09(2)
		$[3C]_2[I_5]_4[I_3]_2\cdot(I_2)_3\cdot(H_2O)_4$		
I4–I3···I17	3.6893(8)	0.93	172.10(4)	76.783(19)
I14–I13···I18	3.5515(12)	0.90	171.96(3)	82.15(3)
		$[1A][1B][Bi_2I_9]\cdot(H_2O)_3$		
C7–S1A···I2	3.740(7)	0.94	149.0(5)	97.17(12)
		$[2C]_2[Bi_4I_{16}]\cdot(I_2)_2\cdot(MeCN)_2$		
C1–S1A···I1	3.610(5)	0.91	166.5(4)	127.76(10)
I10–I9···I8	3.4489(10)	0.87	174.36(2)	115.52(2)
I9–I10···I7	3.5893(11)	0.91	174.86(2)	107.483(16)
		$[3A]_3[Bi_6I_{22}]_2[I_7]\cdot(I_2)\cdot(MeCN)_3\cdot(H_2O)_2$		
I23–I24···I1	3.314(3)	0.84	171.79(11)	114.70(8)
I24–I23···I26	3.697(3)	0.93	154.87(10)	91.62(11)
I26–I25···I1	3.581(3)	0.90	166.80(11)	110.54(7)
		$[4A]_4[I_3]_4\cdot(MeCN)_3$		
I11–I12···I5	3.9103(4)	0.99	167.952(14)	90.975(15)
		$[5B]_2[I_3]_4\cdot(5)_2\cdot(MeCN)$		
C16–S1···I5	3.7064(6)	0.94	156.34(8)	90.567(18)
		$[5C][I_5]_2$		
I4–I5···I2	3.8741(7)	0.98	156.129(16)	90.54(2)
		$[6A]_2[Bi_4I_{16}]\cdot(I_2)_2\cdot(MeCN)_4$		
I10–I9···I8	3.2834(7)	0.83	171.49(2)	114.401(16)
I9–I10···I3	3.6098(7)	0.91	168.69(3)	109.231(15)

Only halogen and chalcogen bonds of Type II geometry are tabulated. R_{XB} and R_{ChB} are calculated using the van der Waals radii of Bondi (S = 1.80 Å and I = 1.98 Å).

Table SI3. Selected hydrogen bonding parameters [Å, °]

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
[1B][I_3]$_2$·(H_2O)$_2$				
N3–H3···O1	0.860(19)	2.03(3)	2.816(5)	151(6)
N4–H4···O2	0.868(19)	1.82(4)	2.683(5)	170(6)
[2C][I_3]$_2$·(2A)				
N1–HN1···N5	0.82(4)	1.89(5)	2.710(4)	173(5)
N4–HN4···N8	0.86(4)	1.88(5)	2.72(5)	166(4)
[2B][I]·(CHI_3)				
N3–HN3···N8	0.87(2)	1.81(7)	2.681(4)	175(6)
N4–HN4···N7	0.87(7)	1.78(7)	2.647(4)	175(6)
N7–HN7···N4	0.87(7)	1.78(7)	2.647(4)	174(5)
N8–HN8···N3	0.88(7)	1.82(7)	2.681(4)	166(6)
[3A][I_5]$_3$·($MeCN$)$_2$				
N4–HN4···N8	0.86(4)	2.23(4)	3.018(6)	152(4)
N5–HN5···N8	0.85(3)	2.02(3)	2.845(7)	163(5)
N6–HN6···N7	0.85(3)	2.15(4)	2.872(6)	143(5)
[3B][I_5]$_4$·(I_2)$_{0.14}$·($MeCN$)$_{2.86}$				
N12–HN12···N14	0.87(5)	2.03(4)	2.820(8)	152(9)
[3C]$_2$[I_5]$_4$[I_3]$_2$·(I_2)$_3$·(H_2O)$_4$				
N10–HN10···O1	0.86(9)	2.0(1)	2.743(11)	145(3)
N4–HN4A···O4	0.880(9)	2.171(7)	2.957(11)	148.5(7)
N4–HN4B···O2	0.88(1)	2.025(10)	2.886(14)	166.5(6)
[1A]$_2$[Bi_8I_{28}]·($MeCN$)$_4$				
N1–HN1···N9	0.86(5)	1.96(4)	2.801(11)	163(8)
N4–HN4···N11	0.86(7)	2.39(7)	2.909(9)	120(6)
N5–HN5···N11	0.880(7)	2.323(7)	2.93(1)	126.2(5)
N4–HN4···N10	0.86(7)	2.21(7)	2.963(10)	147(6)
N5–HN5···N10	0.880(7)	2.150(7)	2.876(9)	139.3(5)
N8–HN8···N12	0.86(5)	2.06(5)	2.830(11)	149(8)
[1A][1B][Bi_2I_9]·(H_2O)$_3$				
N4–H4···O1	0.87(6)	1.78(7)	2.625(15)	163(10)
N7–H7···O2	0.86(4)	1.94(5)	2.77(2)	164(6)
O1–H1A···N3	0.875(10)	2.011(12)	2.661(17)	130.2(10)
[2C]$_2$[Bi_4I_{16}]·(I_2)$_2$·($MeCN$)$_2$				
N1–HN1···N5	0.881(6)	1.931(6)	2.809(9)	174.3(4)
[2C]$_2$[Bi_6I_{22}]·($MeOH$)$_2$				
N1–HN1···O1	0.91(8)	2.21(6)	2.999(6)	144(7)
[3A]$_3$[Bi_6I_{22}]$_2$[I_7]·(I_2)·($MeCN$)$_3$·(H_2O)$_2$				
N4–HN4···O1	0.89(2)	2.01(2)	2.87(3)	163.2(16)
N6–HN6···O1	0.88(2)	2.038(18)	2.89(3)	160.7(17)
N5–HN5···N7	0.88(2)	2.04(3)	2.82(4)	148.7(19)
N18–HN8···N21	0.88(3)	2.21(3)	3.03(5)	154(3)
N19–HN19···N21	0.87(3)	2.30(4)	3.13(5)	159(2)
N11–HN11···N14	0.88(2)	2.08(2)	2.86(3)	146.5(18)
N12–HN12···O2	0.88(2)	1.98(2)	2.82(3)	157.6(17)
N13–HN13···O2	0.88(2)	2.04(2)	2.88(3)	159.6(17)
[4A]$_4$[I_3]$_4$·($MeCN$)$_3$				
N1–HN1A···N24	0.86(5)	2.13(5)	2.969(5)	167(4)
N13–HN13···N12	0.88(3)	2.09(3)	2.957(5)	170(4)
N7–HN7A···N18	0.86(2)	2.08(3)	2.928(5)	168(4)
N19–HN19···N6	0.84(2)	2.16(3)	2.983(5)	168(4)
N3–HN3···N25	0.85(5)	2.11(5)	2.848(5)	145(5)
N9–HN9···N26	0.87(5)	2.14(4)	2.831(5)	137(5)
N21–HN21···N27	0.87(5)	2.21(4)	2.943(4)	142(3)

$[5A]_4[Bi_4I_{16}]\cdot(MeOH)_4$				
N1–HN1B···N9	0.86(14)	2.38(11)	3.167(11)	152(9)
N4–HN4···O1	0.86(7)	1.88(6)	2.723(9)	166(11)
N7–HN7B···N3	0.87(12)	2.46(10)	3.204(11)	144(9)
N10–HN10···O2	0.88(4)	1.84(4)	2.707(10)	169(6)
$[5B]_2[I_3]_4\cdot(5)_2\cdot(MeCN)$				
N10–H1···N8	0.8799(16)	2.3558(15)	3.179(2)	155.73(14)
N5–HN5···N11	0.86(5)	2.11(3)	2.878(3)	148.8(19)
N7–HN7···N12	0.85(3)	2.13(3)	2.957(3)	164(2)
$[6A]_2[Bi_4I_{16}]\cdot(I_2)_2\cdot(MeCN)_4$				
N7–HN7B···N10	0.880(4)	2.735(7)	3.155(8)	110.7(3)
N7–HN7A···N4	0.880(3)	2.501(5)	3.023(6)	118.7(3)
N6–HN6···N9	0.880(5)	2.029(5)	2.880(7)	162.7(4)

Only intermolecular hydrogen bonding interactions involving oxygen and nitrogen atoms are tabulated.

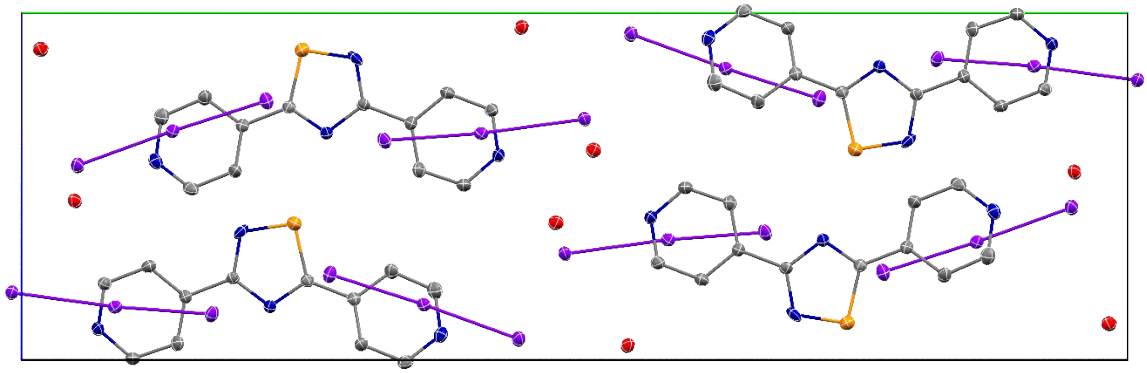

Figure SI1. Unit cell packing of **[1B][I_3]$_2$·(H_2O)$_2$** as viewed down the *a* axis. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

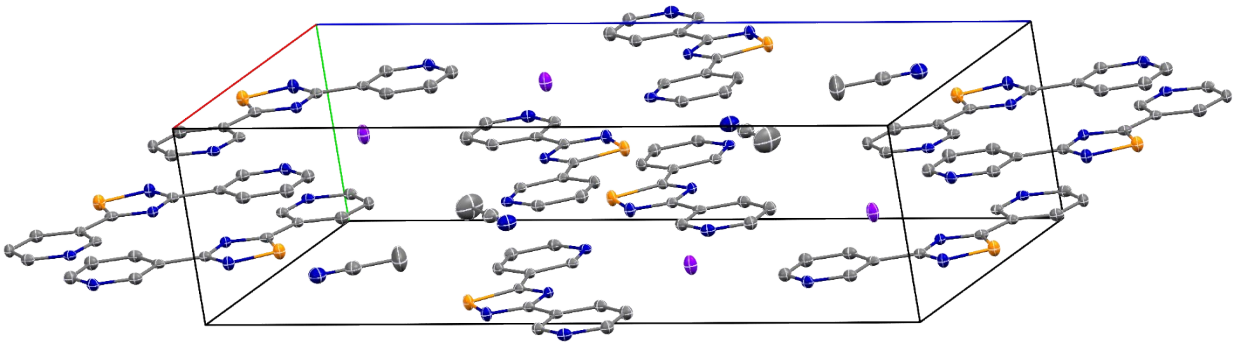

Figure SI2. Unit cell packing of [**2B**][I]·(MeCN). Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

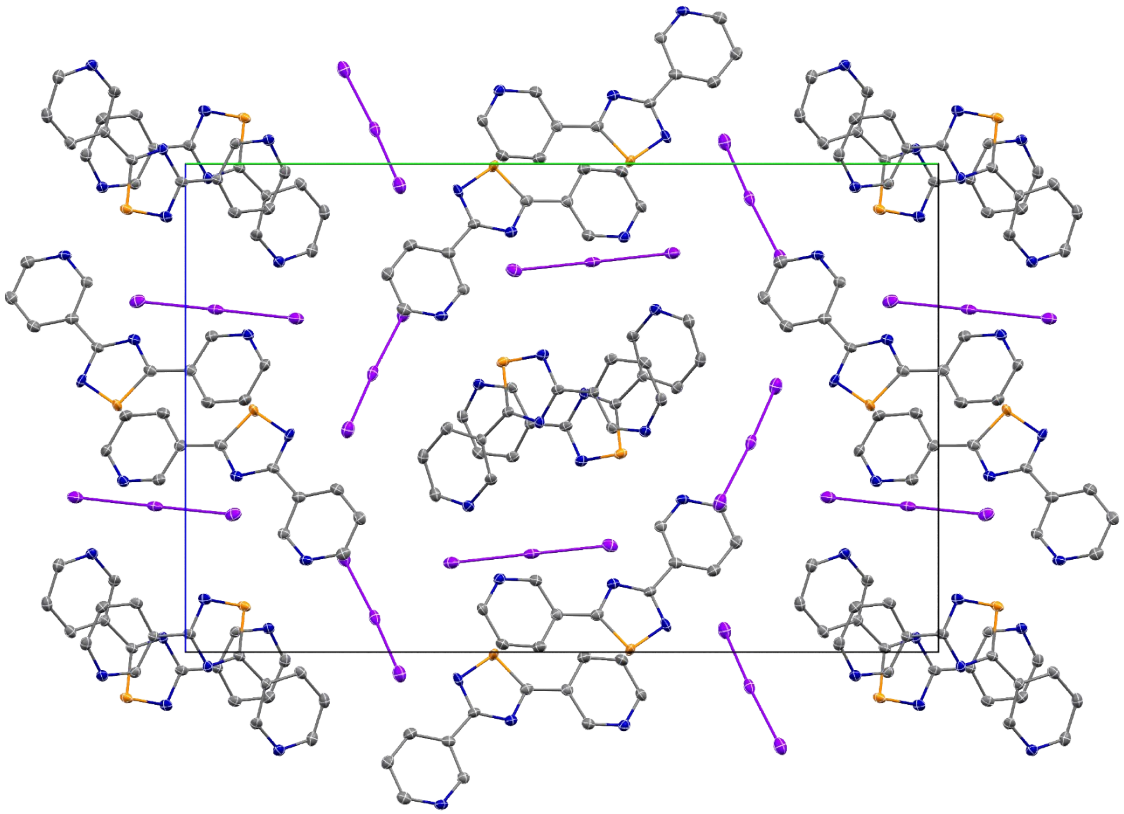

Figure SI3. Unit cell packing of [**2C**][I_3]$_2$·(**2A**) as viewed down the *a* axis. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

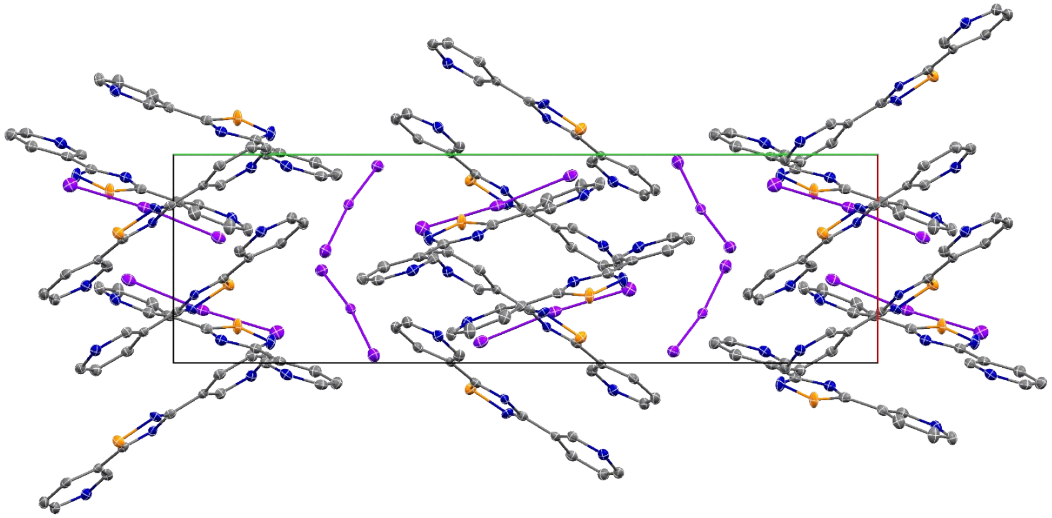

Figure SI4. Unit cell packing of [**2C**][I_3]$_2$·(**2A**) as viewed down the *c* axis. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

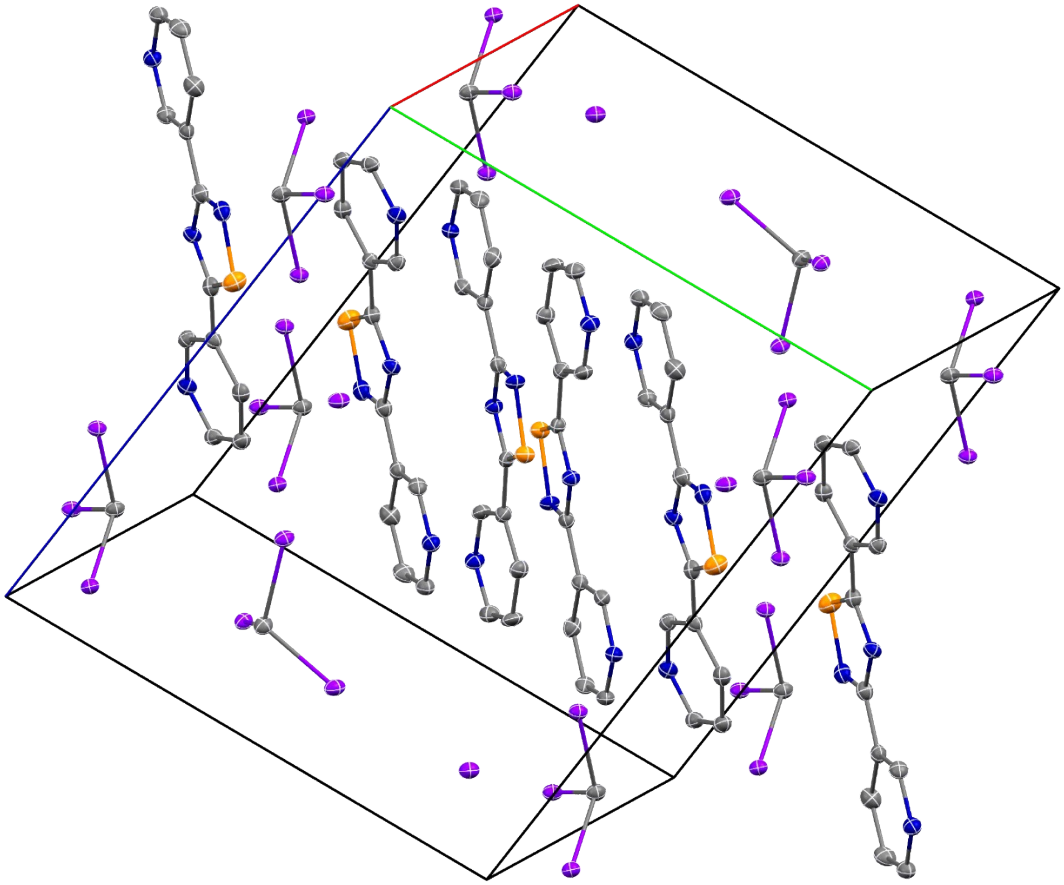

Figure SI5. Unit cell packing of [**2B**][I]·(CHI_3). Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

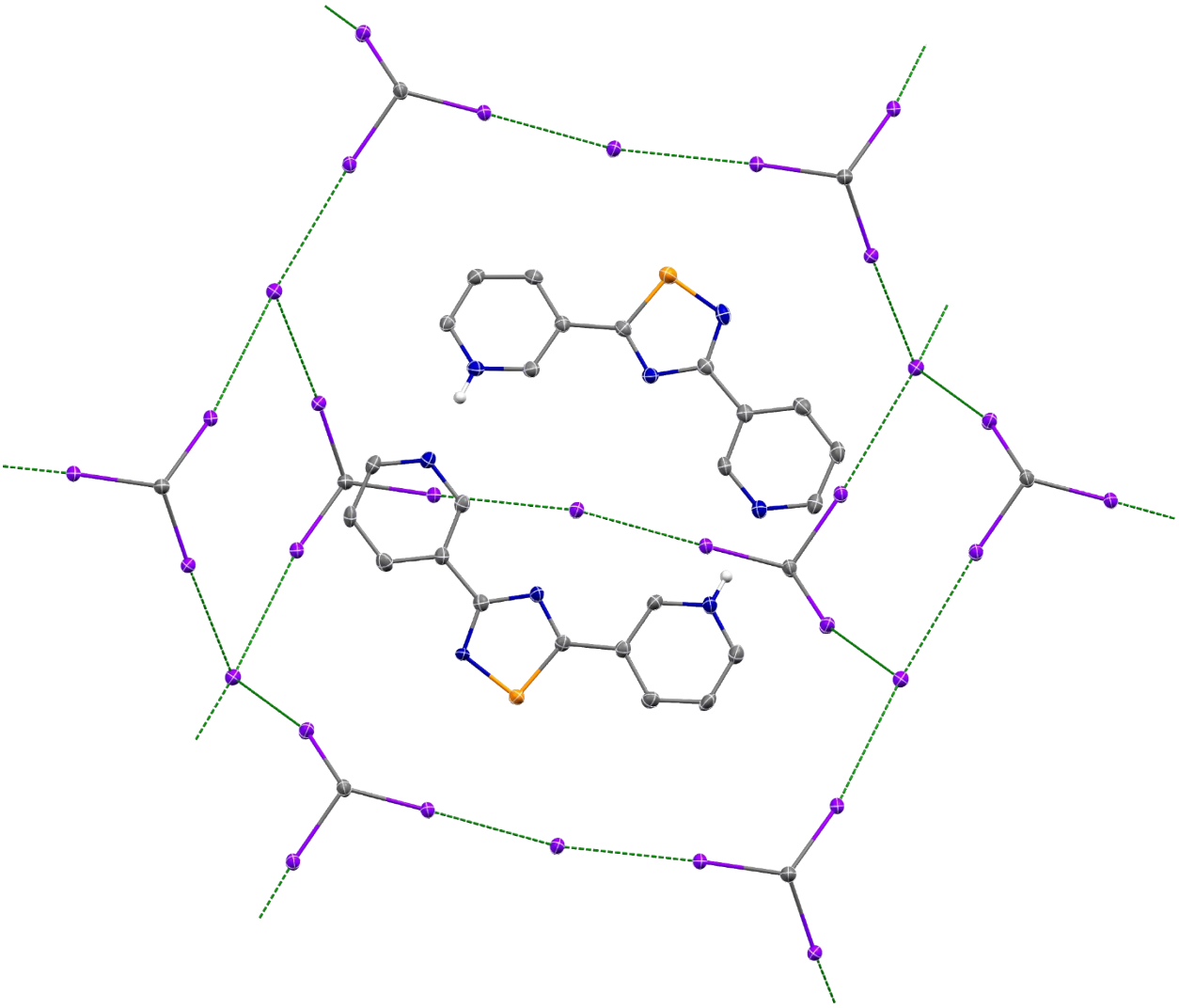

Figure SI6. Halogen bonding rings in [**2B**][I]·(CHI_3). Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

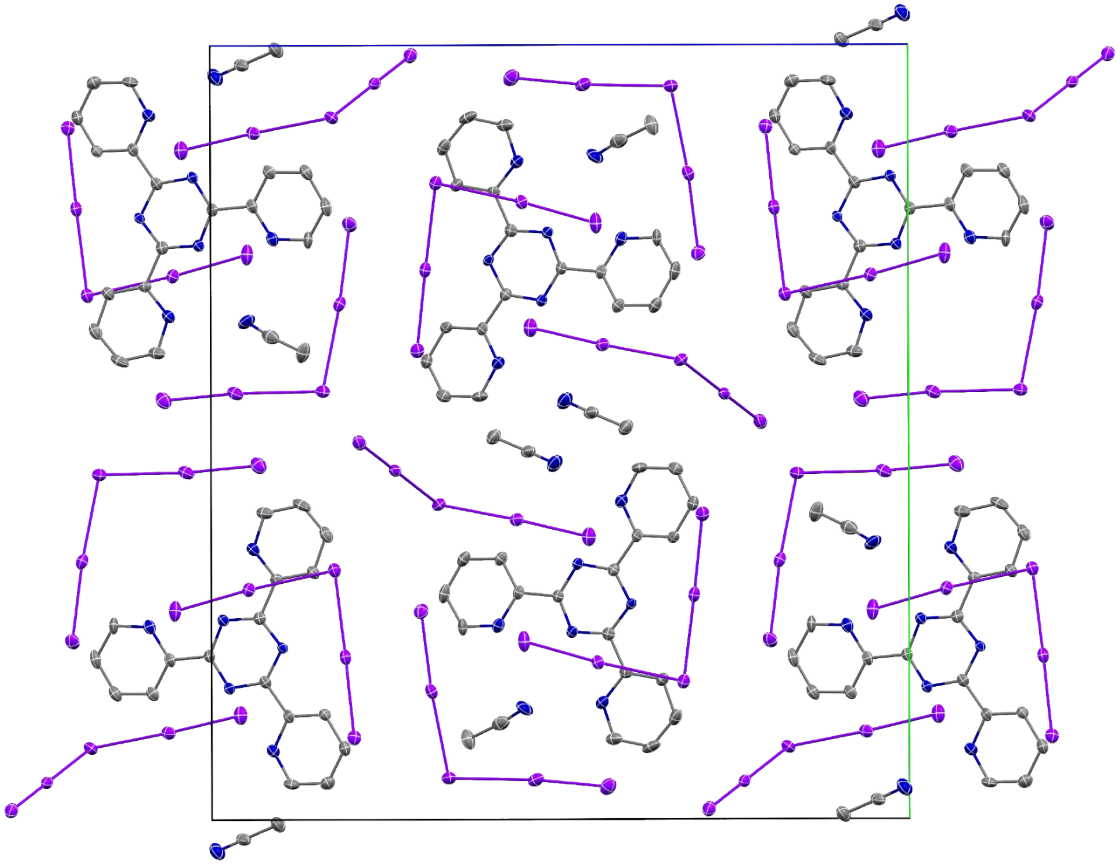

Figure SI7. Unit cell packing of [**3A**][I_5]$_3$·(MeCN)$_2$ as viewed down the *a* axis. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

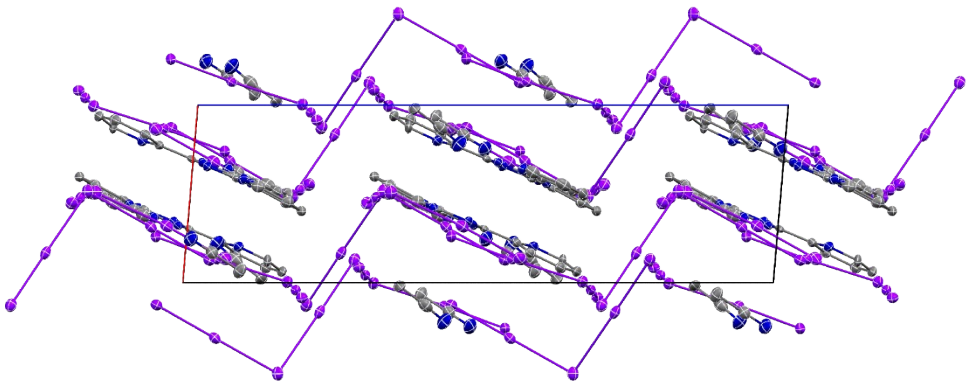

Figure SI8. Unit cell packing of [**3A**][I_5]$_3$·(MeCN)$_2$ as viewed down the *b* axis. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

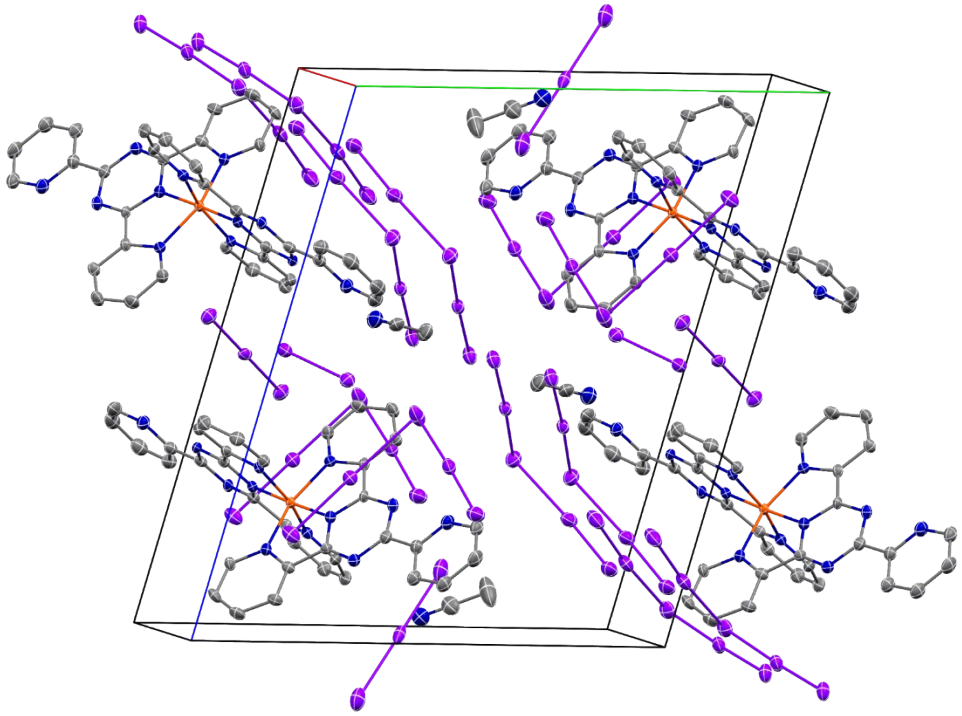

Figure SI9. Unit cell packing of [**3B**][I_3]$_4$·(I_2)$_{4.14}$·(MeCN)$_{2.86}$. The three-part MeCN/MeCN/I_2 disordered region and the hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

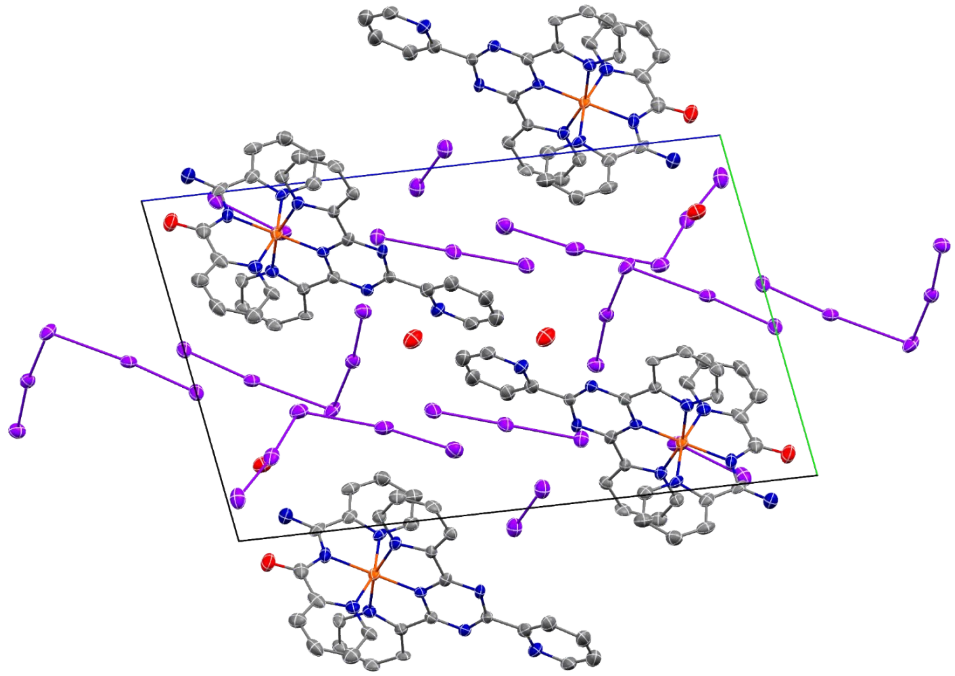

Figure SI10. Unit cell packing of [**3C**]$_2$[I_5]$_6$·(I_2)·(H_2O)$_4$ as viewed down the *a* axis. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

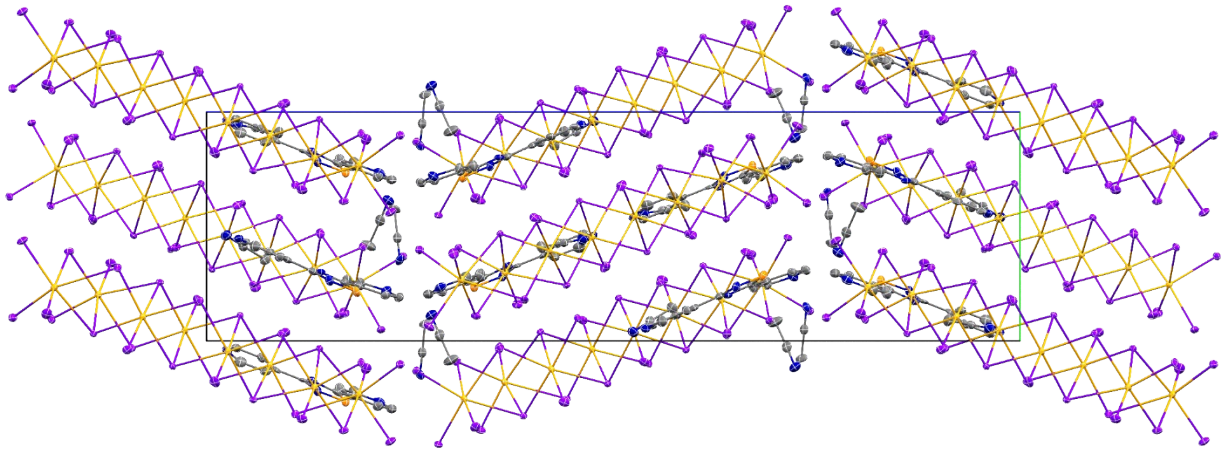

Figure SI11. Unit cell packing of [**1A**]$_2$[Bi_8I_{28}]·$(MeCN)_4$ as viewed down the *a* axis. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

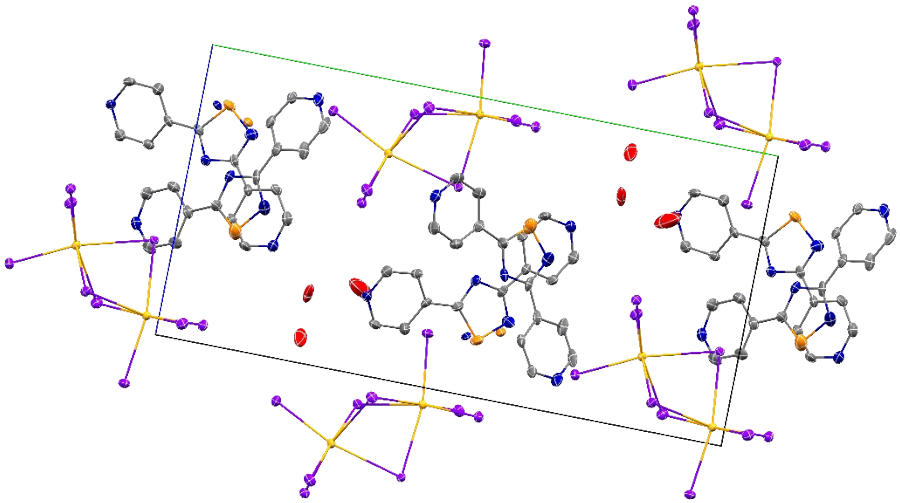

Figure SI12. Unit cell packing of [**1A**][**1B**][Bi_2I_9]·$(H_2O)_3$ as viewed down the *a* axis. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

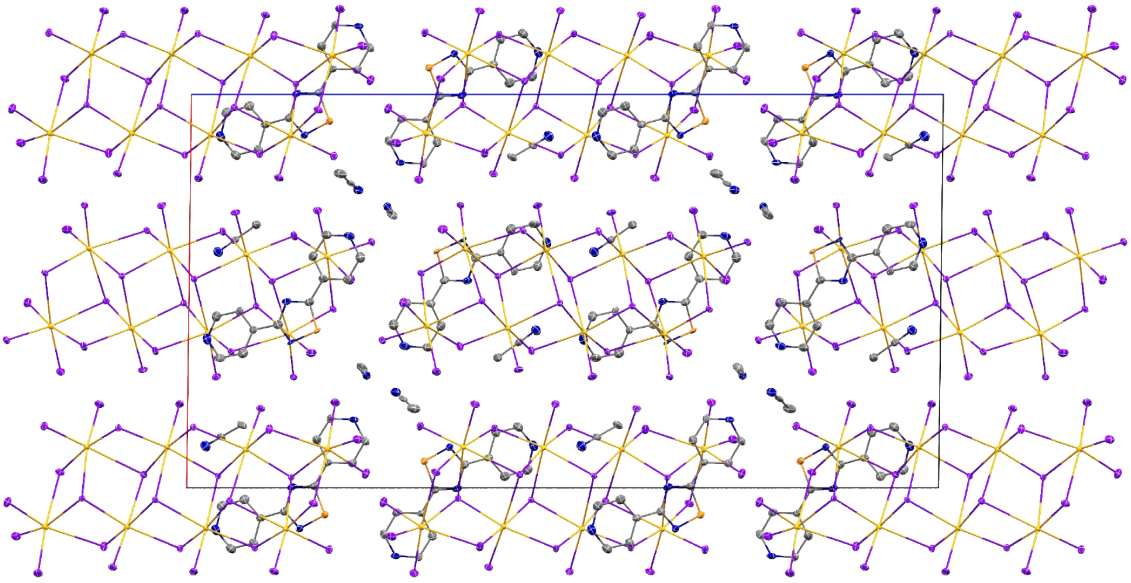

Figure SI13. Unit cell packing of $[\mathbf{1A}]_2[Bi_8I_{28}]\cdot(MeCN)_4$ as viewed down the *b* axis. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

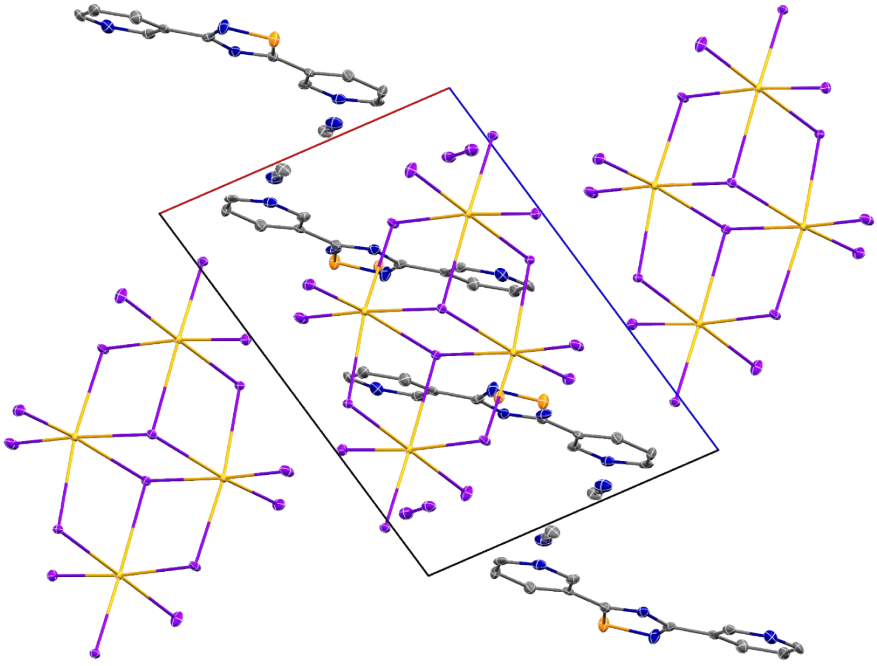

Figure SI14. Unit cell packing of $[\mathbf{2C}]_2[Bi_4I_{16}]\cdot(I_2)_2\cdot(MeCN)_2$ as viewed down the *b* axis. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

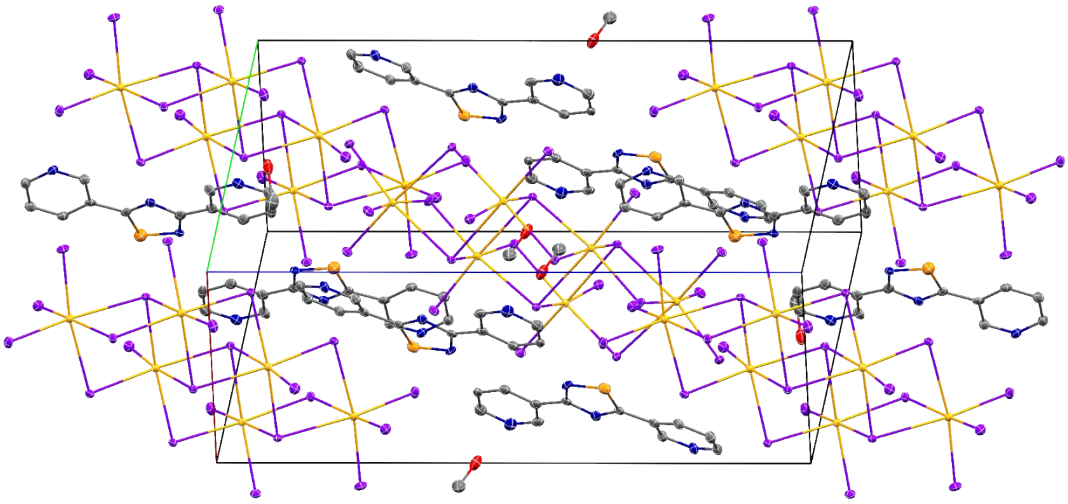

Figure SI15. Unit cell packing of $[\mathbf{2C}]_2[Bi_6I_{22}]\cdot(MeOH)_2$. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

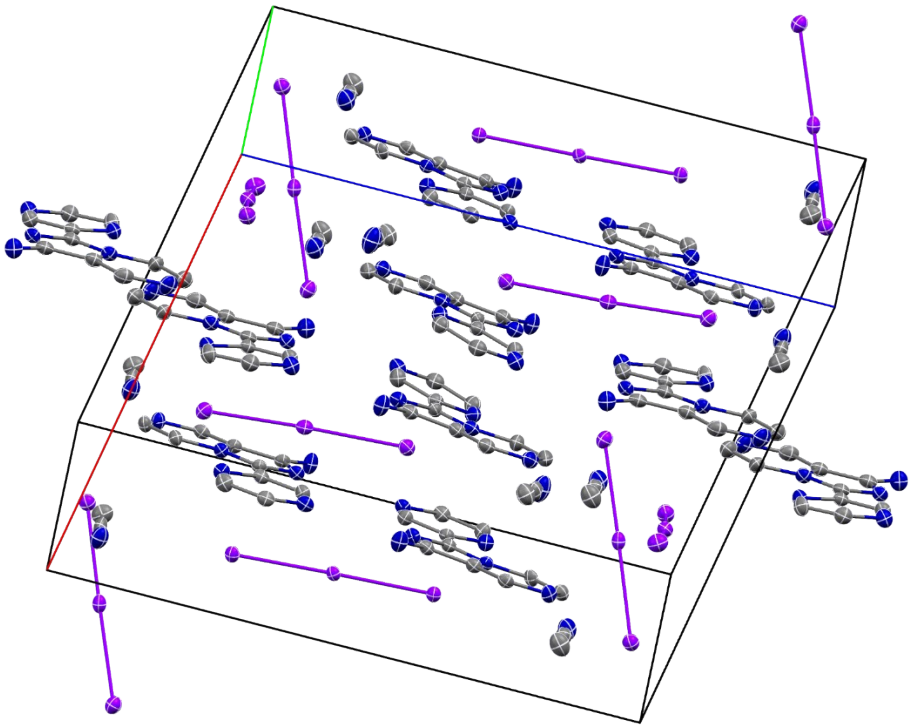

Figure SI16. Unit cell packing of $[\mathbf{4A}]_4[I_3]_4\cdot(MeCN)_3$. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

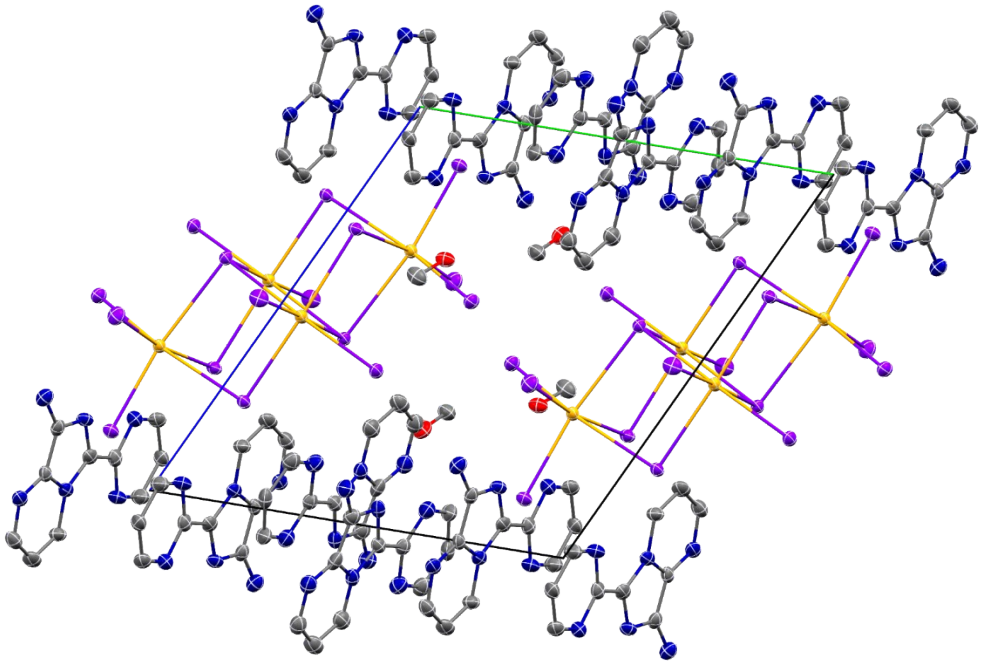

Figure SI17. Unit cell packing of [**5A**]$_4$[Bi_4I_{16}]·$(MeOH)_4$ as viewed down the *a* axis. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

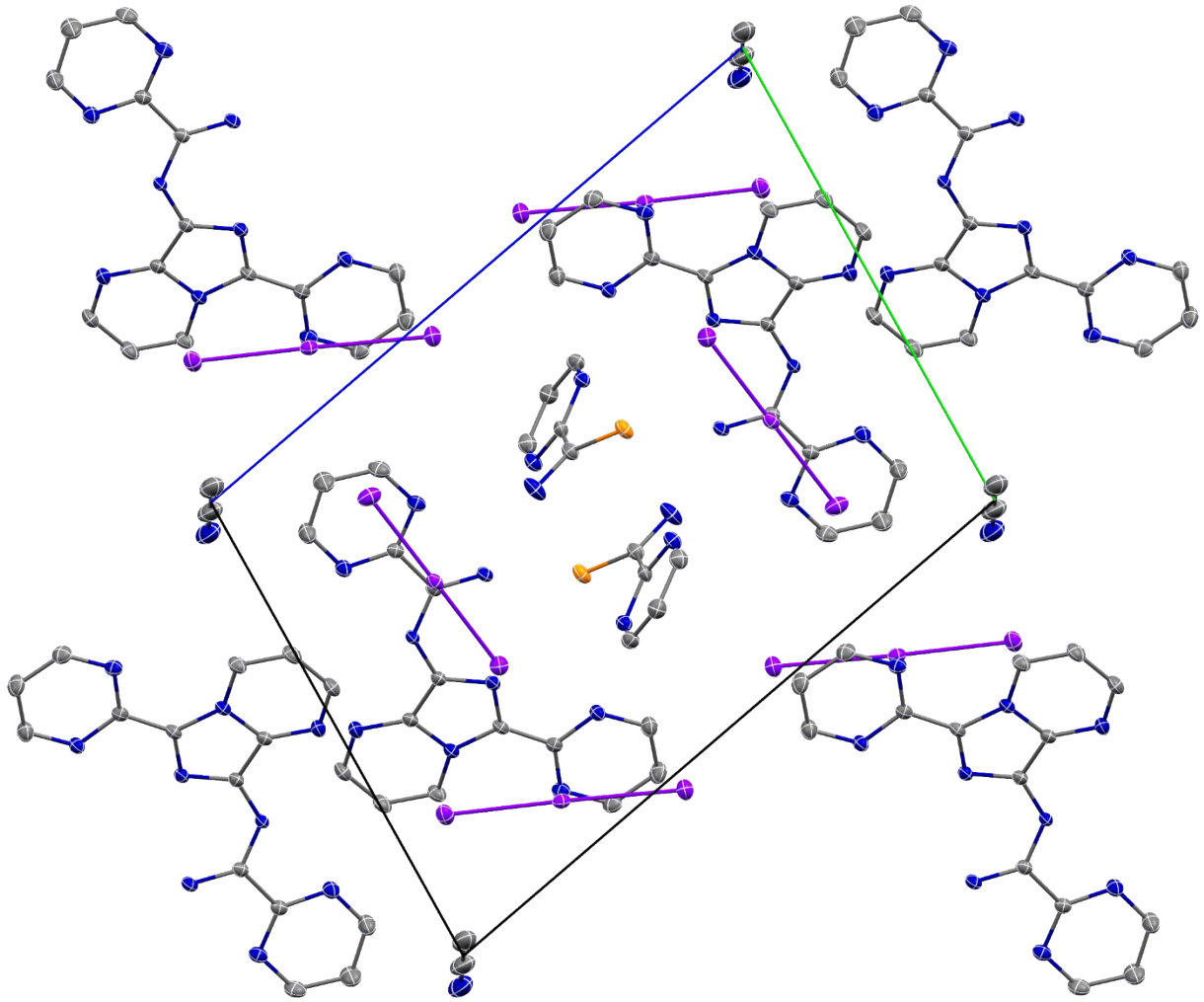

Figure SI18. Unit cell packing of [**5B**]$_2$[I_3]$_4$·(**5**)$_2$·(MeCN) as viewed down the *a* axis. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

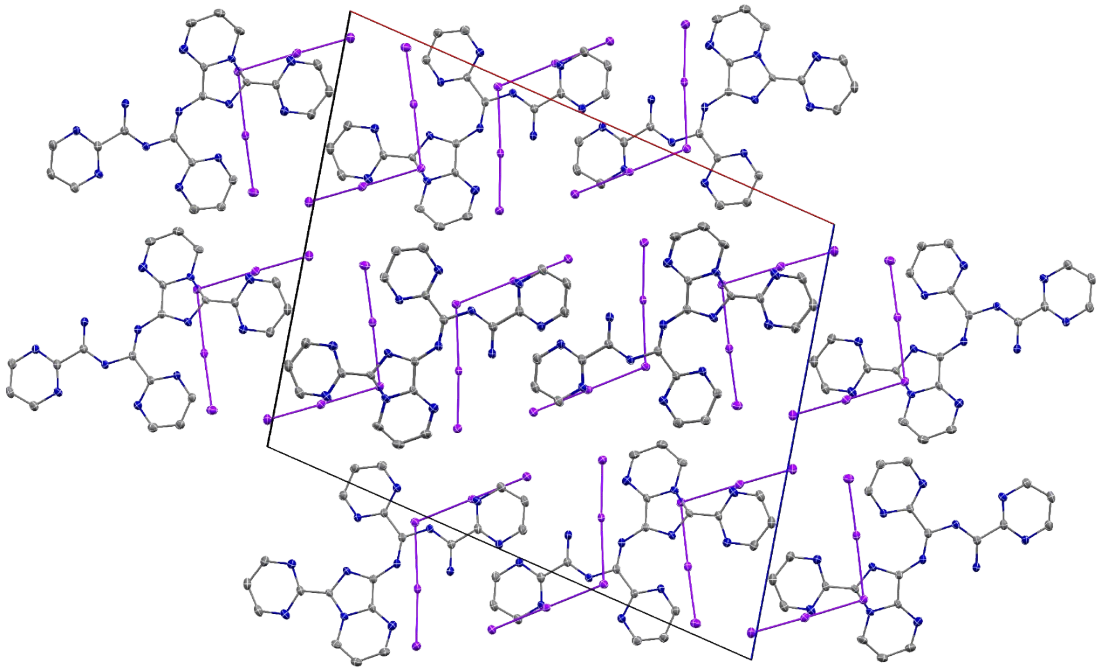

Figure SI19. Unit cell packing of [**5C**][I_5]$_2$ as viewed down the *b* axis. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.

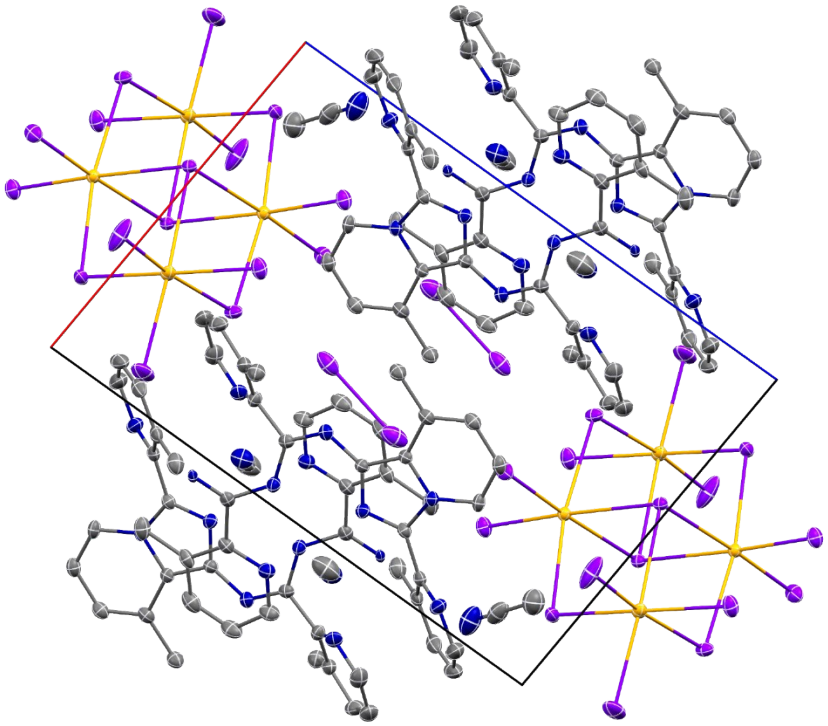

Figure SI20. Unit cell packing of [**6A**]$_2$[Bi_4I_{16}]·(I_2)$_2$ as viewed down the *b* axis. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are shown at the 50% probability level.