Electronic Supplementary Information

Binuclear Bi(III) halide complexes with 4,4-ethylenepyridinium cations: luminescence tuning by reversible solvation

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Table 1S. Bond lengths (*d*, Å) and angles (ω, º) for $[Bi_2Cl_{10}]^{4-}$ and $[Bi_2Br_{10}]^{4-}$ anions in **1** and **2**, respectively.

1		**2**	
Bond	*d*	Bond	*d*
Bi(1)–Cl(1)	2.7683(5)	Bi(1)–Br(1)	2.9077(4)
Bi(1)–Cl(2)	2.5650(5)	Bi(1)–Br(2)	2.7585(4)
Bi(1)–Cl(3)	2.5824(5)	Bi(1)–Br(3)	2.7279(4)
Bi(1)–Cl(4)	2.6173(5)	Bi(1)–Br(4)	2.7897(5)
Bi(1)–Cl(5)	2.9902(5)	Bi(1)–Br(5)	3.0294(4)
Bi(1)–Cl(5)^{i}	2.9023(5)	Bi(1)–Br(5)^{i}	3.0493(4)
Bi(2)–Cl(6)	2.6962(5)		
Bi(2)–Cl(7)	2.6072(5)		
Bi(2)–Cl(8)	2.5996(5)		
Bi(2)–Cl(9)	2.6763(5)		
Bi(2)–Cl(10)	2.8718(5)		
Bi(2)–Cl(10)^{ii}	2.8986(5)		
Angle	ω	Angle	ω
Cl(1)–Bi(1)–Cl(2)	91.401(16)	Br(1)–Bi(1)–Br(2)	88.013(13)
Cl(1)–Bi(1)–Cl(3)	92.165(16)	Br(1)–Bi(1)–Br(3)	89.980(13)
Cl(1)–Bi(1)–Cl(4)	174.626(13)	Br(1)–Bi(1)–Br(4)	175.957(11)
Cl(1)–Bi(1)–Cl(5)	95.710(14)	Br(1)–Bi(1)–Br(5)	88.330(12)
Cl(1)–Bi(1)–Cl(5)^{i}	87.870(15)	Br(1)–Bi(1)–Br(5)^{i}	92.393(13)
Cl(2)–Bi(1)–Cl(3)	87.948(16)	Br(2)–Bi(1)–Br(3)	89.530(13)
Cl(2)–Bi(1)–Cl(4)	87.330(16)	Br(2)–Bi(1)–Br(4)	90.388(14)
Cl(2)–Bi(1)–Cl(5)	171.306(15)	Br(2)–Bi(1)–Br(5)	95.842(12)
Cl(2)–Bi(1)–Cl(5)^{i}	94.409(15)	Br(2)–Bi(1)–Br(5)^{i}	175.779(11)

Cl(3)–Bi(1)–Cl(4)	93.007(16)	Br(3)–Bi(1)–Br(4)	93.721(14)
Cl(3)–Bi(1)–Cl(5)	86.792(15)	Br(3)–Bi(1)–Br(5)	174.307(13)
Cl(3)–Bi(1)–Cl(5)^{i}	177.641(14)	Br(3)–Bi(1)–Br(5)^{i}	86.270(12)
Cl(4)–Bi(1)–Cl(5)	86.039(15)	Br(4)–Bi(1)–Br(5)	88.139(13)
Cl(4)–Bi(1)–Cl(5)^{i}	87.022(15)	Br(4)–Bi(1)–Br(5)^{i}	89.475(13)
Cl(5)–Bi(1)–Cl(5)^{i}	90.857(13)	Br(5)–Bi(1)–Br(5)^{i}	88.370(11)
Cl(6)–Bi(2)–Cl(7)	86.450(15)	Bi(1)–Br(5)–Bi(1)^{i}	91.630(11)
Cl(6)–Bi(2)–Cl(8)	92.617(16)		
Cl(6)–Bi(2)–Cl(9)	172.237(15)		
Cl(6)–Bi(2)–Cl(10)	84.586(14)		
Cl(6)–Bi(2)–Cl(10)^{ii}	89.864(14)		
Cl(7)–Bi(2)–Cl(8)	87.458(16)		
Cl(7)–Bi(2)–Cl(9)	89.323(16)		
Cl(7)–Bi(2)–Cl(10)	98.512(15)		
Cl(7)–Bi(2)–Cl(10)^{ii}	172.478(14)		
Cl(8)–Bi(2)–Cl(9)	93.698(17)		
Cl(8)–Bi(2)–Cl(10)	173.217(15)		
Cl(8)–Bi(2)–Cl(10)^{ii}	86.162(15)		
Cl(9)–Bi(2)–Cl(10)	89.611(15)		
Cl(9)–Bi(2)–Cl(10)^{ii}	95.057(15)		
Cl(10)–Bi(2)–Cl(10)^{ii}	87.650(14)		
Bi(1)–Cl(5)–Bi(1)^{i}	89.143(13)		
Bi(2)–Cl(10)–Bi(2)^{ii}	92.349(14)		

Symmetry codes: **1**) (i) $1-x, 2-y, -z$; (ii) $2-x, 1-y, 1-z$; **2**) (i) $2-x, -y, 1-z$.

Table 2S. Hydrogen-bonding geometry (Å, º) for **1** and **2**.

1				
D–H···*A*	d(*D*–H)	d(H···*A*)	d(*D*···*A*)	∠(*D*–H···*A*)
O(1W)–H(1WB)···O(2W)	0.819(16)	2.021(17)	2.829(2)	169(2)
O(1W)–H(1WA)···Cl(10)	0.80(3)	2.68(3)	3.2788(17)	132(2)
O(2W)–H(2WA)···Cl(1)	0.81(2)	2.52(2)	3.2587(16)	151(2)
O(2W)–H(2WB)···Cl(5)	0.85(3)	2.33(3)	3.1702(16)	168(2)
N(1)–H(1)···O(1W)	0.88	1.86	2.686(2)	155.1
N(3)–H(3)···O(2W)	0.88	2.18	2.895(2)	137.6
N(1)–H(1)···Cl(4)^{i}	0.88	2.98	3.5239(17)	121.7
N(2)–H(2)···Cl(2)^{ii}	0.88	2.69	3.3606(18)	133.9
N(2)–H(2)···Cl(3)^{ii}	0.88	2.51	3.2194(18)	138.7
N(3)–H(3)···Cl(6)	0.88	2.69	3.3248(17)	130.2
N(4)–H(4)···Cl(7)^{iii}	0.88	2.62	3.3117(17)	135.7
N(4)–H(4)···Cl(8)^{iii}	0.88	2.58	3.2656(18)	135.9
C(1)–H(1A)···Cl(4)^{i}	0.95	2.83	3.461(2)	124.7
C(1)–H(1A)···Cl(8)^{iv}	0.95	2.77	3.479(2)	132.4
C(4)–H(4)···Cl(9)^{v}	0.95	2.85	3.752(2)	158.3
C(5)–H(5)···Cl(9)^{vi}	0.95	2.63	3.556(2)	165.2
C(6)–H(6)···Cl(2)^{ii}	0.95	2.91	3.482(2)	119.8
C(6)–H(6)···Cl(7)^{vii}	0.95	2.68	3.402(2)	132.9
C(10)–H(10)···Cl(3)^{ii}	0.95	3.00	3.472(2)	112.4
C(10)–H(10)···Cl(6)^{viii}	0.95	2.71	3.467(2)	137.0
C(12)–H(12A)···Cl(4)^{ix}	0.99	2.80	3.586(2)	137.2
C(13)–H(13)···Cl(1)	0.95	2.72	3.661(2)	172.6
C(14)–H(14)···Cl(1)^{x}	0.95	2.75	3.669(2)	161.8
C(16)–H(16)···Cl(3)^{xi}	0.95	2.98	3.527(2)	117.6
C(17)–H(17)···Cl(3)^{xi}	0.95	2.79	3.424(2)	124.8
C(17)–H(17)···Cl(6)	0.95	2.83	3.405(2)	120.0
C(18)–H(18)···Cl(4)^{xii}	0.95	2.62	3.392(2)	138.2
C(18)–H(18)···Cl(8)^{iii}	0.95	2.89	3.430(2)	117.3
C(22)–H(22)···Cl(2)^{xiii}	0.95	2.77	3.393(2)	124.1
C(22)–H(22)···Cl(7)^{iii}	0.95	2.97	3.492(2)	115.9

C(24)–H(24B)···Cl(6)^{xiv}	0.99	2.79	3.463(2)	125.7
		2		
O(1W)–H(1WB)···O(1W)^{i}	0.87(2)	2.24(5)	2.992(7)	142(6)
O(1W)–H(1WA)···Br(1)^{ii}	0.90(2)	2.74(5)	3.444(3)	136(6)
O(1W)–H(1WC)···Br(5)^{ii}	0.89(2)	2.67(4)	3.433(4)	145(5)
N(1)–H(1)···O(1W)	0.88	2.03	2.788(4)	143.9
N(1)–H(1)···Br(1)	0.88	3.01	3.615(3)	127.3
N(2)–H(2)···Br(2)^{iii}	0.88	2.78	3.492(3)	139.3
N(2)–H(2)···Br(3)^{iii}	0.88	2.78	3.422(3)	131.3
C(1)–H(1A)···Br(1)	0.95	2.91	3.580(4)	128.5
C(1)–H(1A)···Br(3)^{iv}	0.95	3.00	3.637(3)	125.8
C(2)–H(2A)···Br(3)^{iv}	0.95	3.03	3.656(4)	125.0
C(5)–H(5)···Br(4)^{v}	0.95	2.85	3.788(3)	170.6
C(6)–H(6)···Br(2)^{vi}	0.95	2.83	3.625(3)	141.4
C(9)–H(9)···Br(1)^{vii}	0.95	3.04	3.654(4)	123.5
C(10)–H(10)···Br(1)^{vii}	0.95	2.88	3.575(3)	131.0
C(10)–H(10)···Br(3)^{iii}	0.95	2.87	3.485(4)	123.0

Symmetry codes: **1**) (i) $1-x, 2-y, -z$; (ii) $x, 1+y, 1+z$; (iii) $2-x, -y, -z$; (iv) $x-1, 1+y, z$; (v) $x, 1+y, z$; (vi) $2-x, 1-y, 1-z$; (vii) $1-x, 2-y, 1-z$; (viii) $2-x, 2-y, 1-z$; (ix) $x, y, 1+z$; (x) $1-x, 1-y, -z$; (xi) $2-x, 1-y, -z$; (xii) $x, y-1, z$; (xiii) $1+x, y-1, z$; (xiv) $2-x, 1-y, 1-z$; **2**) (i) $1-x, -y, 1-z$; (ii) $1-x, -y, 1-z$; (iii) $1-x, 2-y, -z$; (iv) $2-x, 1-y, -z$; (v) $x-1, y, z$; (vi) $x, 1+y, z-1$; (vii) $x-1, 1+y, z$.

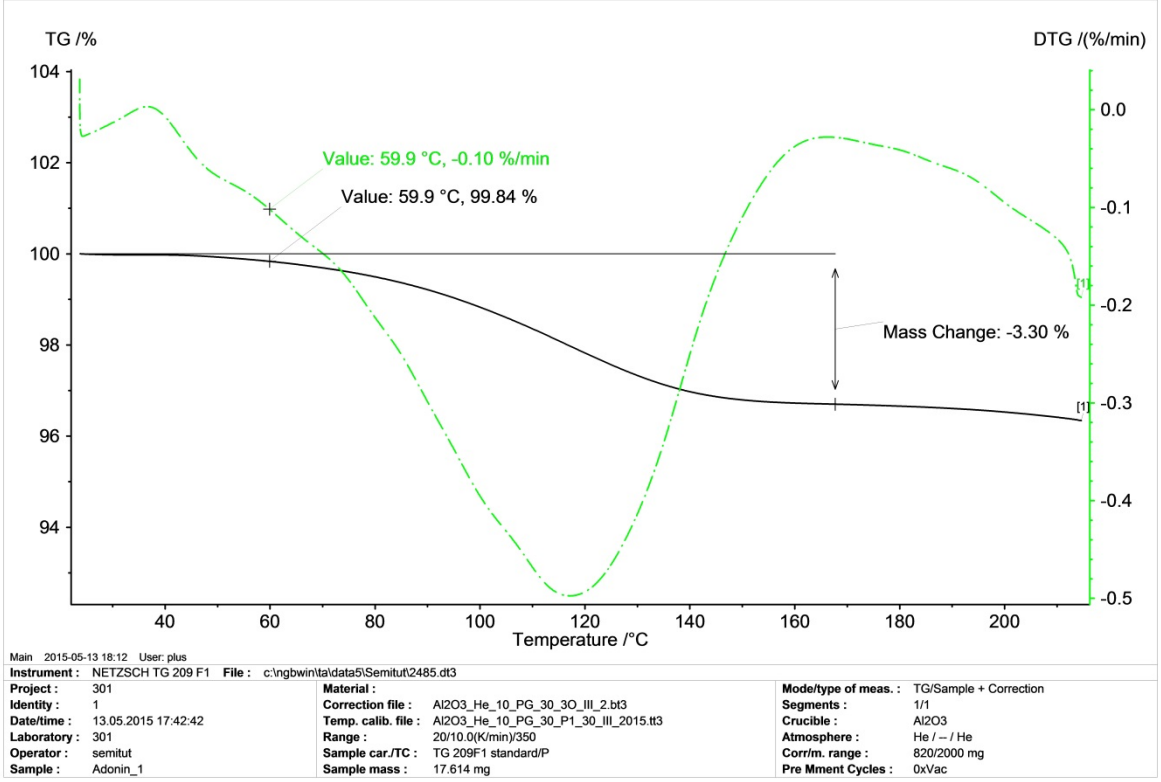

Figure 1S. Thermogravimetric analysis of **1**

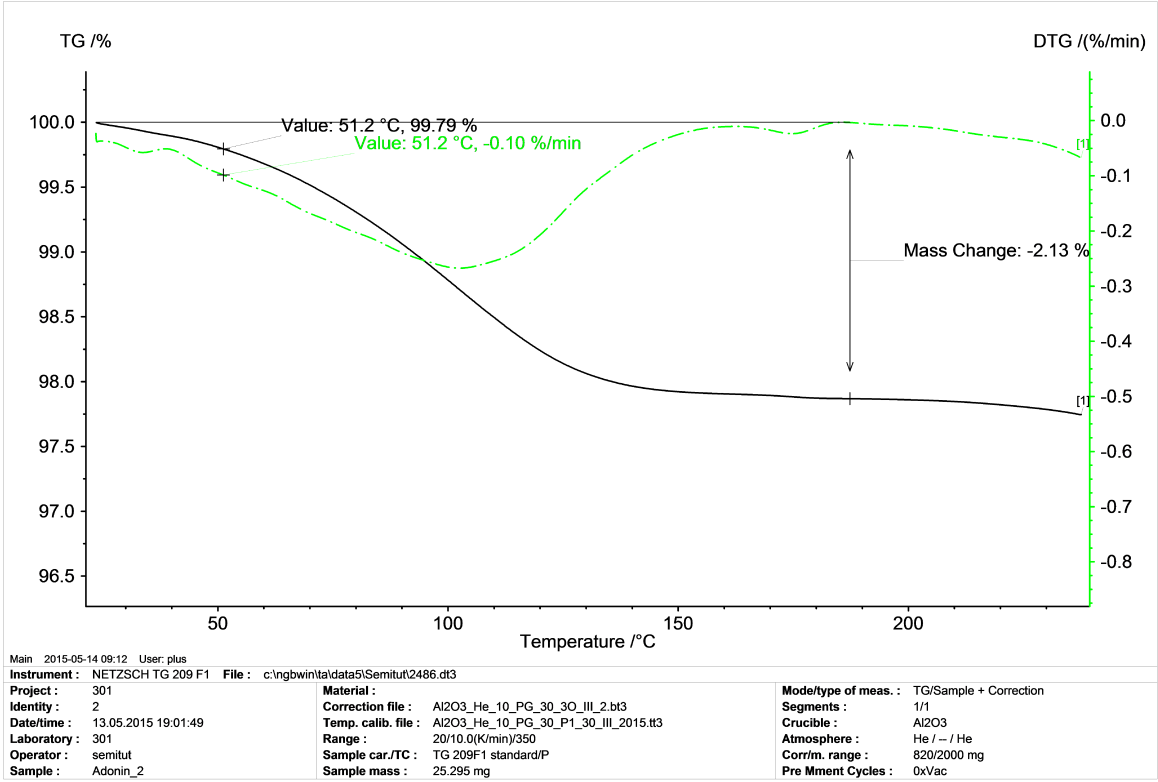

Figure 2S. Thermogravimetric analysis of **2**