Supporting Information

Influence of Crystal Structure and Composition on Optical and Electronic Properties of Pyridinium-based Bismuth Iodide Complexes

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Table SI 1. *Elemental analysis of obtained pyridinium iodibismuthates*.

Compound	Mass average[1]/C:H:N	Mole ratios (Experimental result)[1]	Mole ratios (Theoretical result)[2]
4-AmpyBiI_3	9.14:3.73:0.98	5.71:7.24:2	5:7:2
4-MetpyBiI_3	8.84: 0.96: 1.62	6.37:8.24: 1	6:8:1
4-DimetpyBiI_3	14.49: 1.9: 4.68	7.2:11.25: 2	7:11:2
4-CNpyBiI_3	9.46:3.21:0.861	6.88:7.4:6:2	6:5:2

[1]Elemental analysis
[2]Protonated organic moiety

Table SI2. *Summary of TG-DTG results.*

Compound	Δm [%]	$T_{decomposition}$		
		T_{start} , [°C]	$T_{max,}$ [°C]	$T_{end,}$ [°C]
4-AmpyBiI_3	99.98 % (24 °C – 500 °C)	236.4	400.2	405.7
4-MepyBiI_3	99.81% (24 °C – 500 °C)	231.1	371.8	378.3
4-DmapyBiI_3	93.93% (24 °C – 500 °C)	282.9	416.5	449.5
4-CNpyBiI_3	23 % (24 °C – 246°C)	93.3	239.7	245.7
	76.98 % (246 °C - 400 °C)	246	350	400
pyBiI_3	26.88% (24 °C – 159.03°C)	78	141	159.03
	73.34% (159.03 °C – 274.98°C)	159.03	233.89	274.98

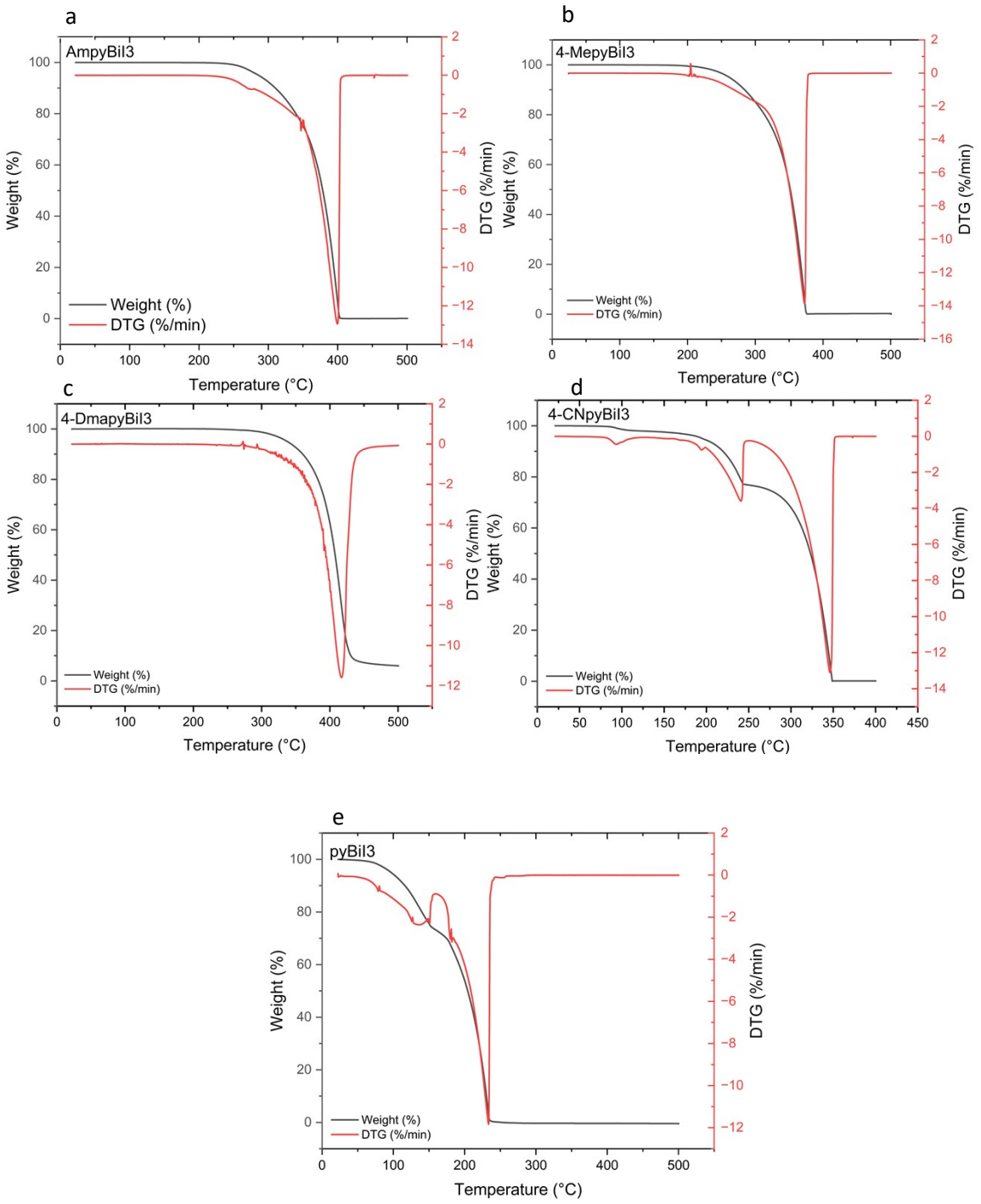


***Figure SI 1**. TG-DTA of a) 4-AmpyBiI$_3$ b) 4-MetpyBiI$_3$ c) 4-DmapyBiI$_3$ d)4-CNpyBiI3 e) pyBiI$_3$.*

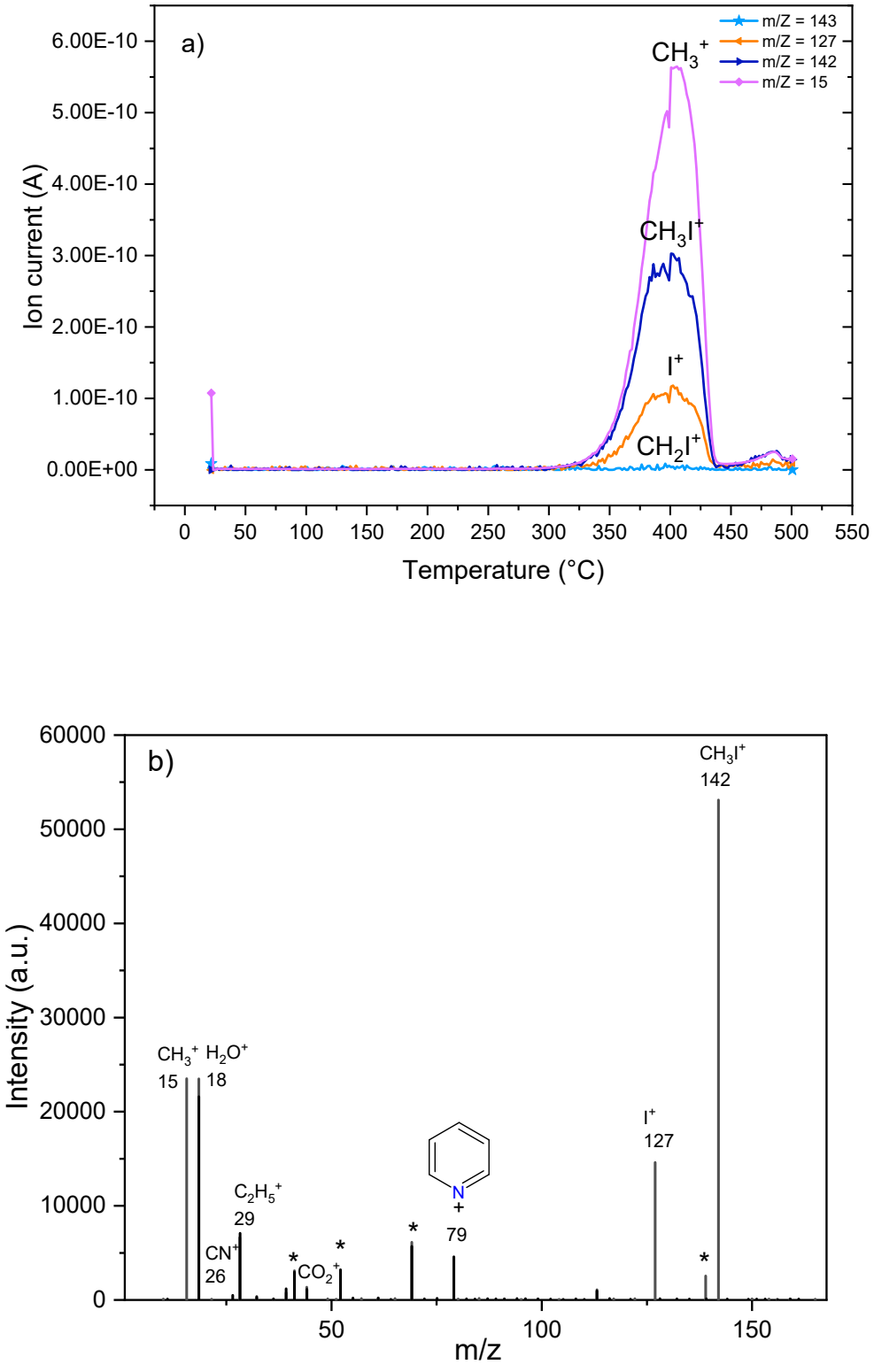


***Figure SI 2**. (a) TGA-Mass spectrum of 4-DmapyBiI$_3$, (b) GC-Mass spectrum of 4-MepyBiI$_3$.*

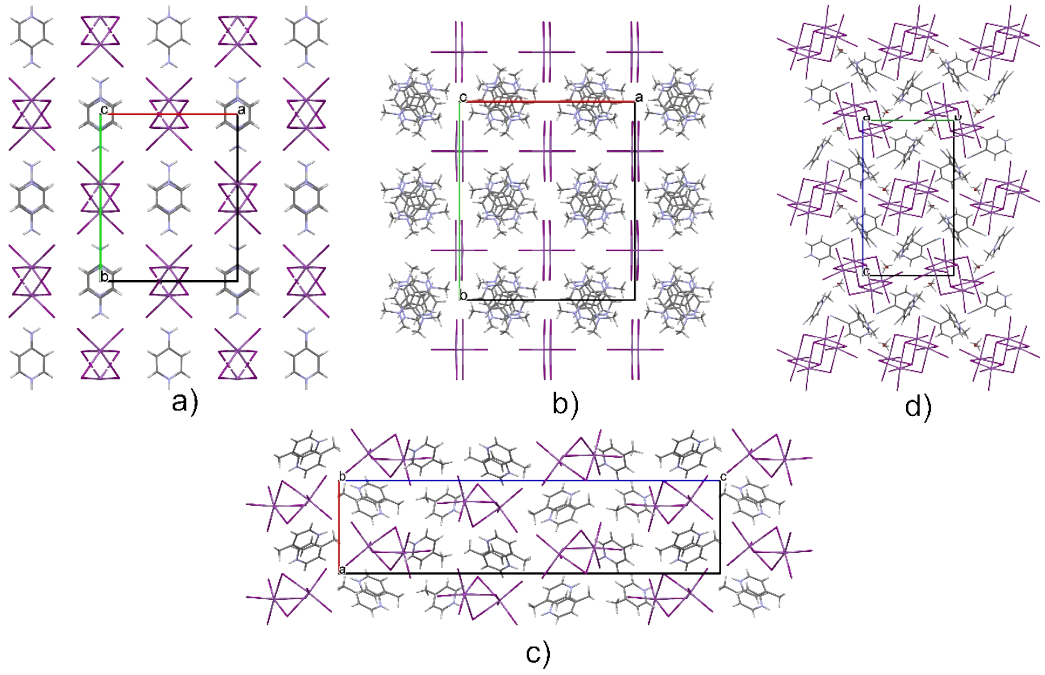


Figure SI 3. Packing of the structural components in a) 4-AmpyBiI$_3$ along [001], b) 4-DmapyBiI$_3$ along [001], c) 4-CNpyBiI$_3$ along [010], d) 4-MepyBiI$_3$ along [100].

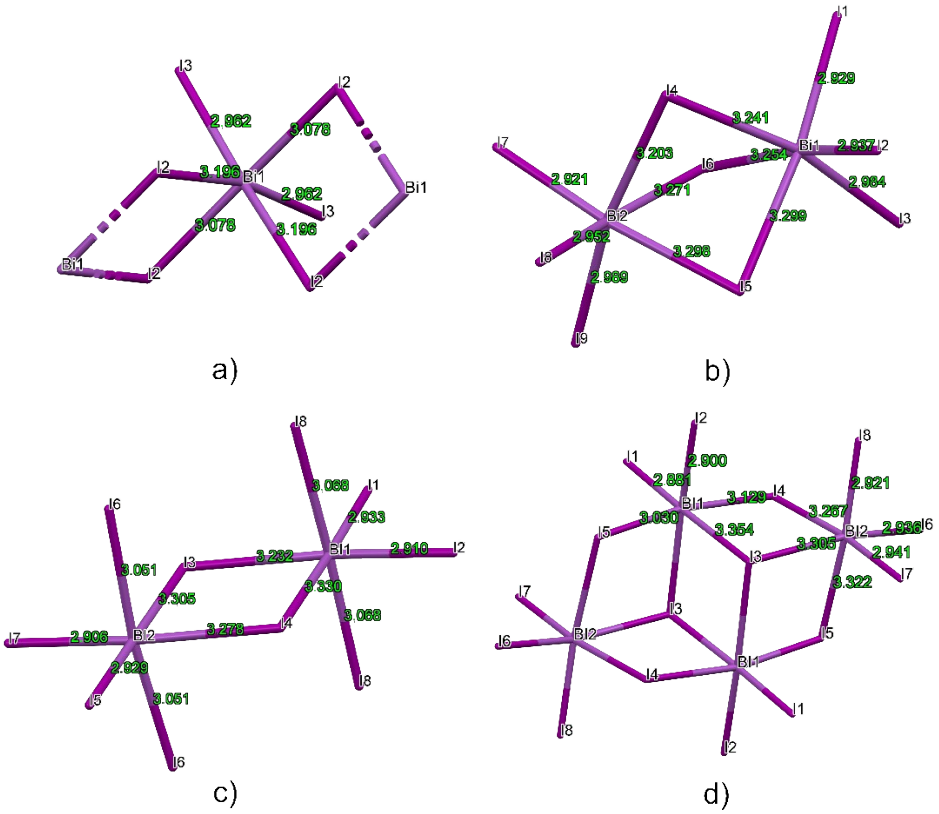


Figure SI 4. a) $[BiI_4]_n$ in 4-AmpyBiI$_3$ along [001], b) Bi_2I_9 in 4-DmapyBiI$_3$ along [001], c) Bi_2I_{10} in 4-CNpyBiI$_3$ along [010], d) Bi_4I_{16} in 4-MepyBiI$_3$ along [100].

***Table SI3**. Geometry of weak interactions in 4-AmpyBiI$_3$ (1) [Å/°]*

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N(8)-H(8)...I(3)	0.88	3.06	3.715(3)	133.0
N(8)-H(8)...I(3)#1	0.88	3.06	3.715(3)	133.0
N(4)-H(4A)...I(3)#4	0.87(2)	2.93(5)	3.7242(18)	153(9)
C(7)-H(7)...I(2)#5	0.95	3.31	3.805(3)	114.5
C(5)-H(5)...I(2)#6	0.95	3.10	3.947(3)	149.7
Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+3/2 #2 -x+1,-y+2,-z+1 #3 x,-y+2,z+1/2 #4 -x+1,-y+1,-z+2 #5 -x+1/2,-y+3/2,z+1/2 #6 -x+1/2,y-1/2,z				

***Table SI4**. Geometry of weak interactions in 4-DmapyBiI$_3$ [Å/°]*

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C(3A)-H(3A)···I(8)#2	0.95	3.08	3.965(3)	155.8
C(6A)-H(6A)···I(6)#3	0.95	3.06	3.723(3)	128.6
C(6A)-H(6A)···I(8)	0.95	3.29	3.827(3)	118.0
C(8A)-H(8A2)···I(1)#4	0.98	3.26	4.110(4)	146.6
N(1A)-H(1A)···I(3)	0.88	2.92	3.702(3)	148.2
N(1B)-H(1B)···I(4)	0.88	2.74	3.528(3)	149.2
C(2B)-H(2B)···I(6)#3	0.95	3.12	3.853(3)	135.5
C(2A)-H(2A)···I(2)#2	0.95	3.08	4.002(3)	164.2
C(5B)-H(5B)···I(8)#5	0.95	3.22	4.090(3)	152.3
C(7B)-H(7B1)···I(2)#6	0.98	3.26	3.774(4)	114.2
C(7B)-H(7B2)···I(5)#7	0.98	3.33	3.966(4)	124.7
C(7B)-H(7B3)···I(7)#3	0.98	3.22	3.796(5)	119.5
C(5A)-H(5A)···I(6)#3	0.95	3.30	3.841(3)	118.3
Symmetry transformations used to generate equivalent atoms: #1 x,-y+1/2,z; #2 x-1/2,y,-z+3/2; #3 -x+1,-y+1,-z+1; #4 -x+1/2,-y+1,z-1/2; #5 x+1/2,y,-z+3/2; #6 -x+3/2,-y+1,z-1/2; #7 -x+3/2,-y+1,z+1/2				

***Table SI5**. Geometry of weak interactions in 4-CNpyBiI$_3$ [Å/°]*

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C(6A)-H(6A)...I(2)#2	0.93	3.33	4.170(8)	151.7
C(3A)-H(3A)...I(6)	0.93	3.25	4.012(8)	140.1
C(2A)-H(2A)...I(4)	0.93	3.23	4.100(8)	157.0
C(2A)-H(2A)...I(5)	0.93	3.31	3.774(7)	113.0
O(1)-H(1)...I(7)	0.82	2.91	3.597(10)	142.8
C(6B)-H(6B)...N(2B)#3	0.93	2.45	3.079(16)	125.2
N(1B)-H(1B)...O(1)	0.86	1.85	2.631(15)	149.5
C(2B)-H(2B)...I(6)#4	0.93	3.14	3.966(13)	149.2
C(3B)-H(3B)...I(7)#4	0.93	3.13	4.058(13)	175.4
C(1)-H(1D)...I(1)#5	0.96	2.94	3.843(14)	157.1
C(7A)-H(7AB)...I(4)	0.96	3.17	4.082(10)	158.3
Symmetry transformations used to generate equivalent atoms: #1 #2 x-1/2,-y+1/2,z-1/2 #3 -x+3/2,y+1/2,-z+1/2 #4 -x+2,-y,-z+1 #5 x+1,y,z				

***Table SI6**. Geometry of weak interactions in (3) [Å/°]*

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N(1A)-H(1A)···I(9)#1	0.88	2.70	3.560(10)	166.0
C(6A)-H(6A)···I(6)#2	0.95	3.25	4.085(11)	147.9
C(2C)-H(2C)···I(4)#3	0.95	3.24	3.991(12)	137.2
C(2C)-H(2C)···I(1)#3	0.95	3.22	3.710(11)	114.0
N(1B)-H(1B) ···I(5)	0.88	2.75	3.604(11)	163.6
N(1C)-H(1C)···I(3)	0.88	2.71	3.545(11)	159.0
C(2A)-H(2A)···I(9)#4	0.95	3.15	3.946(12)	143.0
C(3A)-H(3A)···I(5)#4	0.95	3.30	4.187(11)	157.1
C(6B)-H(6B)···I(4)	0.95	3.07	3.797(13)	134.0
C(6C)-H(6C)···I(8)#5	0.95	3.22	4.118(13)	158.9
C(5A)-H(5A)···I(1)#2	0.95	3.14	4.051(12)	160.3
C(5B)-H(5B)···I(1)#2	0.95	3.03	3.791(11)	138.7
C(5B)-H(5B)···I(2)#6	0.95	3.27	3.941(12)	129.2
C(5C)-H(5C)···I(7)#7	0.95	3.13	4.073(13)	170.1
Symmetry transformations used to generate equivalent atoms: #1 x-1/2,-y+3/2,-z+1; #2 x,y+1,z; #3 x+1,y,z ; #4 x-1,y,z; #5 x,y-1,z; #6 -x,y+1/2,-z+1/2; #7 x+1/2,-y+1/2,-z+1				

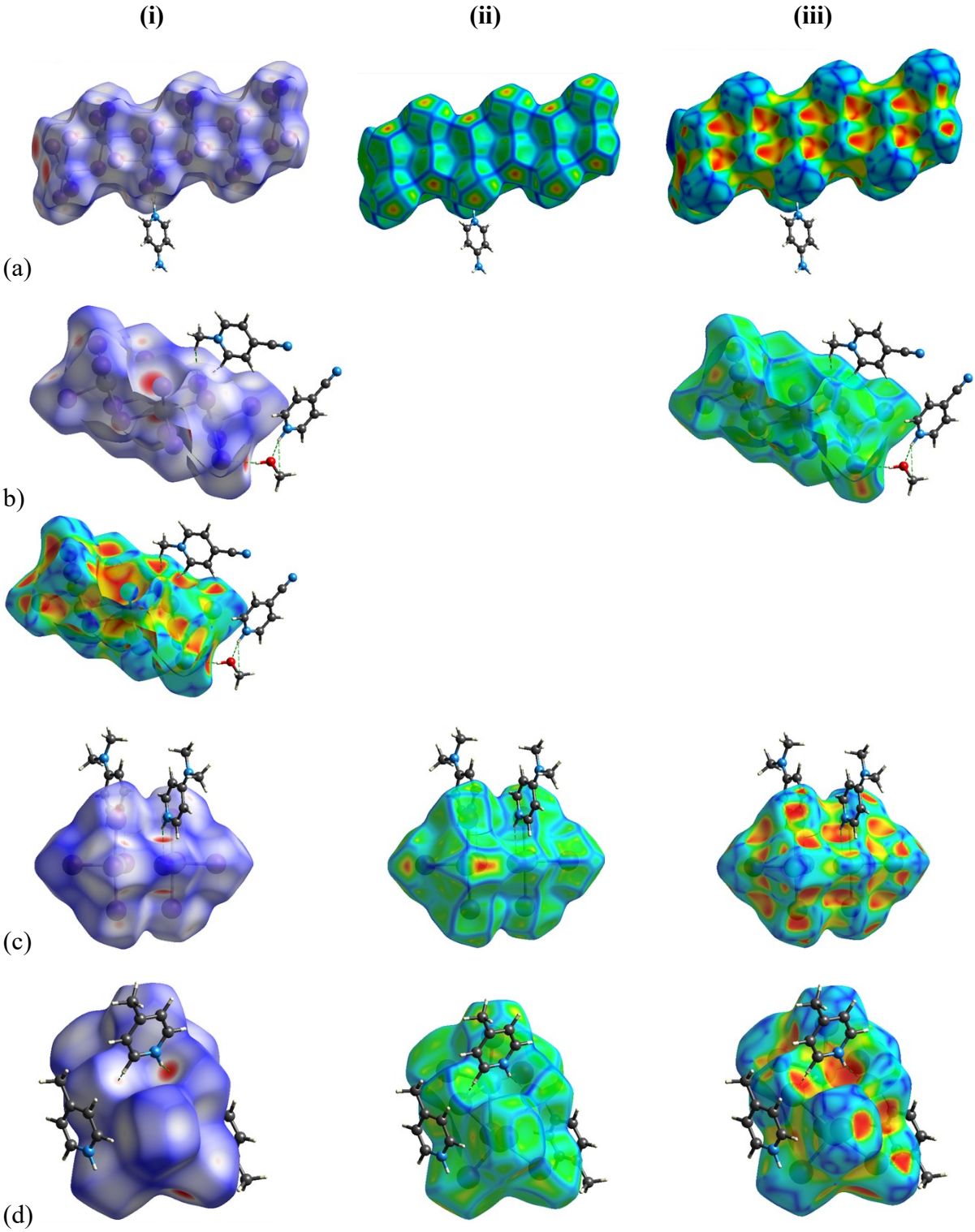
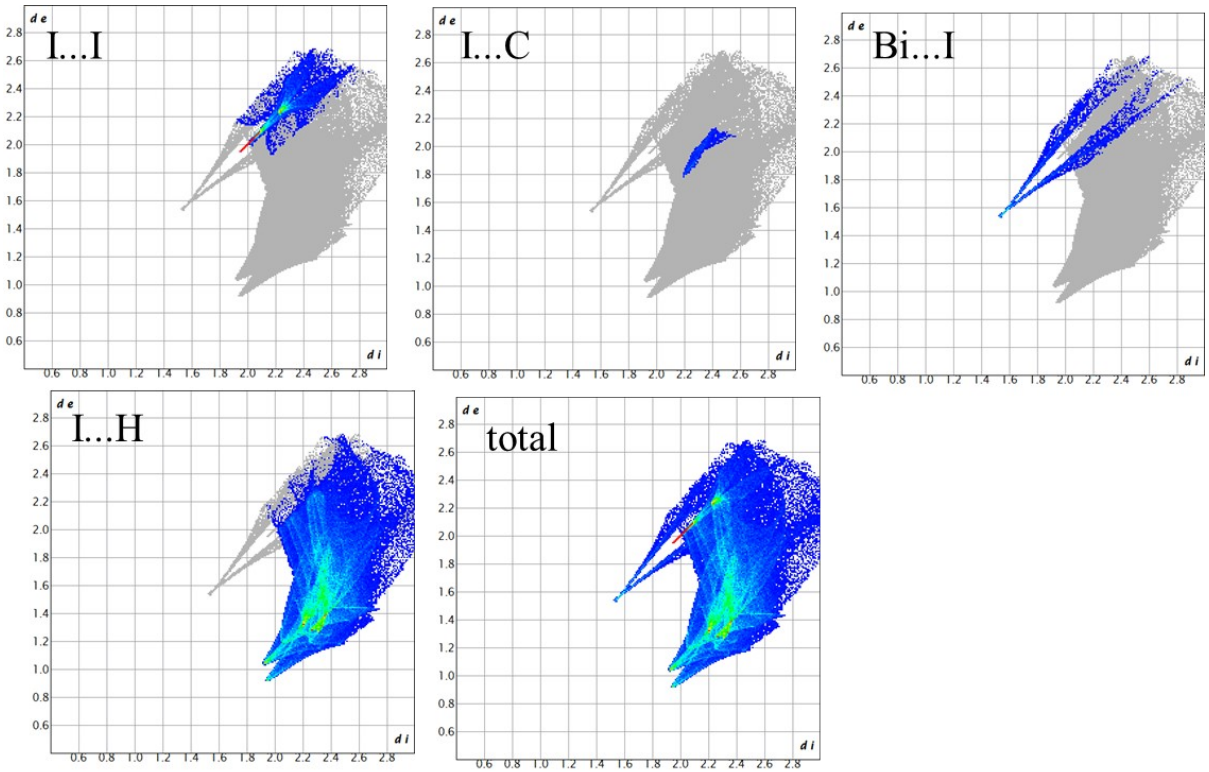
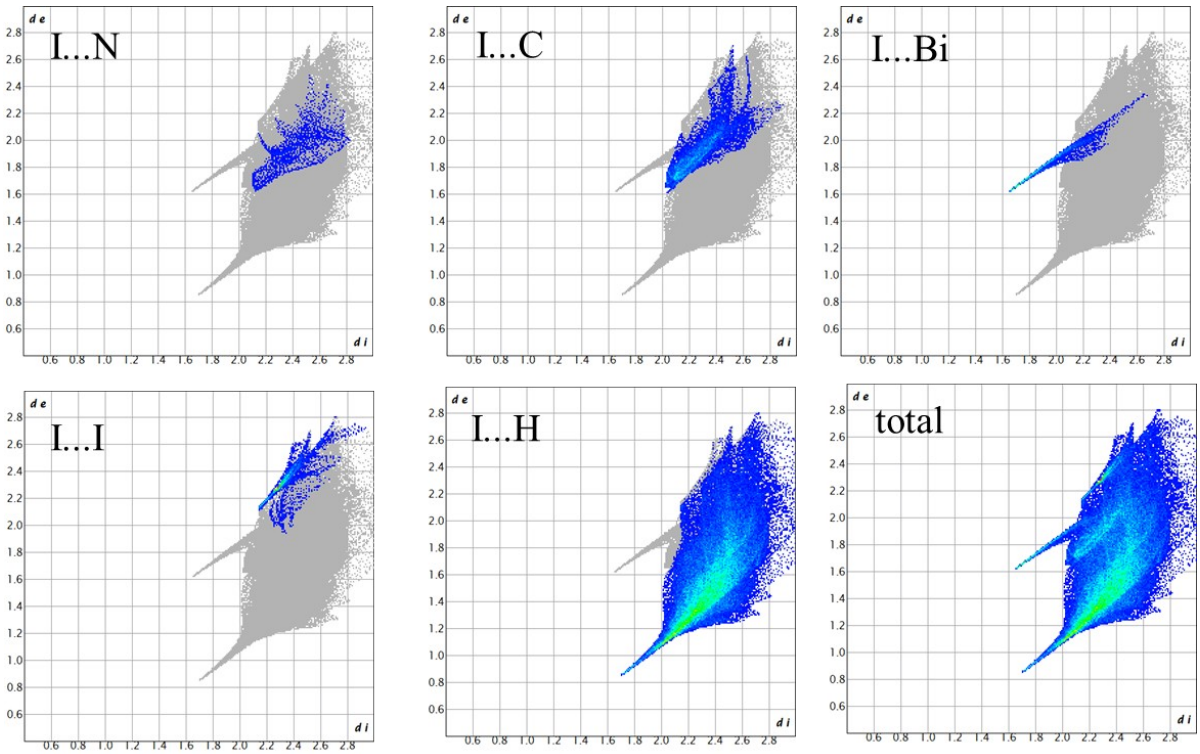


Figure SI 5. ***(i)*** *3D d_{norm} surface of (a) 4-AmpyBiI$_3$ in the range -0.4527 to 1.1099, (b) 4-MetpyBiI$_3$ ranging from -0.3428 to 1.2451 (c) 4-DmetpyBiI$_3$ in the range -0.3012 to 1.1518, (d) 4-CNpyBiI$_3$ in the range of -0.3383 a.u. (red) to 1.3823a.u. (blue),* ***(ii)*** *curvedness in the range of (-4.0000 to 0.4000),* ***(iii)*** *shape index in the range of (-1.0000 to 1.0000).*

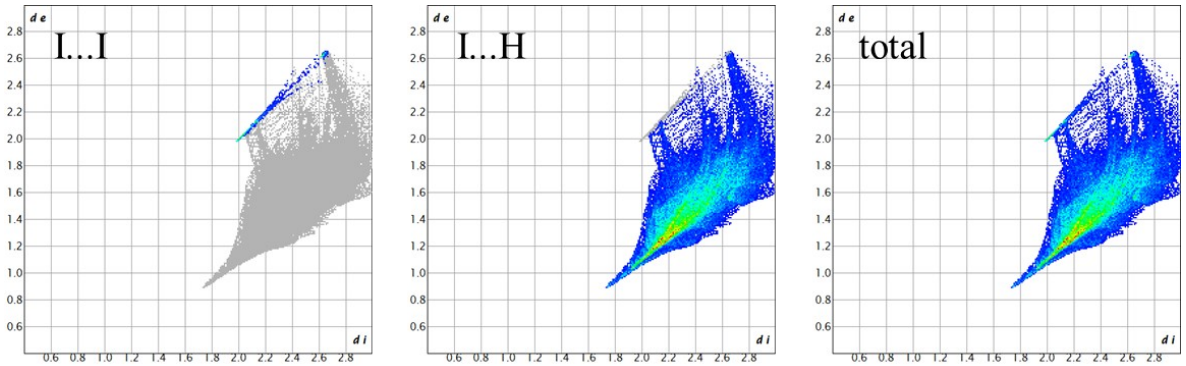
(a)



(b)



(c)



(d)

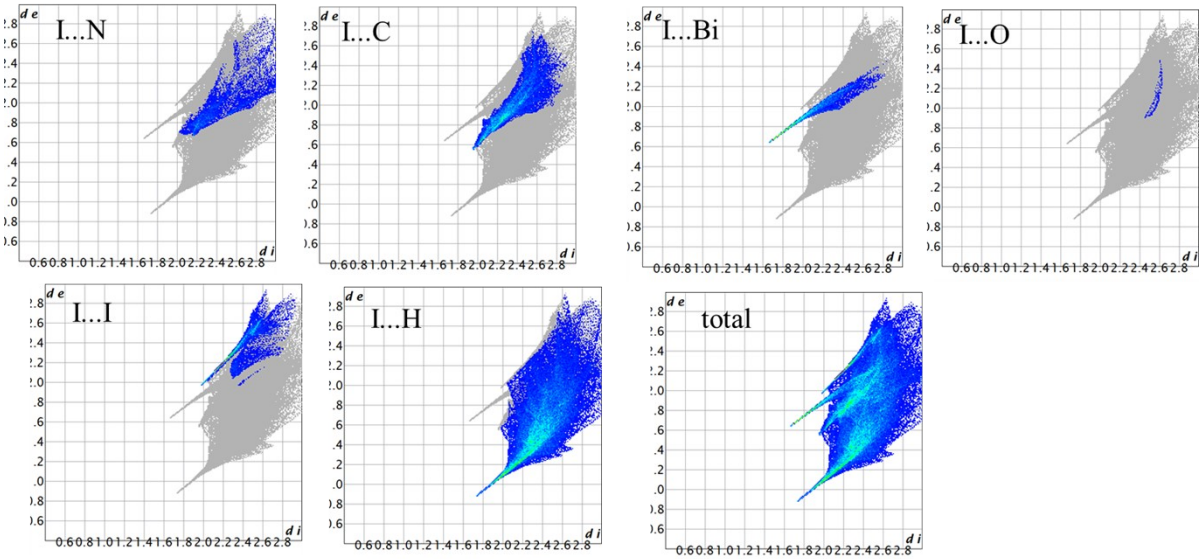


***Figure SI 6**. Fingerprint plots of (a) 4-AmpyBiI$_3$, (b) 4-MetpyBiI$_3$ (c) 4-DmetpyBiI$_3$, (d) 4-CNpyBiI$_3$.*

***Table SI** 7. Percentage contributions of the various intermolecular contacts contributing to Hirshfeld's surfaces of the structures.*

Percentage of interaction	4-AmpyBiI$_3$	4-MepyBiI$_3$	4-DMepyBiI$_3$	4-CNpyBiI$_3$
I···I	12.5	4.5	2	8.7
I···H	82.5	81	98	59.9
I···N	0.3	2	-	6.5
I···C	0.8	9.5	-	16.9
Bi···I	3.9	3	-	7.7
Bi-O	-	-	-	0.3

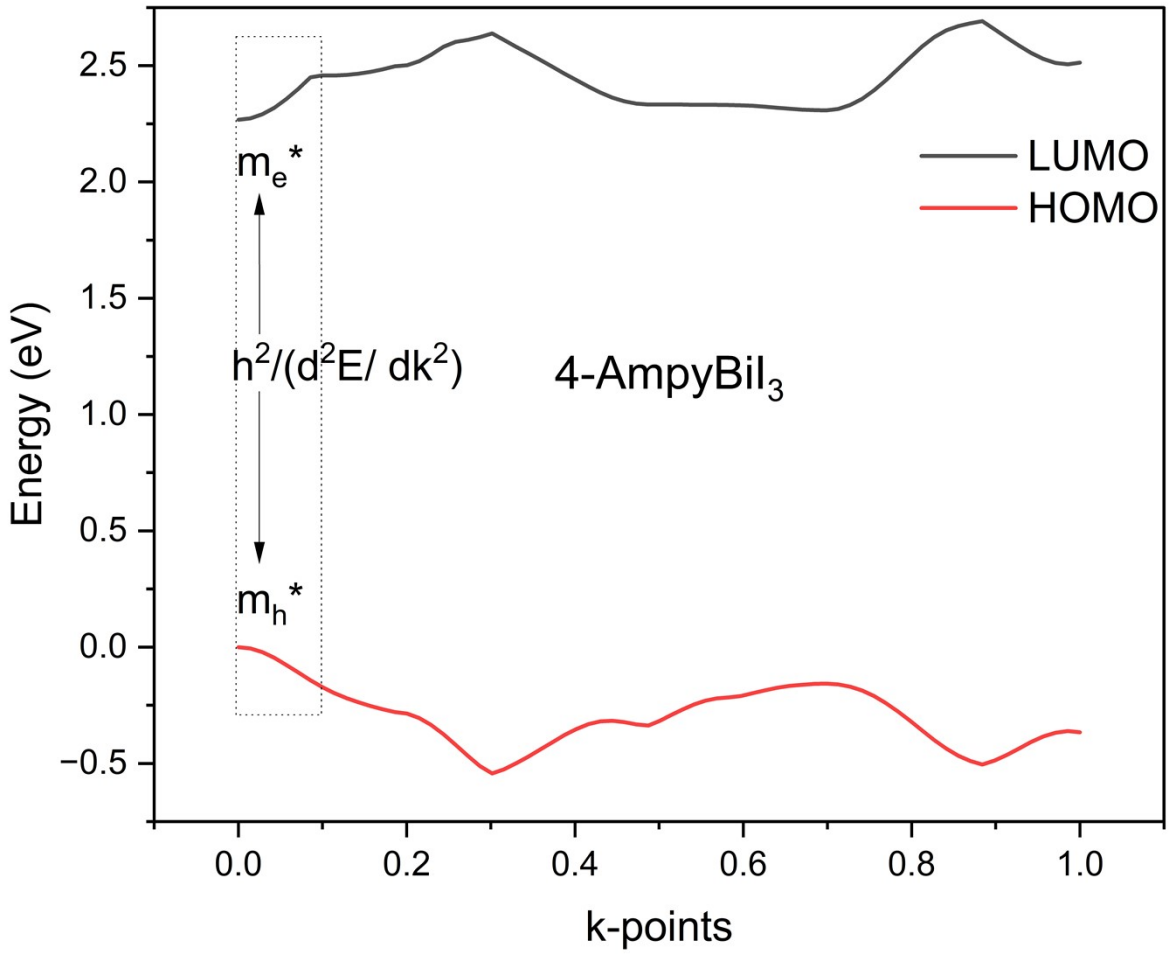


***Figure SI 7.** Minimum conduction band and maximum valence band structure and the dashed rectangular shows the region for calculation of the effective mass by the second derivative of the region.*

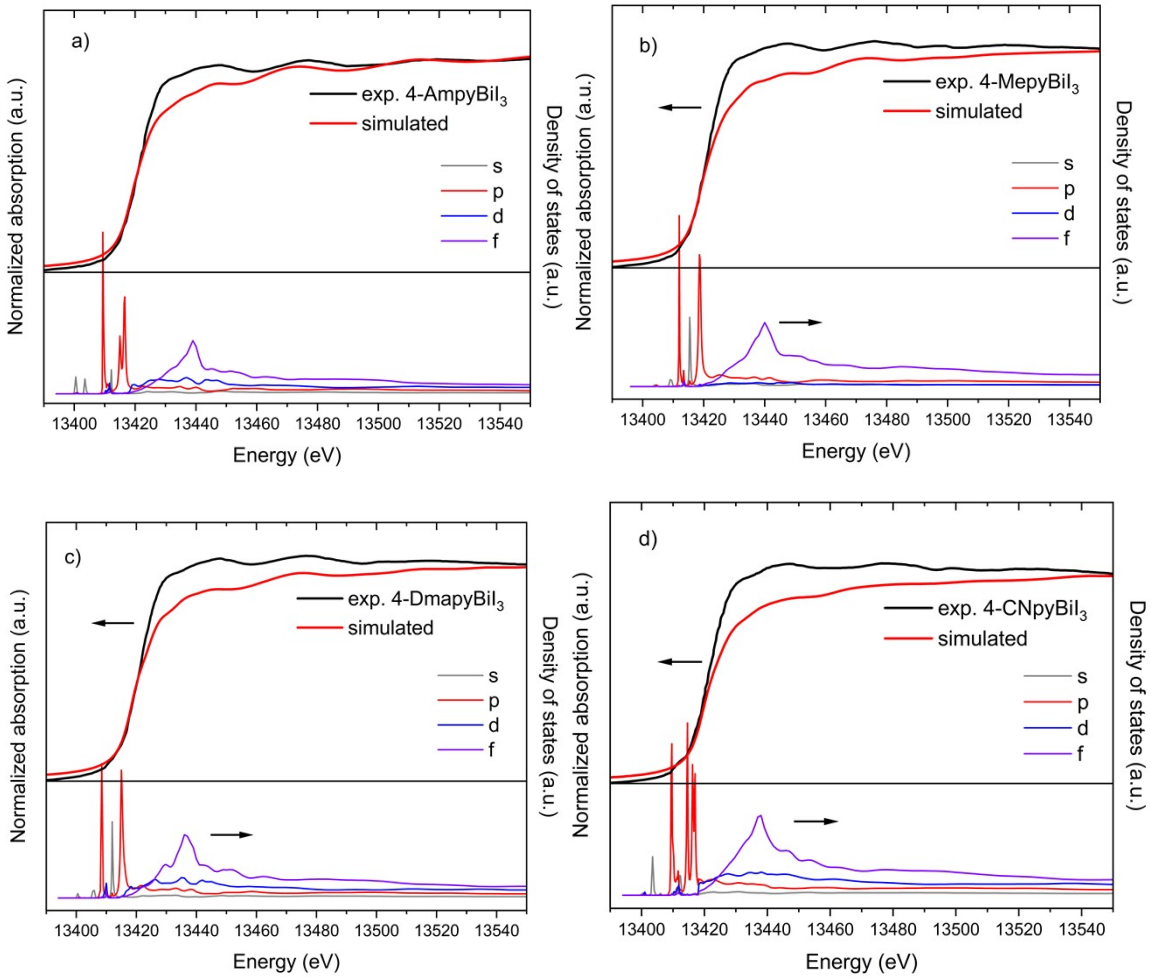


Figure SI 8. *Experimental (black) and DFT-calculated (red) XAS spectra for 4-AmpyBiI$_3$ (a), 4-MepyBiI$_3$ (b), 4-DmapyBiI$_3$ (c) and 4-CNpyBiI$_3$ (d) at L3-edge are plotted on the left axis. The partial densities of the states projected on the absorbing Bi atom are also presented on the right axis.*

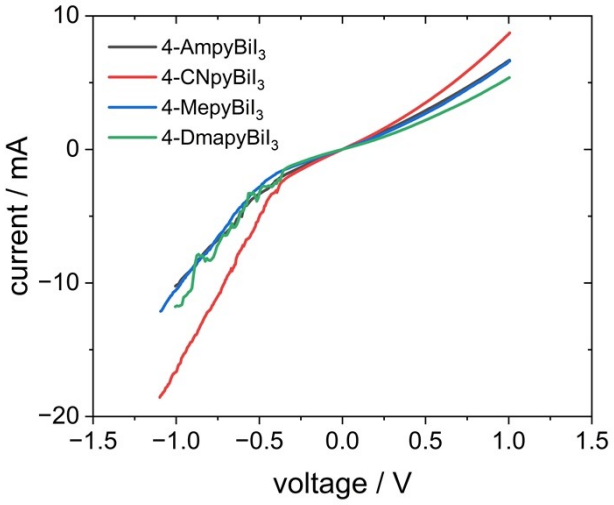


Figure SI 9. *Current-voltage dependencies (linear scale) for all studied bismuth complexes recorded at 298 K.*