Photochromism, Electrical Properties and Structural Investigations of a Series of Hydrated Methylviologen HaloBismuthate Hybrids: Influence of the Anionic Oligomer Size and Iodide Doping on the Photo-Induced Properties and on the Dehydration Process.

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Supporting Information

I- $(MV)_3Bi_4Cl_{18}$, $1.7H_2O$ (1a) and $(MV)_4Bi_4Cl_{18}$ (1b)

I-A- Summary of crystallographic data

Table I-A-1. Crystal data and structure refinement for 1a

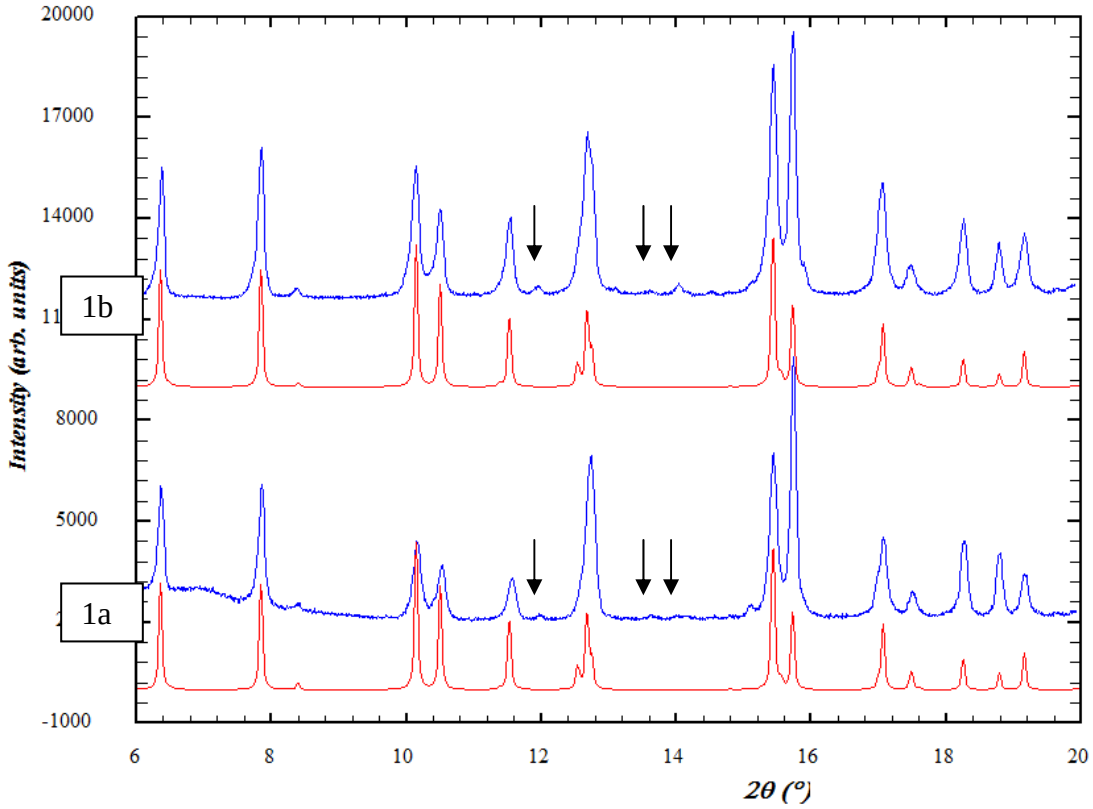
Empirical formula	C36 H42 Bi4 Cl18 N6 O1.7
Formula weight	2060.03
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.2783(4) A alpha = 72.478(8) deg. b = 12.5784(11) A beta = 89.874(7) deg. c = 14.6518(11) A gamma = 71.994(5) deg.
Volume	1542.95(19) A^3
Z, Calculated density	1, 2.222 Mg/m^3
Absorption coefficient	12.186 mm^-1
F(000)	954
Crystal size	0.323 x 0.096 x 0.066 mm
Theta range for data collection	3.33 to 29.99 deg.
Limiting indices	-13<=h<=13, -17<=k<=17, -20<=l<=20
Reflections collected / unique	55262 / 8766 [R(int) = 0.0576]
Completeness to theta = 29.99	97.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.898 and 0.305
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8766 / 0 / 310
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0472
R indices (all data)	R1 = 0.0766, wR2 = 0.0555
Extinction coefficient	0.0000(5)
Largest diff. peak and hole	1.062 and -1.071 e.A^-3

Table I-A-2. Crystal data and structure refinement for 1b

Empirical formula	C36 H42 Bi4 Cl18 N6
Formula weight	2032.83
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.2588(7) A alpha = 72.336(5) deg. b = 12.5306(9) A beta = 89.811(6) deg. c = 14.5781(4) A gamma = 71.266(6) deg.
Volume	1517.87(16) A^3
Z, Calculated density	1, 2.224 Mg/m^3
Absorption coefficient	12.383 mm^-1
F(000)	938
Crystal size	0.323 x 0.096 x 0.066 mm
Theta range for data collection	2.34 to 30.02 deg.
Limiting indices	-12<=h<=13, -17<=k<=17, -20<=l<=20
Reflections collected / unique	61586 / 8813 [R(int) = 0.0766]
Completeness to theta = 30.02	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.898 and 0.305
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8813 / 0 / 292
Goodness-of-fit on F^2	1.150
Final R indices [I>2sigma(I)]	R1 = 0.0356, wR2 = 0.0853
R indices (all data)	R1 = 0.0820, wR2 = 0.1257
Largest diff. peak and hole	1.635 and -2.014 e.A^-3

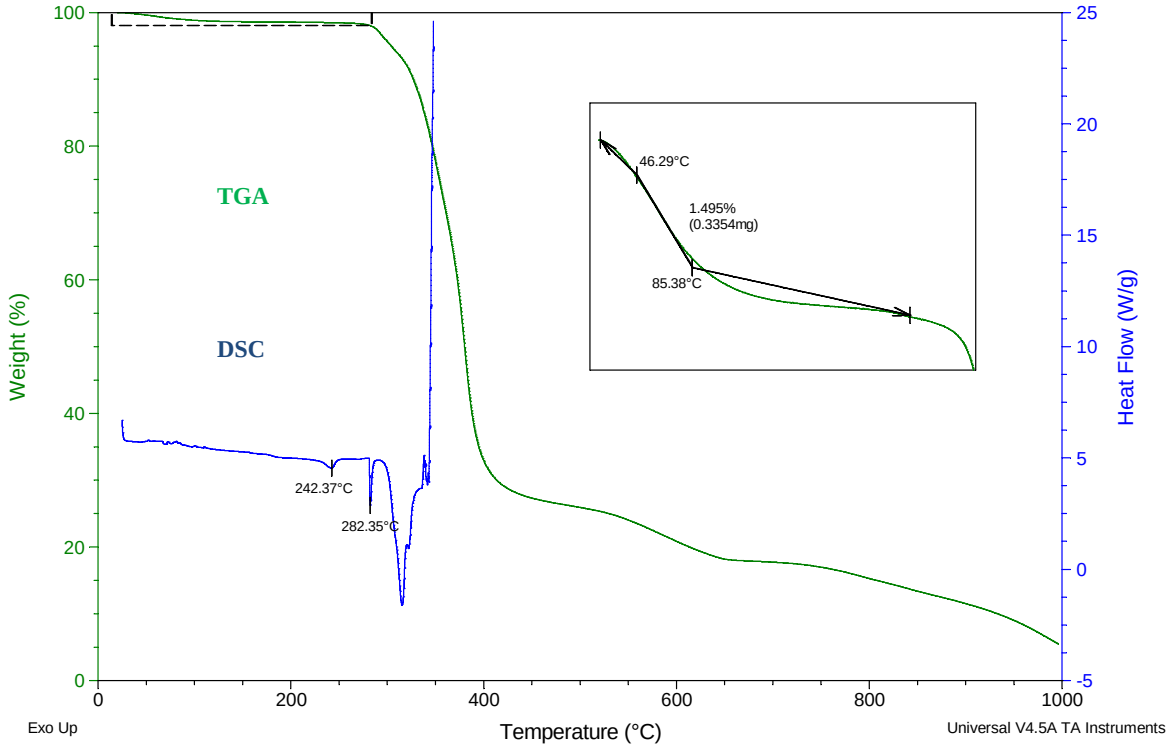
I-B- XRPD of 1a and 1b: theoretical (red) and experimental (blue)

Arrows: impurities

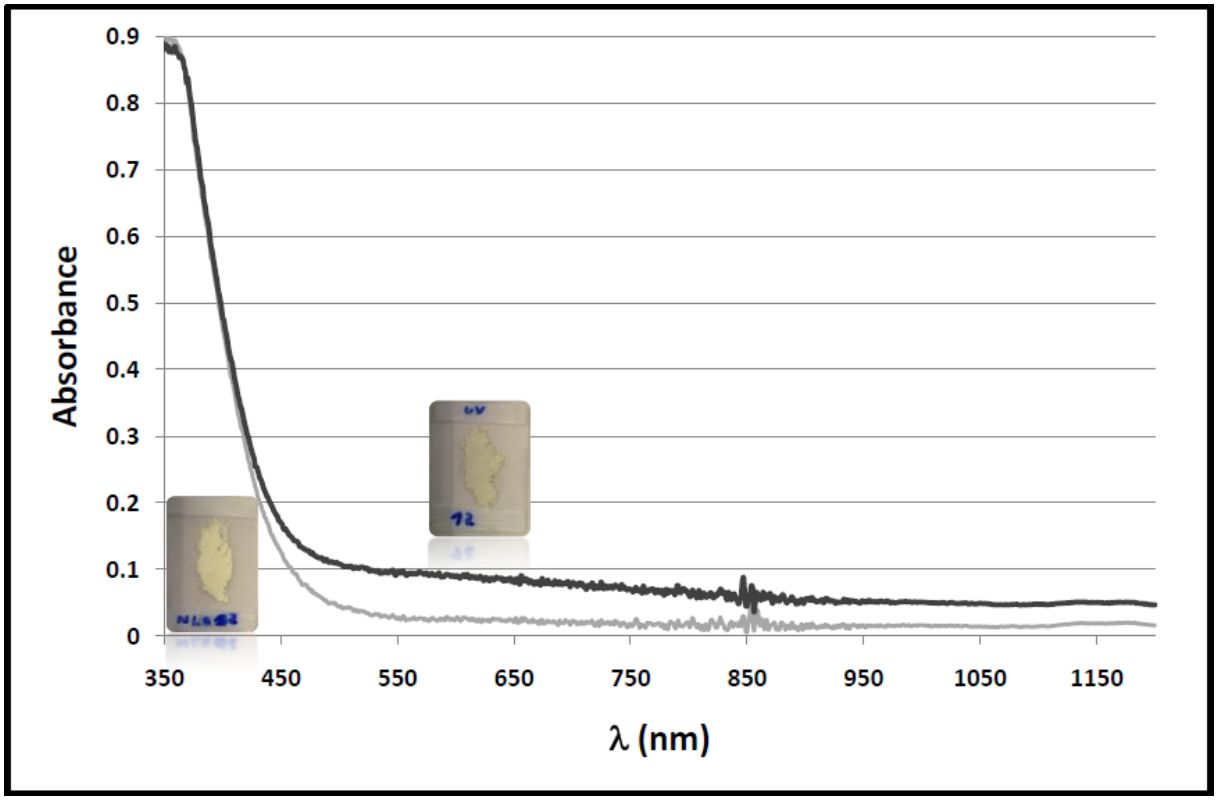


I-C- TGA-DSC of 1a

1a : 1.495% = 1.714 H_2O



I-D- UV-VIS spectra of 1a and 1a post UV (≅1b)



I-E- Crystal structure: Figures

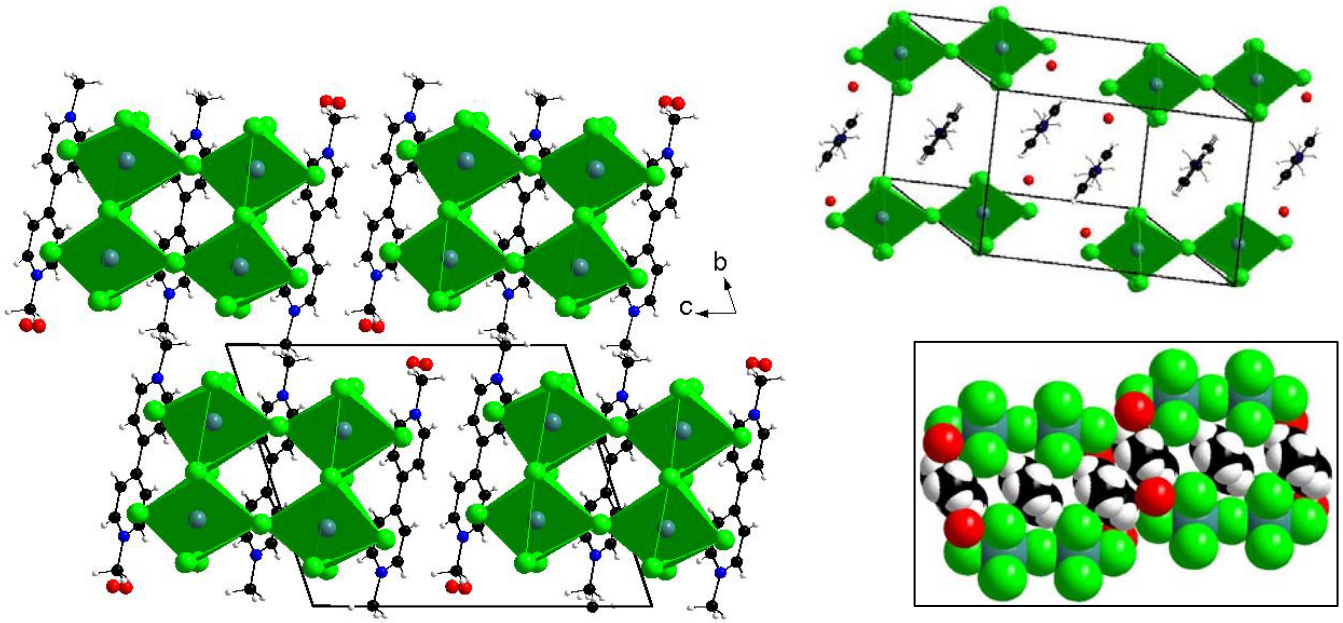


Figure S1: Crystal Structure of 1a: general view along a (left) and part of the structure showing an organic-inorganic layer (right), ball and stick (top) and space filling (bottom) representations

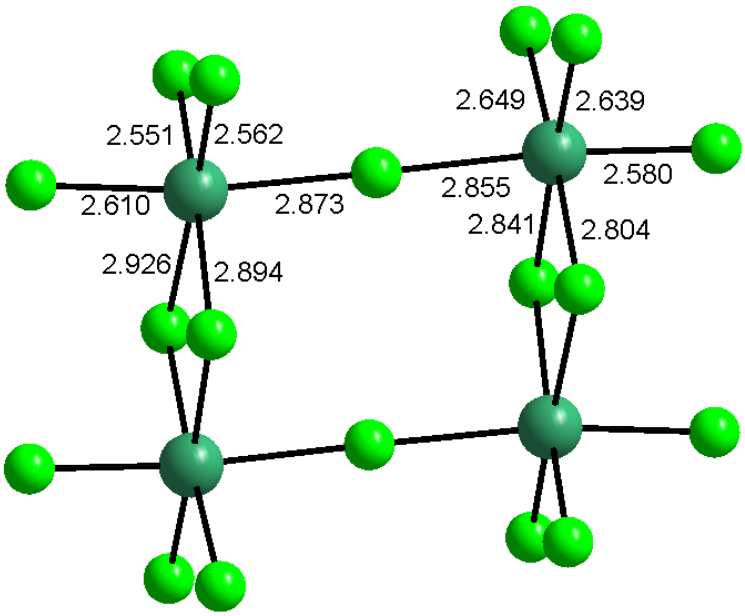


Figure S2: Crystal Structure of 1b: bond distances in the $[Bi_4Cl_{18}]^{6-}$ cluster

II- $(MV)_4Bi_6Cl_{26}$, $1.7H_2O$ (2a) and $(MV)_4Bi_6Cl_{26}$ (2b)

II-A- Summary of crystallographic data

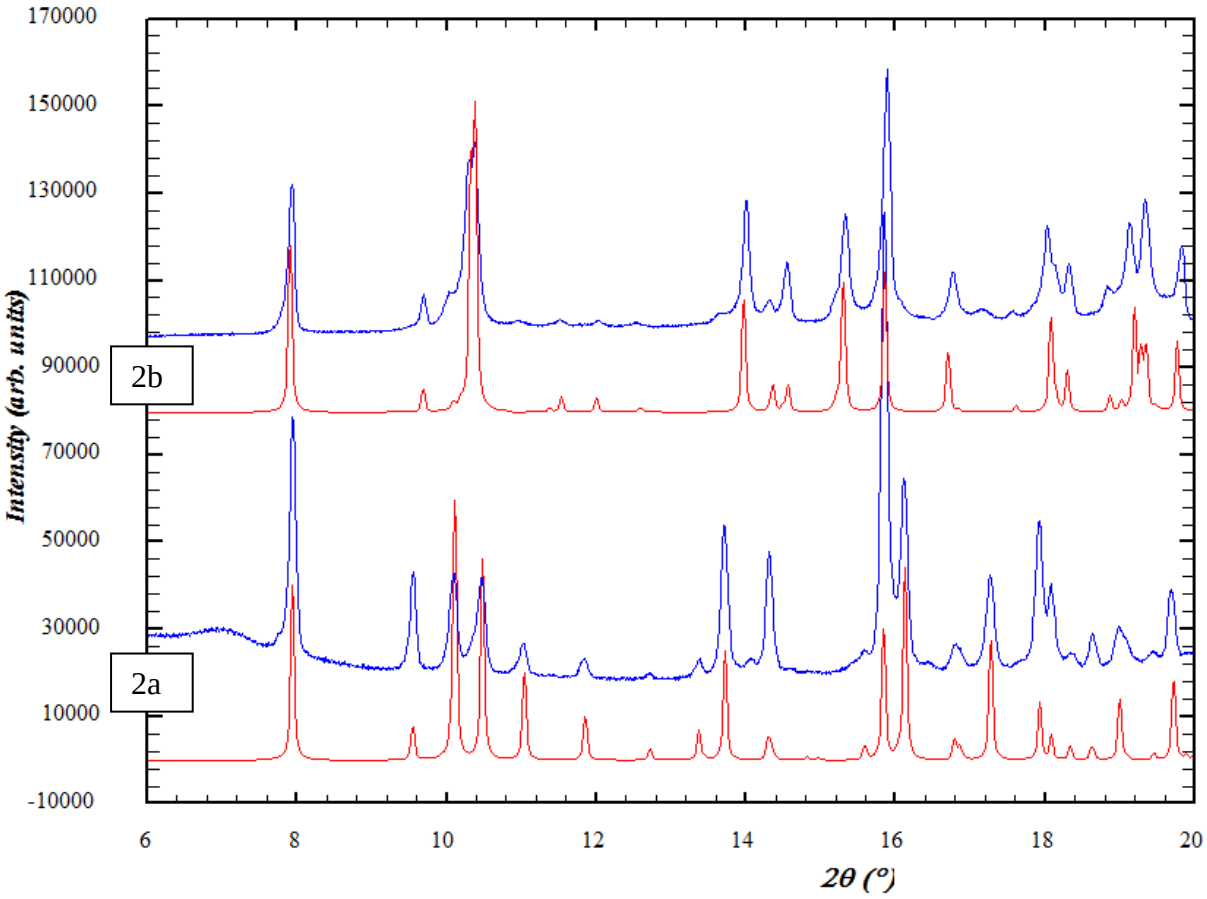
Table II-A-1. Crystal data and structure refinement for 2a

Empirical formula	C48 H56 Bi6 Cl26 N8 O1.7
Formula weight	2947.87
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.3993(5) A alpha = 99.774(8) deg.
	b = 12.6132(13) A beta = 103.196(7) deg.
	c = 19.8496(18) A gamma = 108.088(6) deg.
Volume	2103.0(3) A^3
Z, Calculated density	1, 2.331 Mg/m^3
Absorption coefficient	13.373 mm^-1
F(000)	1356
Crystal size	0.18 x 0.094 x 0.07 mm
Theta range for data collection	2.42 to 31.01 deg.
Limiting indices	-13<=h<=13, -18<=k<=18, -28<=l<=28
Reflections collected / unique	55725 / 13325 [R(int) = 0.0570]
Completeness to theta = 31.01	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.898 and 0.305
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13325 / 0 / 420
Goodness-of-fit on F^2	1.008
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0583
R indices (all data)	R1 = 0.1073, wR2 = 0.0726
Extinction coefficient	0.00002(3)
Largest diff. peak and hole	1.560 and -1.051 e.A^-3

Table II-A-2. Crystal data and structure refinement for 2b

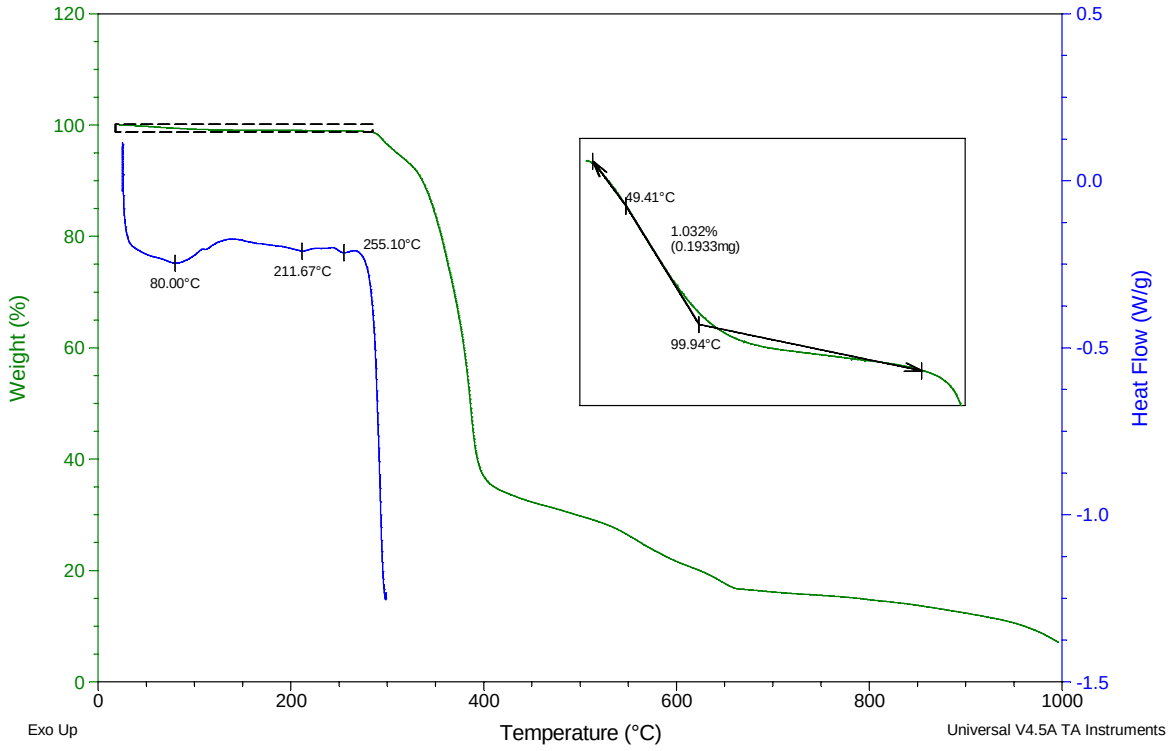
Empirical formula	C48 H56 Bi6 Cl26 N8
Formula weight	2920.67
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.3871(8) A alpha = 103.068(10) deg.
	b = 12.5062(11) A beta = 96.160(10) deg.
	c = 19.070(3) A gamma = 108.004(10) deg.
Volume	2035.7(4) A^3
Z, Calculated density	1, 2.386 Mg/m^3
Absorption coefficient	13.812 mm^-1
F(000)	1344
Crystal size	0.18 x 0.094 x 0.07 mm
Theta range for data collection	1.78 to 30.07 deg.
Limiting indices	-13<=h<=13, -17<=k<=17, -26<=l<=26
Reflections collected / unique	70592 / 11888 [R(int) = 0.0697]
Completeness to theta = 30.07	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.898 and 0.305
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11888 / 0 / 401
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0381, wR2 = 0.0732
R indices (all data)	R1 = 0.0826, wR2 = 0.0888
Largest diff. peak and hole	1.755 and -1.054 e.A^-3

II-B- XRPD of 2a (down) and 2b (top): theoretical (red) and experimental (blue)



II-C- TGA-DSC of 2a

2a : 1.032% = 1.692 H_2O



II-D- Crystal structure: Figures

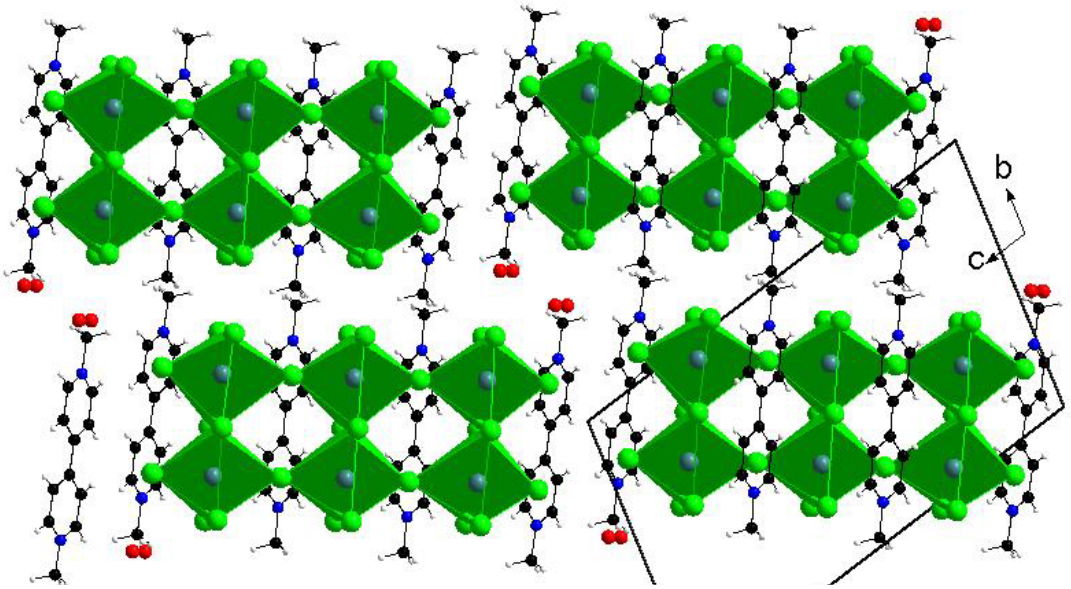


Figure S3: Crystal Structure of 2a: general view along a

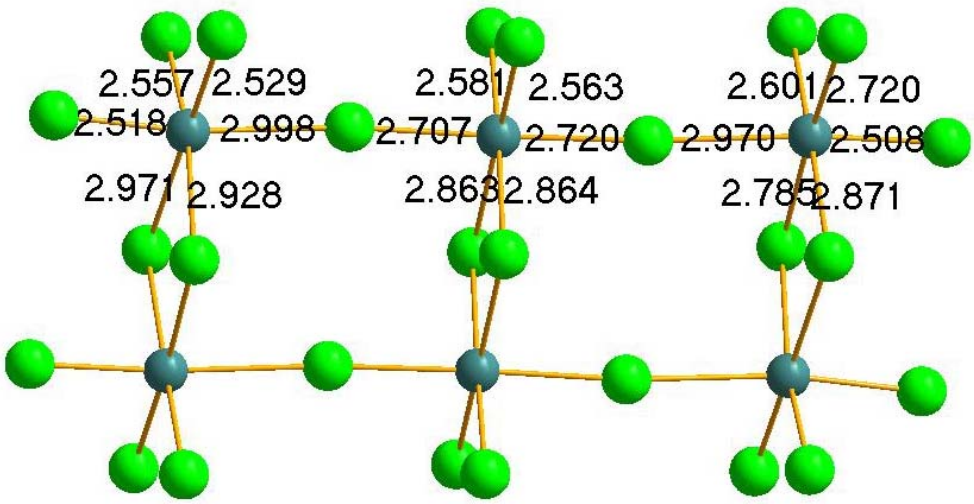
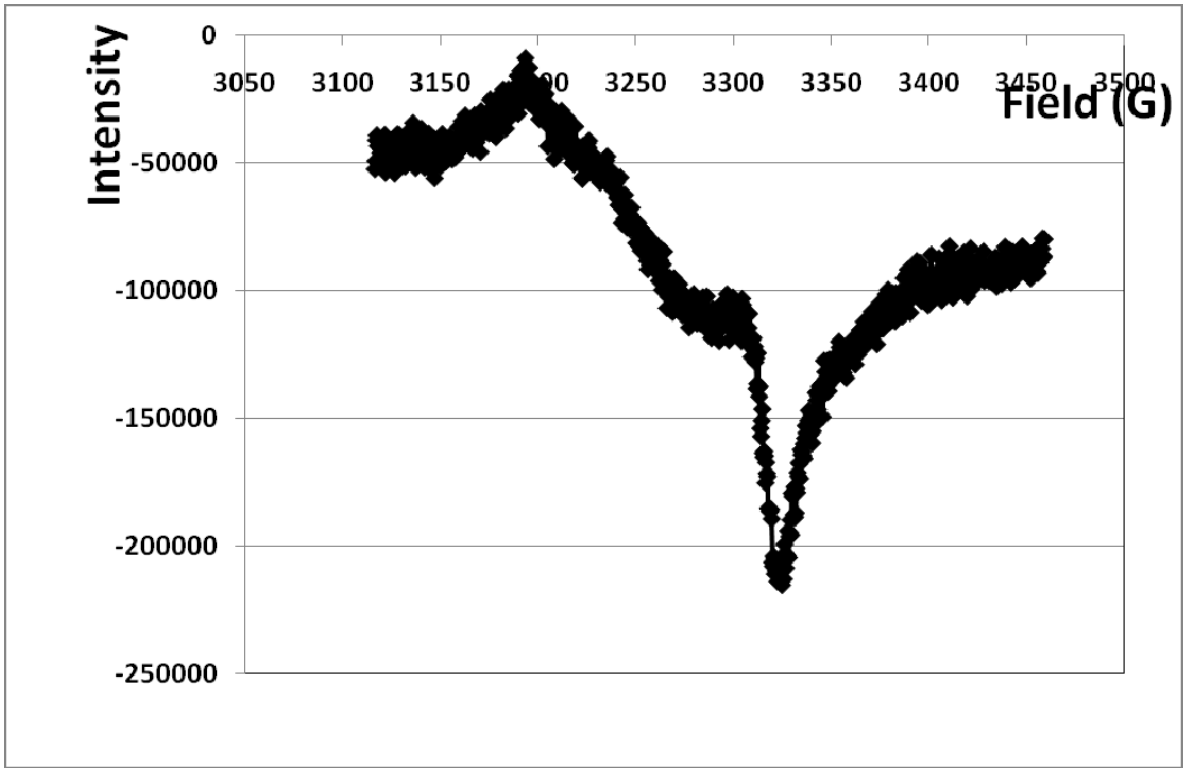


Figure S4: Crystal Structure of 2b: bond distances in the $[Bi_6Cl_{26}]^{8-}$ cluster

Figure S5: EPR spectrum of irradiated single crystals sample of **2b** collected at 6K.



EPR experimental parameters:

* Data Ranges and Resolutions:
XPTS 1024
XMIN 3116.800000
XWID 342.400000
* Documentational Text:
*
TITL 'MV4... cristaux (5K)'
IRNAM 'Intensity'
XNAM 'Field'
IRUNI ''
XUNI 'G'
****
#SPL 1.2 * STANDARD PARAMETER LAYER
STAG C
EXPT CW
OXS1 IADC
AXS1 B0VL
AXS2 NONE
AXS3
A1CT 0.3288
A1SW 0.03424
MWFQ 9.41975e+09

MWPW 0.02
AVGS 10
RESO CO150310
SPTP 0.08192
RCAG 95
RCHM 1
B0MA 0.0001
B0MF 100000
RCPH 0.0
RCOF -11.4
A1RS 1024
RCTC 0.02048
****
*
#DSL 1.0 * DEVICE SPECIFIC LAYER
.DVC acqStart, 1.0
.DVC fieldCtrl, 1.0
CenterField 3288.00 G
Delay 0.0 s
FieldFlyback On
FieldWait Wait LED off
GFactor 2.000000
SetToSampleG False
SweepDirection Up
SweepWidth 342.4 G
.DVC fieldSweep, 1.0
.DVC freqCounter, 1.0
FrequencyMon 9.419750 GHz
.DVC mwBridge, 1.0
AcqFineTuning Never
Power 20.00 mW
PowerAtten 10 dB
.DVC recorder, 1.0
BaselineCorr Off
NbScansAcc 10
NbScansDone 10
NbScansToDo 10
ReplaceMode Off
.DVC scanEnd, 1.0
.DVC signalChannel, 1.0
AFCTrap True
Calibrated True
ConvTime 81.92 ms
DModAFCTrap True
DModAmp 1.00 G
DModCalibrated True
DModDetectSCT First
DModEliDelay 1.0 us
DModExtLockIn False
DModExtTrigger False

DModFieldMod	First
DModGain	60 dB
DModHighPass	True
DModIntegrator	True
DModModOutput	Internal
DModSignalInput	Internal
DModTimeConst	1.28 ms
DoubleModFreq	5.00 kHz
DoubleModPhase	0.0
DoubleMode	False
EliDelay	1.0 us
ExtLockIn	False
ExtTrigger	False
Gain	95 dB
Harmonic	1
HighPass	True
Integrator	True
ModAmp	1.00 G
ModFreq	100.00 kHz
ModInput	Internal
ModOutput	Internal
ModPhase	0.0
Offset	-11.4 %
QuadMode	False
QuadPhase	90.0
Resolution	1024
Resonator	1
SctNorm	False
SignalInput	Internal
SweepTime	83.89 s
TimeConst	20.48 ms
TuneCaps	38

III- $(MV)_4Bi_6Cl_{25.6}I_{0.4}$, $1.5H_2O$ (3a) and $(MV)_4Bi_6Cl_{25.6}I_{0.4}$ (3b)

III-A- Summary of crystallographic data

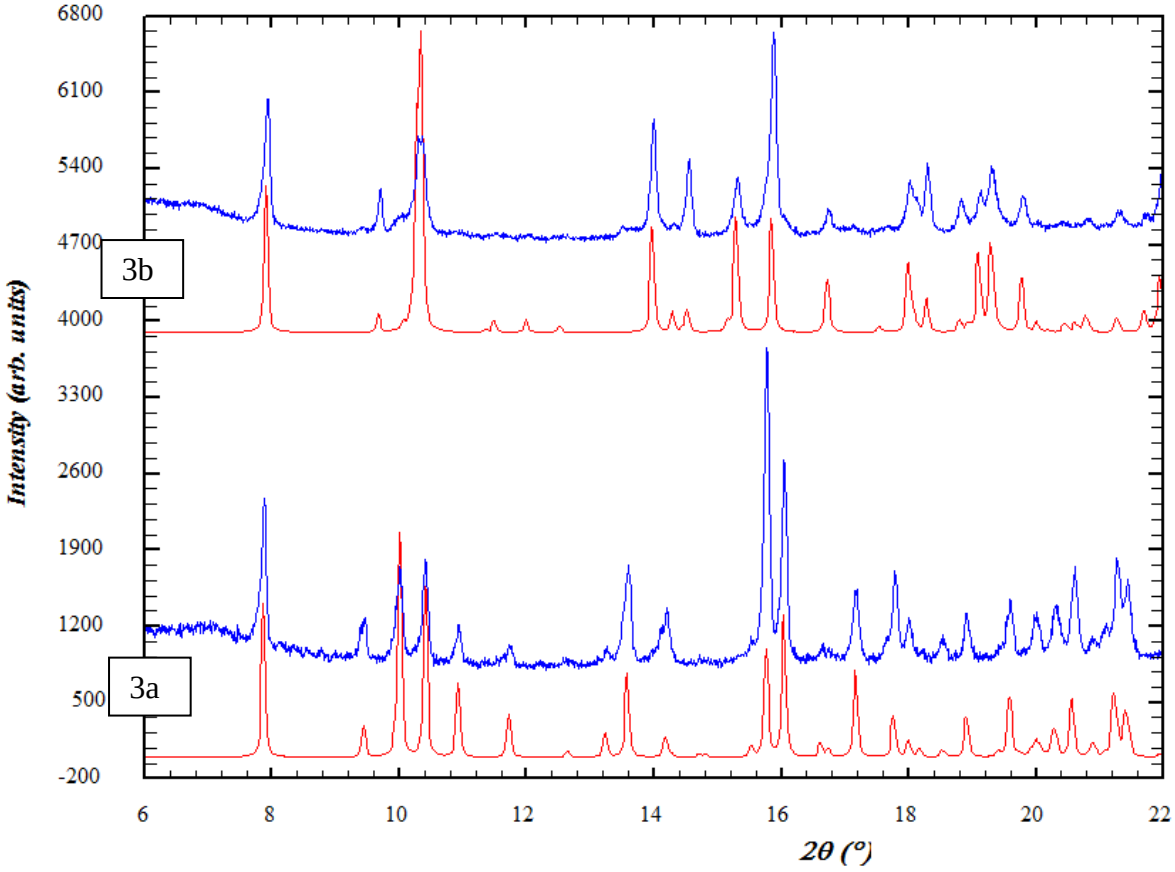
Table III-A-1. Crystal data and structure refinement for 3a

Empirical formula	C48 H56 Bi6 Cl25.6 I0.4 N8 O1.5
Formula weight	2981.25
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.3866(11) A alpha = 99.518(8) deg. b = 12.6026(8) A beta = 103.518(10) deg. c = 19.868(2) A gamma = 108.027(7) deg.
Volume	2100.0(4) A^3
Z, Calculated density	1, 2.435 Mg/m^3
Absorption coefficient	13.760 mm^-1
F(000)	1409
Crystal size	0.257 x 0.114 x 0.087 mm
Theta range for data collection	2.75 to 30.01 deg.
Limiting indices	-13<=h<=13, -17<=k<=17, -27<=l<=27
Reflections collected / unique	48931 / 12243 [R(int) = 0.0805]
Completeness to theta = 30.01	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6189 and 0.2253
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12243 / 0 / 452
Goodness-of-fit on F^2	0.964
Final R indices [I>2sigma(I)]	R1 = 0.0454, wR2 = 0.0564
R indices (all data)	R1 = 0.1392, wR2 = 0.0718
Largest diff. peak and hole	1.477 and -0.862 e.A^-3

Table III-A-2. Crystal data and structure refinement for 3b

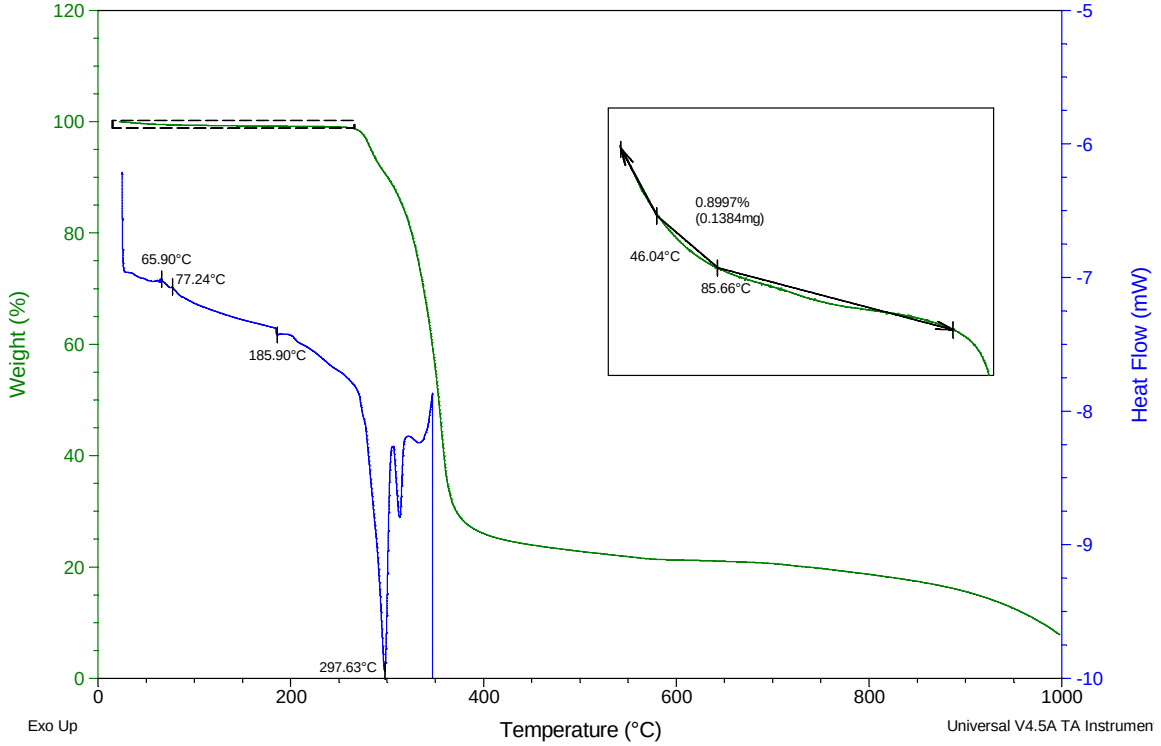
Empirical formula	C48 H56 Bi6 Cl25.6 I0.4 N8
Formula weight	2957.25
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.3912(9) A alpha = 103.027(7) deg. b = 12.5094(9) A beta = 96.320(9) deg. c = 19.094(2) A gamma = 108.018(8) deg.
Volume	2038.7(4) A^3
Z, Calculated density	1, 2.482 Mg/m^3
Absorption coefficient	14.171 mm^-1
F(000)	1393
Crystal size	0.257 x 0.114 x 0.087 mm
Theta range for data collection	3.25 to 30.03 deg.
Limiting indices	-13<=h<=13, -17<=k<=17, -26<=l<=26
Reflections collected / unique	45909 / 11819 [R(int) = 0.0962]
Completeness to theta = 30.03	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.898 and 0.305
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11819 / 0 / 412
Goodness-of-fit on F^2	1.014
Final R indices [I>2sigma(I)]	R1 = 0.0574, wR2 = 0.0832
R indices (all data)	R1 = 0.1604, wR2 = 0.1043
Largest diff. peak and hole	1.733 and -1.239 e.A^-3

III-B- XRPD of 3a (down) and 3b (top): theoretical (red) and experimental (blue)

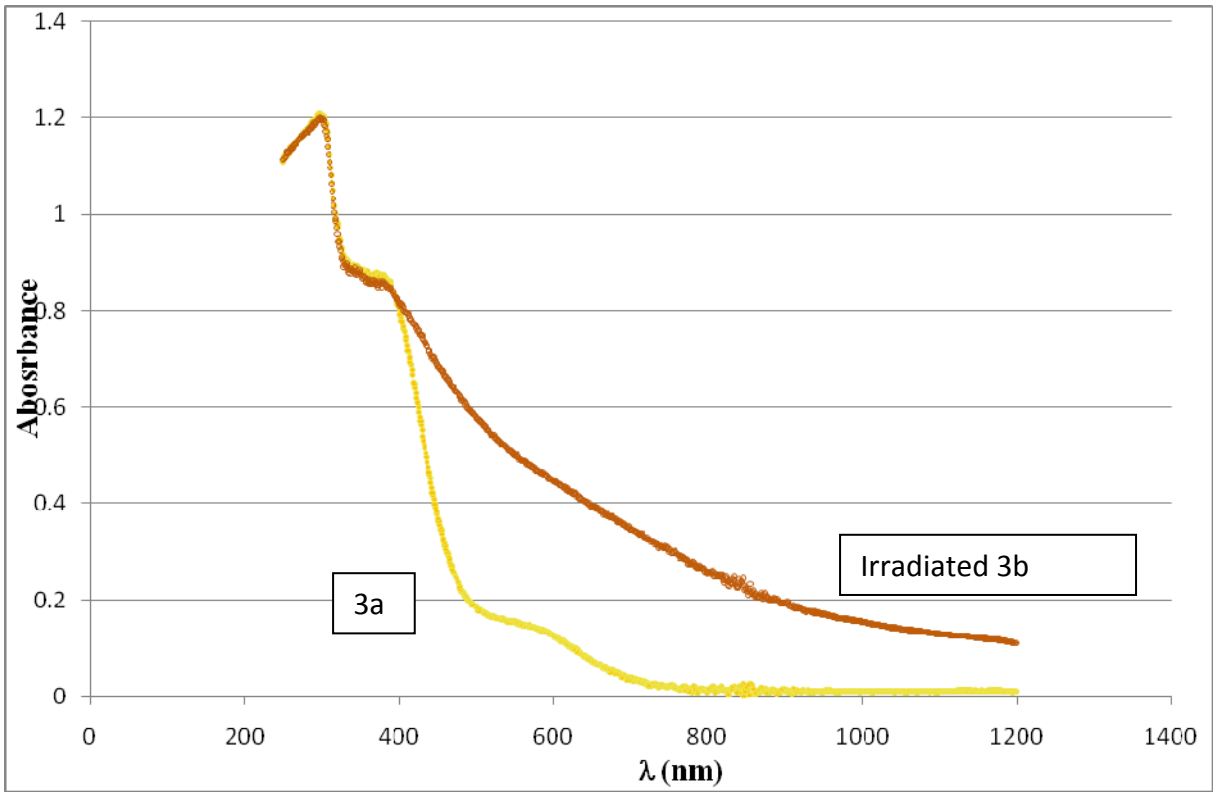


III-C- TGA-DSC of 3a

3a : 0.8997% = 1.491 H_2O



III-D- UV-VIS spectra of 3a and 3a post UV=3b



III-E- Crystal structure: Figures

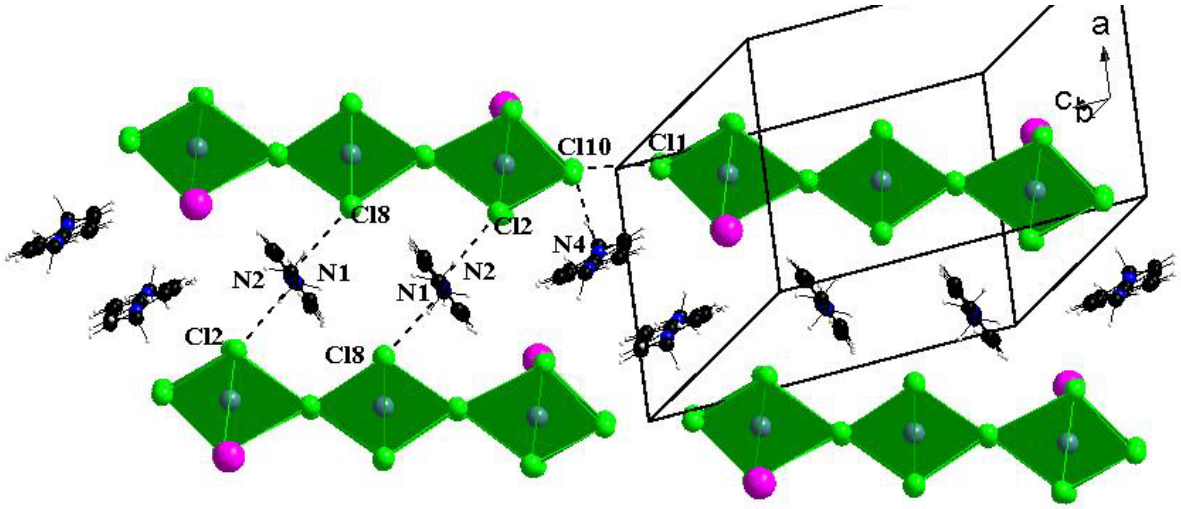


Figure S6: Crystal Structure of 3b: part of the structure showing an organic-inorganic layer

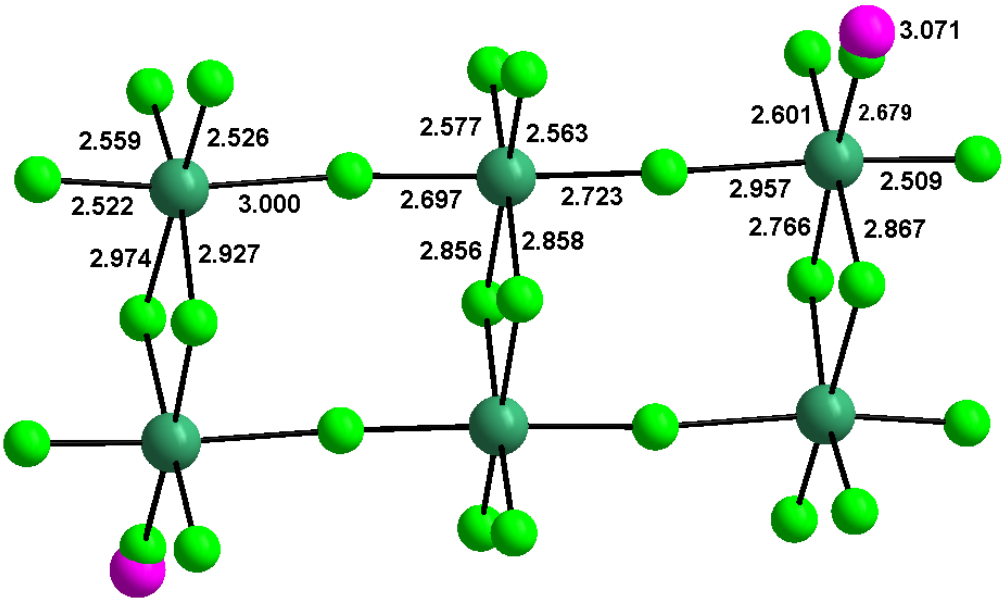


Figure S7: Crystal Structure of 3b: bond distances in the $[Bi_6Cl_{25.6}I_{0.4}]^{8-}$ cluster

IV- $(MV)_4Bi_6Cl_{24.6}I_{1.4}$, $1.3H_2O$ (4a(y=1.3), $(MV)_4Bi_6Cl_{24.6}I_{1.4}$, $0.65H_2O$ (4a(y=0.65) and $(MV)_4Bi_6Cl_{24.6}I_{1.4}$ (4b).

IV-A- Summary of crystallographic data

Table IV-A-1. Crystal data and structure refinement for 4a(y=1.3)

Empirical formula	C48 H56 Bi6 Cl24.6 I1.4 N8 O1.3
Formula weight	3069.50
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.4162(8) A alpha = 107.724(7) deg. b = 12.6502(9) A beta = 103.171(8) deg. c = 19.955(2) A gamma = 72.189(6) deg.
Volume	2131.7(3) A^3
Z, Calculated density	1, 2.360 Mg/m^3
Absorption coefficient	13.522 mm^-1
F(000)	1386
Crystal size	0.204 x 0.102 x 0.052 mm
Theta range for data collection	2.42 to 30.02 deg.
Limiting indices	-13<=h<=13, -17<=k<=17, -28<=l<=28
Reflections collected / unique	71308 / 12237 [R(int) = 0.0547]
Completeness to theta = 30.02	98.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6189 and 0.2253
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12237 / 0 / 452
Goodness-of-fit on F^2	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.0577
R indices (all data)	R1 = 0.1004, wR2 = 0.0692
Largest diff. peak and hole	1.191 and -0.717 e.A^-3

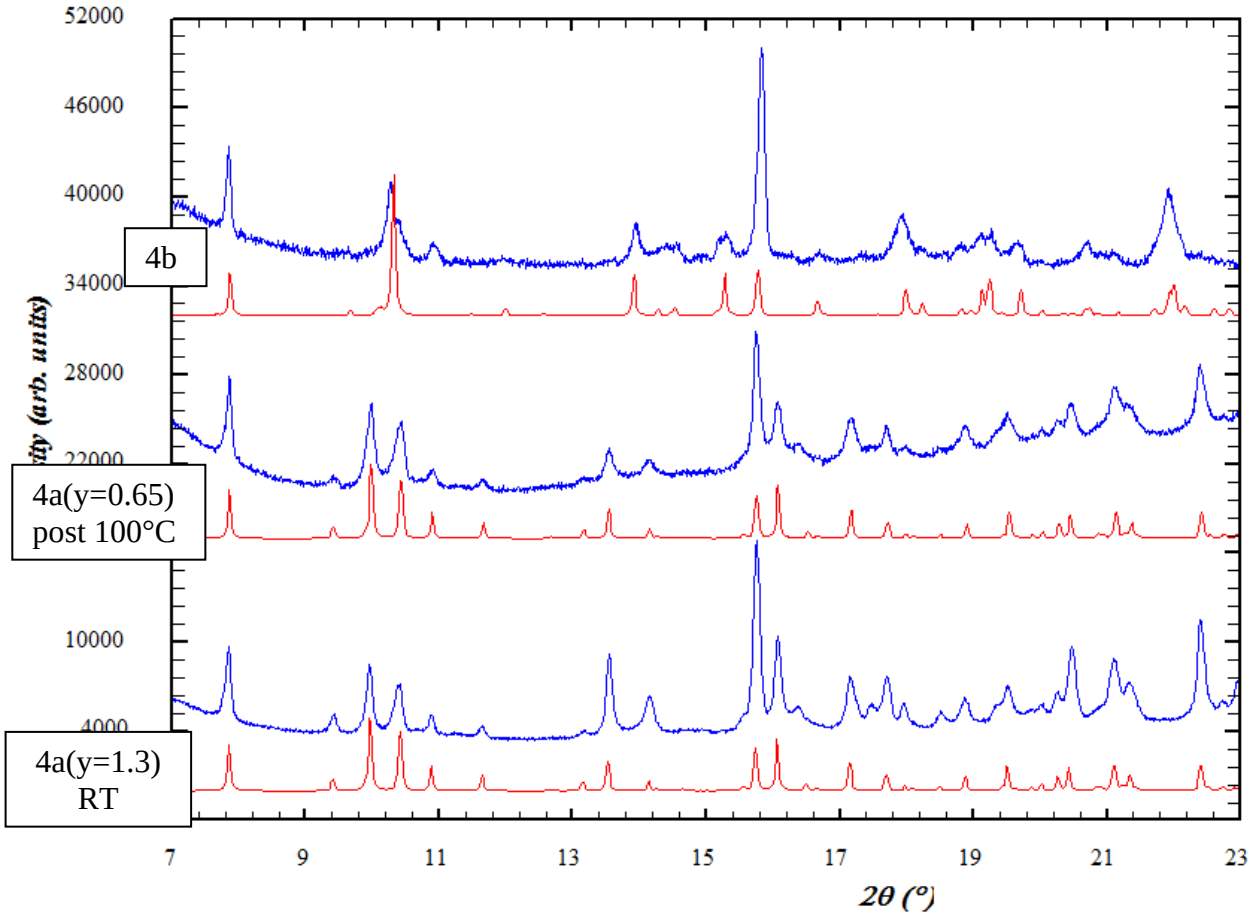
Table IV-A-2. Crystal data and structure refinement for 4a(y=0.65)

Empirical formula	C48 H56 Bi6 Cl24.6 I1.4 N8 O0.65
Formula weight	3059.10
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.4030(3) A alpha = 107.773(6) deg. b = 12.6265(7) A beta = 103.222(6) deg. c = 19.9238(16) A gamma = 72.146(4) deg.
Volume	2120.1(2) A^3
Z, Calculated density	1, 2.373 Mg/m^3
Absorption coefficient	13.596 mm^-1
F(000)	1386
Crystal size	0.204 x 0.102 x 0.052 mm
Theta range for data collection	2.42 to 30.11 deg.
Limiting indices	-13<=h<=13, -17<=k<=17, -28<=l<=28
Reflections collected / unique	76028 / 12381 [R(int) = 0.0832]
Completeness to theta = 30.11	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6189 and 0.2253
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12381 / 0 / 444
Goodness-of-fit on F^2	1.003
Final R indices [I>2sigma(I)]	R1 = 0.0569, wR2 = 0.1451
R indices (all data)	R1 = 0.1264, wR2 = 0.1749
Extinction coefficient	0.00036(10)
Largest diff. peak and hole	3.719 and -1.374 e.A^-3

Table IV-A-3. Crystal data and structure refinement for 4b

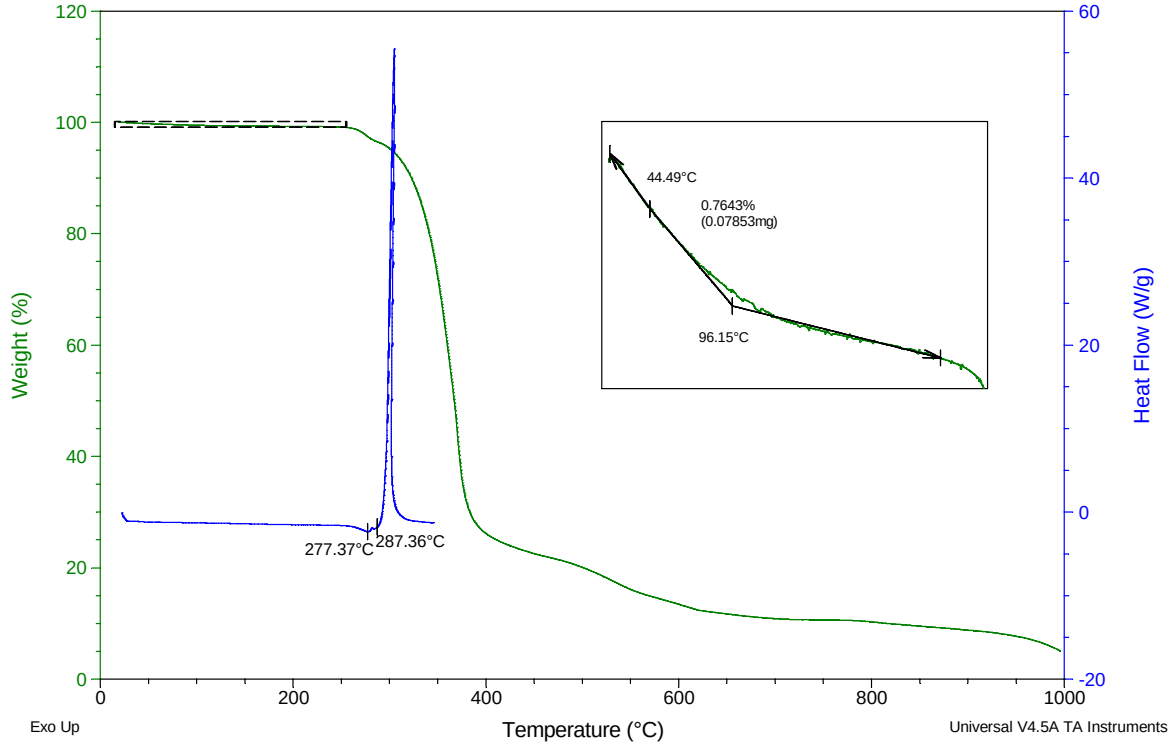
Empirical formula	C48 H56 Bi6 Cl24.6 I1.4 N8
Formula weight	3039.56
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.4244(10) A alpha = 102.979(10) deg.
	b = 12.5997(10) A beta = 96.181(12) deg.
	c = 19.156(3) A gamma = 108.223(6) deg.
Volume	2066.2(4) A^3
Z, Calculated density	1, 2.449 Mg/m^3
Absorption coefficient	13.982 mm^-1
F(000)	1393
Crystal size	0.204 x 0.102 x 0.052 mm
Theta range for data collection	2.43 to 30.03 deg.
Limiting indices	-13<=h<=13, -17<=k<=17, -26<=l<=26
Reflections collected / unique	65174 / 11924 [R(int) = 0.0741]
Completeness to theta = 30.03	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6189 and 0.2253
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11924 / 0 / 434
Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0487, wR2 = 0.0883
R indices (all data)	R1 = 0.1126, wR2 = 0.1039
Largest diff. peak and hole	2.078 and -1.501 e.A^-3

IV-B- XRPD of 4a(y=1.3) at RT and post 100°C (4a(y=0.65)) and and 4b (top): theoretical (red) and experimental (blue)



IV-C- TGA-DSC of 4a

4a : 0.7643% = 1.304 H_2O



IV-D- Crystal structure: Figures

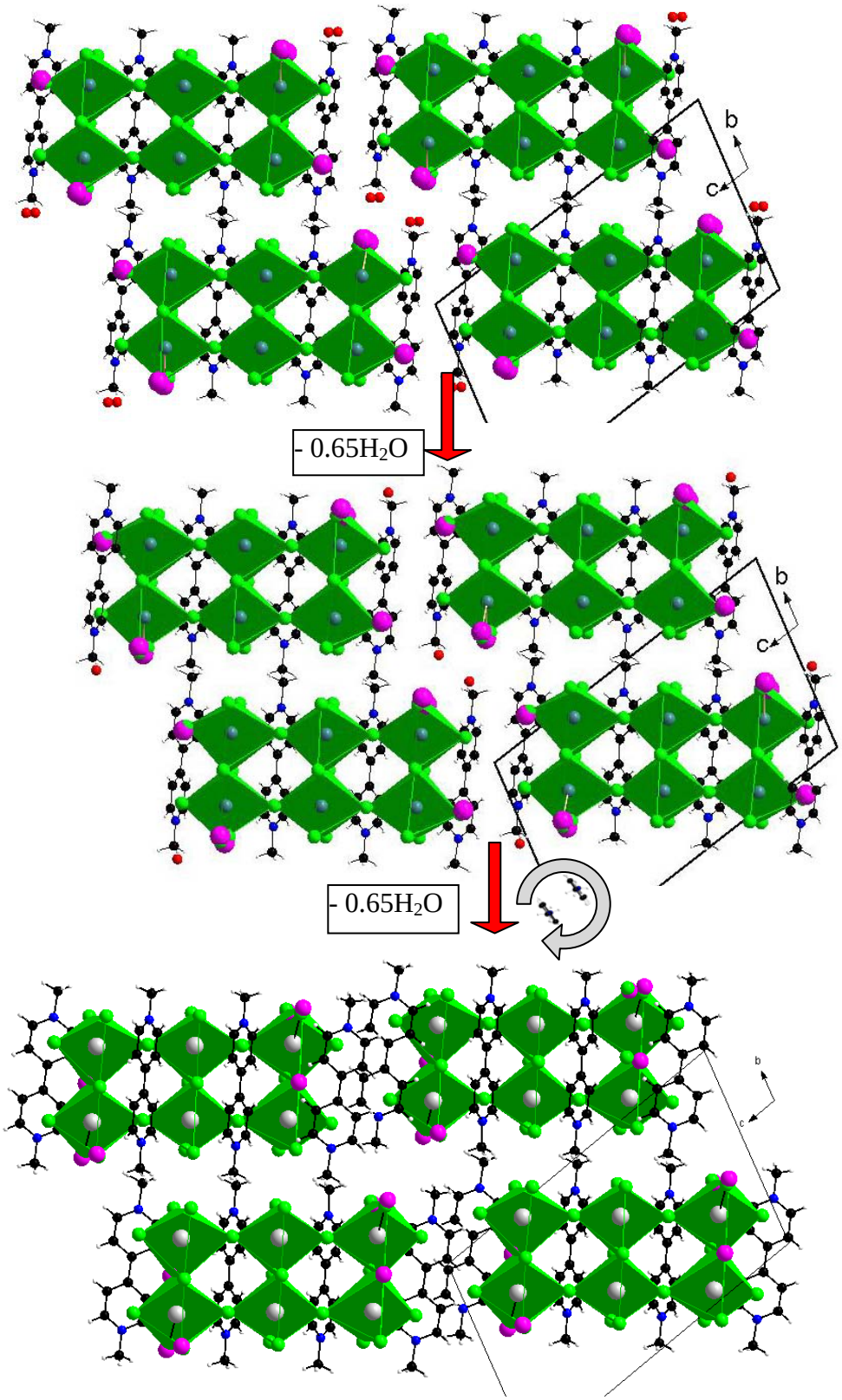


Figure S8: Dehydration process of 4a at the molecular level: general view of structures, from 4a(y=1.3) -RT (top) to 4a(y=0.65) -post 100°C (middle) to 4b (bottom).

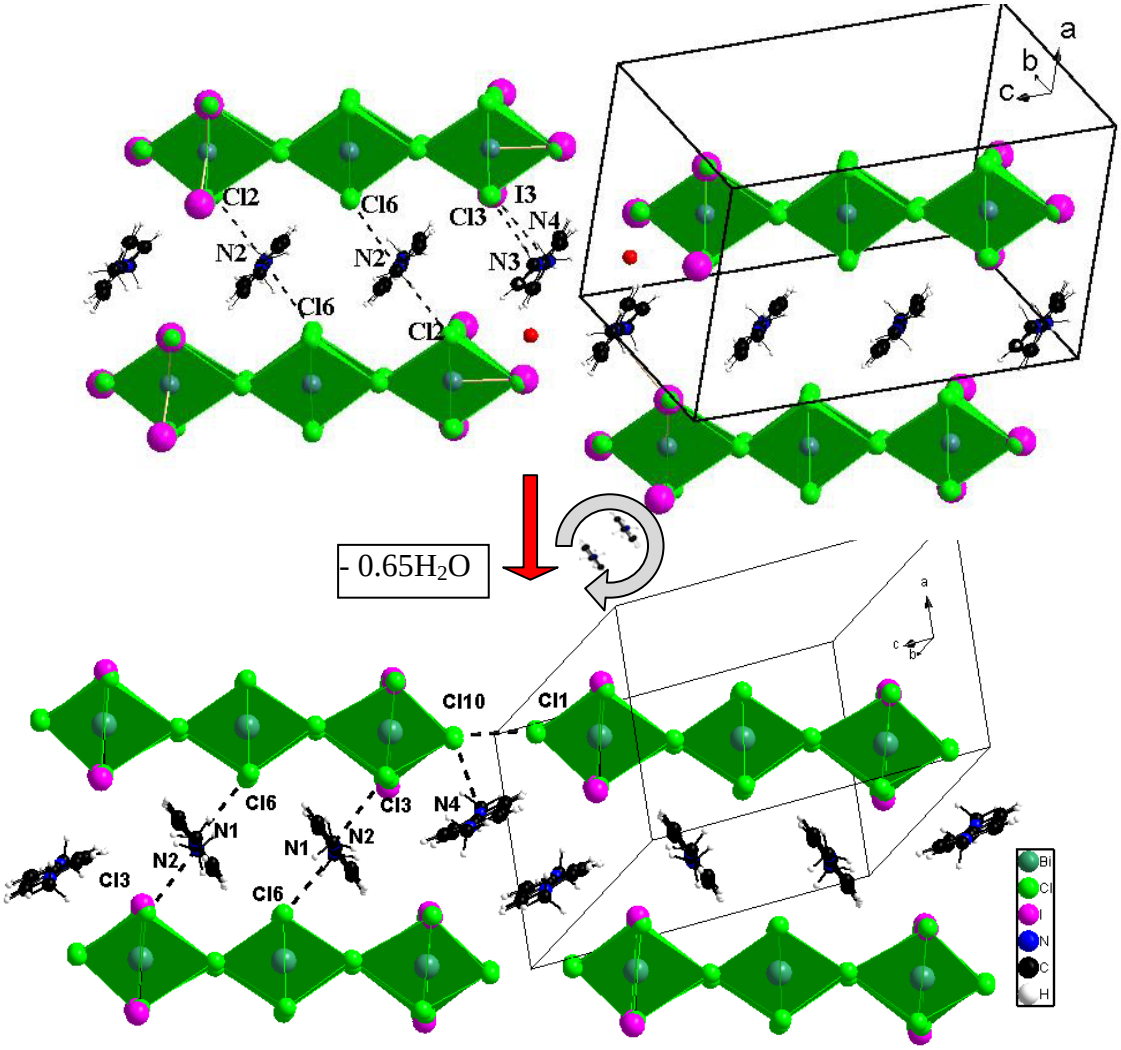


Figure S9: Dehydration process of 4a: part of structures showing one organic-inorganic layer, from 4a (y=0.65) -post 100°C (top) to 4b (bottom).

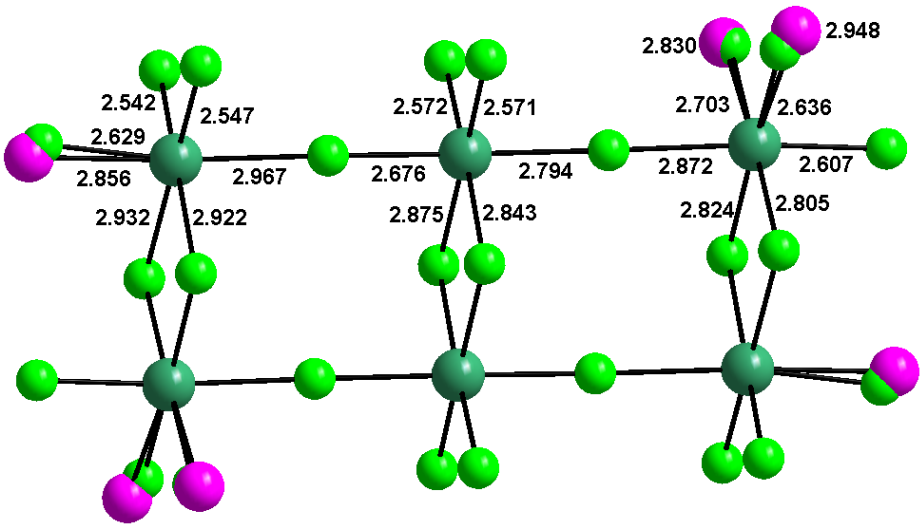


Figure S10: Crystal Structure of **4a**: bond distances in the $[Bi_6Cl_{24.6}I_{1.4}]^{8-}$ cluster

V- Crystal Structure of (MV)[Bi_2Cl_8]

IV-A- Summary of crystallographic data

Table IV-A-1. Crystal data and structure refinement for (MV)Bi2Cl8 (synthesized with iodide containing solution)

Empirical formula	C12 H14 Bi2 Cl8 I N2
Formula weight	1014.71
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	monoclinic, C2/m
Unit cell dimensions	a = 9.58390(10) A alpha = 90 deg. b = 21.8894(10) A beta = 100.7960(10) deg. c = 5.52510(10) A gamma = 90 deg.
Volume	1138.57(6) A^3
Z, Calculated density	4, 5.920 Mg/m^3
Absorption coefficient	35.462 mm^-1
F(000)	1820
Crystal size	0.3 x 0.1 x 0.06 mm
Theta range for data collection	4.07 to 32.01 deg.
Limiting indices	-14<=h<=13, -32<=k<=32, -8<=l<=8
Reflections collected / unique	13796 / 2018 [R(int) = 0.0316]
Completeness to theta = 32.01	99.4 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2018 / 0 / 60
Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0204, wR2 = 0.0398
R indices (all data)	R1 = 0.0265, wR2 = 0.0416
Largest diff. peak and hole	0.770 and -0.783 e.A^-3

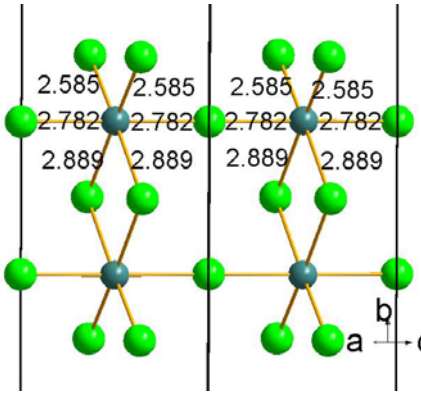


Figure S11: Crystal Structure of (MV)[Bi_2Cl_8]: bond distances in the 1D inorganic chain