Supporting Information

Solvent Mediated Crystallization of $(TMS)_2BiBr_5$.DMSO: A New 0D hybrid Perovskite

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Table S1: Atomic Parameters along with the site occupancy factor (SOF) of $(TMS)_2BiBr_5$.DMSO.

Atom	Wyck.	Site	S.O.F.	x/a	y/b	z/c	U [Å²]
Bi1	2i	1		0.26337(4)	0.75242(3)	0.25020(2)	
Br1	2i	1		0.05869(13)	0.54385(10)	0.21545(7)	
Br2	2i	1		0.27306(14)	0.66045(11)	0.43038(6)	
Br3	2i	1		0.46728(13)	0.96211(11)	0.28638(7)	
Br4	2i	1		0.29271(13)	0.80027(11)	0.06567(6)	
Br5	2i	1		-0.00955(12)	0.97385(10)	0.27263(7)	
S1	2i	1		0.5171(3)	0.3878(3)	0.25038(18)	
S2	2i	1		-0.2923(3)	0.7873(3)	0.51589(17)	
S3	2i	1	0.278	0.8551(13)	0.7210(11)	-0.0039(7)	
S4	2i	1	0.722	0.7156(4)	0.7921(4)	-0.0121(2)	
O1	2i	1		0.5131(8)	0.5486(7)	0.2272(5)	
C1	2i	1		0.6562(19)	0.3436(13)	0.3334(8)	
C2	2i	1		0.647(2)	0.2901(14)	0.1682(8)	
C3	2i	1		-0.2401(17)	0.9575(11)	0.4854(7)	
C4	2i	1		-0.1434(15)	0.7238(12)	0.5939(7)	
C5	2i	1		-0.2235(14)	0.6789(10)	0.4233(6)	
C6	2i	1	0.278	0.738(6)	0.807(4)	-0.091(2)	
C7	2i	1	0.722	0.9077(19)	0.7900(16)	-0.0710(11)	
C8	2i	1	0.722	0.736(5)	0.607(2)	0.0201(18)	
C9	2i	1	0.278	0.748(10)	0.574(6)	0.023(4)	
C10	2i	1	0.722	0.747(4)	0.879(3)	0.0871(12)	
C11	2i	1	0.278	0.782(10)	0.845(6)	0.083(3)	
H1A	2i	1		0.76046	0.36794	0.31516	0.1650
H1B	2i	1		0.67119	0.23966	0.34630	0.1650
H1C	2i	1		0.61441	0.39845	0.38511	0.1650
H2A	2i	1		0.59968	0.31398	0.11179	0.1680
H2B	2i	1		0.65885	0.18587	0.17917	0.1680
H2C	2i	1		0.75408	0.31729	0.16892	0.1680
H3A	2i	1		-0.12379	0.94326	0.47107	0.1290
H3B	2i	1		-0.26616	1.02524	0.53340	0.1290
H3C	2i	1		-0.30189	0.99713	0.43518	0.1290

H4A	2i	1		-0.15644	0.62781	0.61485	0.1190
H4B	2i	1		-0.15716	0.79117	0.64221	0.1190
H4C	2i	1		-0.03490	0.71749	0.56750	0.1190
H5A	2i	1		-0.29145	0.71451	0.37447	0.0980
H5B	2i	1		-0.23077	0.57797	0.43579	0.0980
H5C	2i	1		-0.11057	0.68510	0.40903	0.0980
H6A	2i	1	0.278	0.76600	0.74973	-0.14334	0.1310
H6B	2i	1	0.278	0.62205	0.81405	-0.07674	0.1310
H6C	2i	1	0.278	0.76079	0.90427	-0.10065	0.1310
H7A	2i	1	0.722	0.91175	0.88771	-0.09261	0.1190
H7B	2i	1	0.722	0.99795	0.75770	-0.03252	0.1190
H7C	2i	1	0.722	0.91643	0.72354	-0.11963	0.1190
H8A	2i	1	0.722	0.72164	0.54834	-0.02974	0.1180
H8B	2i	1	0.722	0.84486	0.57256	0.04265	0.1180
H8C	2i	1	0.722	0.65437	0.59719	0.06487	0.1180
H9A	2i	1	0.278	0.80104	0.51651	0.07077	0.0960
H9B	2i	1	0.278	0.63526	0.61419	0.03943	0.0960
H9C	2i	1	0.278	0.75069	0.51167	-0.02746	0.0960
H10A	2i	1	0.722	0.73778	0.98284	0.07692	0.1130
H10B	2i	1	0.722	0.66433	0.86235	0.13025	0.1130
H10C	2i	1	0.722	0.85482	0.83772	0.10804	0.1130
H11A	2i	1	0.278	0.83725	0.81018	0.13570	0.0980
H11B	2i	1	0.278	0.80336	0.94122	0.06775	0.0980
H11C	2i	1	0.278	0.66461	0.85100	0.09166	0.0980

Table S2: Anisotropic displacement parameters, in $Å^2$ of $(TMS)_2BiBr_5$.DMSO.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Bi1	0.04400(19)	0.03186(17)	0.03148(17)	-0.00188(12)	-0.00060(12)	-0.00220(12)
Br1	0.0728(6)	0.0505(6)	0.0603(6)	-0.0200(5)	-0.0103(5)	-0.0049(5)
Br2	0.0914(7)	0.0590(6)	0.0347(5)	-0.0205(5)	-0.0070(5)	0.0053(4)
Br3	0.0663(6)	0.0656(6)	0.0639(7)	-0.0272(5)	0.0006(5)	-0.0071(5)
Br4	0.0800(7)	0.0651(6)	0.0332(5)	-0.0060(5)	0.0024(4)	-0.0003(4)
Br5	0.0536(5)	0.0525(6)	0.0636(6)	0.0083(4)	0.0009(4)	-0.0105(5)
S1	0.0576(15)	0.0485(14)	0.0741(18)	-0.0003(11)	-0.0038(13)	0.0054(12)

S2	0.0592(15)	0.0604(15)	0.0566(15)	-0.0116(12)	0.0024(12)	-0.0053(12)
S3	0.067(7)	0.066(7)	0.080(8)	-0.003(5)	-0.004(5)	-0.018(5)
S4	0.056(2)	0.048(2)	0.049(2)	-0.0060(16)	0.0029(15)	-0.0010(15)
O1	0.075(5)	0.045(4)	0.084(5)	0.004(3)	0.011(4)	0.018(3)
C1	0.184(15)	0.081(8)	0.066(8)	-0.016(9)	-0.067(9)	0.016(6)
C2	0.187(13)	0.079(8)	0.061(7)	-0.003(8)	0.013(8)	-0.017(6)
C3	0.156(12)	0.046(6)	0.058(7)	-0.026(7)	0.003(7)	0.000(5)
C4	0.115(10)	0.072(7)	0.053(7)	-0.021(7)	-0.020(6)	0.005(5)
C5	0.093(8)	0.052(6)	0.049(6)	-0.007(5)	-0.015(5)	-0.006(5)
C6	0.14(3)	0.05(2)	0.08(2)	-0.03(2)	-0.03(2)	0.011(17)
C7	0.086(11)	0.061(9)	0.094(12)	-0.029(8)	0.046(9)	-0.020(8)
C8	0.090(15)	0.037(12)	0.104(17)	-0.001(10)	0.017(12)	0.012(10)
C9	0.08(3)	0.014(17)	0.10(4)	-0.02(2)	0.01(3)	-0.007(15)
C10	0.106(18)	0.073(15)	0.039(9)	0.007(13)	-0.004(8)	-0.002(8)
C11	0.08(4)	0.03(2)	0.08(2)	-0.01(2)	0.00(2)	-0.020(19)

Table S3: Selected bond distances of $(TMS)_2BiBr_5$.DMSO.

Atoms 1,2	**d 1,2 [Å]**	**Atoms 1,2**	**d 1,2 [Å]**
Bi1—Br1	2.8541(10)	S4—C10	1.766(16)
Bi1—Br2	2.8572(9)	C1—H1A	0.9600
Bi1—Br3	2.8624(10)	C1—H1B	0.9600
Bi1—Br4	2.8465(9)	C1—H1C	0.9600
Bi1—Br5	2.7472(9)	C2—H2A	0.9600
Bi1—O1	2.525(6)	C2—H2B	0.9600
S1—O1	1.513(6)	C2—H2C	0.9600
S1—C1	1.724(10)	C3—H3A	0.9600
S1—C2	1.762(12)	C3—H3B	0.9600
S2—C3	1.757(10)	C3—H3C	0.9600
S2—C4	1.746(10)	C4—H4A	0.9600
S2—C5	1.755(10)	C4—H4B	0.9600
S3—C6	1.75(2)	C4—H4C	0.9600
S3—C9	1.79(2)	C5—H5A	0.9600
S3—C11	1.77(2)	C5—H5B	0.9600
S4—C7	1.791(14)	C5—H5C	0.9600

S4—C8	1.749(19)	C6—H6A	0.9600
C6—H6B	0.9600	C9—H9A	0.9600
C6—H6C	0.9600	C9—H9B	0.9600
C7—H7A	0.9600	C9—H9C	0.9600
C7—H7B	0.9600	C10—H10A	0.9600
C7—H7C	0.9600	C10—H10B	0.9600
C8—H8A	0.9600	C10—H10C	0.9600
C8—H8B	0.9600	C11—H11A	0.9600
C8—H8C	0.9600	C11—H11B	0.9600
		C11—H11C	0.9600

Table S4: Selected bond angles of $(TMS)_2BiBr_5$.DMSO.

Atoms 1,2,3	**Angle 1,2,3 [°]**	**Atoms 1,2,3**	**Angle 1,2,3 [°]**
Br1—Bi1—Br2	89.51(3)	C6—S3—C9	101.(2)
Br2—Bi1—Br3	90.12(3)	C6—S3—C11	101.(2)
Br3—Bi1—Br4	91.97(3)	C11—S3—C9	101.(2)
Br4—Bi1—Br5	94.27(3)	C8—S4—C7	101.2(13)
Br1—Bi1—Br5	91.17(3)	C8—S4—C10	102.4(12)
Br1—Bi1—Br3	179.54(3)	C10—S4—C7	102.2(13)
Br1—Bi1—Br4	88.43(3)	H1A—C1—H1B	109.500
Br4—Bi1—Br2	170.52(3)	H1A—C1—H1C	109.500
Br5—Bi1—Br2	95.03(3)	H1B—C1—H1C	109.500
Br5—Bi1—Br3	88.58(3)	H2A—C2—H2B	109.500
S1—O1—Bi1	124.3(4)	H2A—C2—H2C	109.500
O1—Bi1—Br1	88.46(16)	H2B—C2—H2C	109.500
O1—Bi1—Br2	85.76(16)	H3A—C3—H3B	109.500
O1—Bi1—Br3	91.80(16)	H3A—C3—H3C	109.500
O1—Bi1—Br4	84.93(16)	H3B—C3—H3C	109.500
O1—Bi1—Br5	179.12(16)	H4A—C4—H4B	109.500
O1—S1—C1	106.6(5)	H4A—C4—H4C	109.500
O1—S1—C2	104.2(5)	H4B—C4—H4C	109.500
C1—S1—C2	95.3(7)	H5A—C5—H5B	109.500
C5—S2—C3	101.9(5)	H5A—C5—H5C	109.500
C4—S2—C5	103.8(5)	H5B—C5—H5C	109.500

C4—S2—C3	101.1(6)	H6A—C6—H6B	109.500
H6A—C6—H6C	109.500	S2—C4—H4A	109.500
H6B—C6—H6C	109.500	S2—C4—H4B	109.500
H7A—C7—H7B	109.500	S2—C4—H4C	109.500
H7A—C7—H7C	109.500	S2—C5—H5A	109.500
H7B—C7—H7C	109.500	S2—C5—H5B	109.500
H8A—C8—H8B	109.500	S2—C5—H5C	109.500
H8A—C8—H8C	109.500	S3—C6—H6A	109.500
H8B—C8—H8C	109.500	S3—C6—H6B	109.500
H9A—C9—H9B	109.500	S3—C6—H6C	109.500
H9A—C9—H9C	109.500	S4—C7—H7A	109.500
H9B—C9—H9C	109.500	S4—C7—H7B	109.500
H10A—C10—H10B	109.500	S4—C7—H7C	109.500
H10A—C10—H10C	109.500	S4—C8—H8A	109.500
H10B—C10—H10C	109.500	S4—C8—H8B	109.500
H11A—C11—H11B	109.500	S4—C8—H8C	109.500
H11A—C11—H11C	109.500	S3—C9—H9A	109.500
H11B—C11—H11C	109.500	S3—C9—H9B	109.500
S1—C1—H1A	109.500	S3—C9—H9C	109.500
S1—C1—H1B	109.500	S4—C10—H10A	109.500
S1—C1—H1C	109.500	S4—C10—H10B	109.500
S1—C2—H2A	109.500	S4—C10—H10C	109.500
S1—C2—H2B	109.500	S3—C11—H11A	109.500
S1—C2—H2C	109.500	S3—C11—H11B	109.500
S2—C3—H3A	109.500	S3—C11—H11C	109.500
S2—C3—H3B	109.500		
S2—C3—H3C	109.500		

Table S5: Modes of vibration present in $(TMS)_2BiBr_5$.DMSO compound

Modes of Vibration	Raman Shifts (cm^{-1}) Reported in literature (Reference 1)	Observed Raman modes of $(TMS)_2BiBr_5$.DMSO compound (cm^{-1})
Br—Bi—Br	67	69.8
Bi—Br stretching vibration	158	154.2
Bi—Br stretching vibration	172	175.1
SC_3 deformation	290	284.4
SC_3 deformation	311	314.4
SC_3 symmetric stretching (A_1)	653	656.2
SC_3 symmetric stretching (A_1)	690	683.9
SC_3 asymmetric stretching (E)	727	731.5
CH_3 symmetric deformation	1056	1050
CH_3 asymmetric deformation	1425	1422
CH_3 symmetric stretching.	2919	2921
CH_3 asymmetric stretching.	3010	3010

1. J. W. Ypenburg, E. van Der Leij-Van Wirdum and H. Gerding, Recl. des Trav. Chim. des Pays-Bas, 1971, 90, 896–900

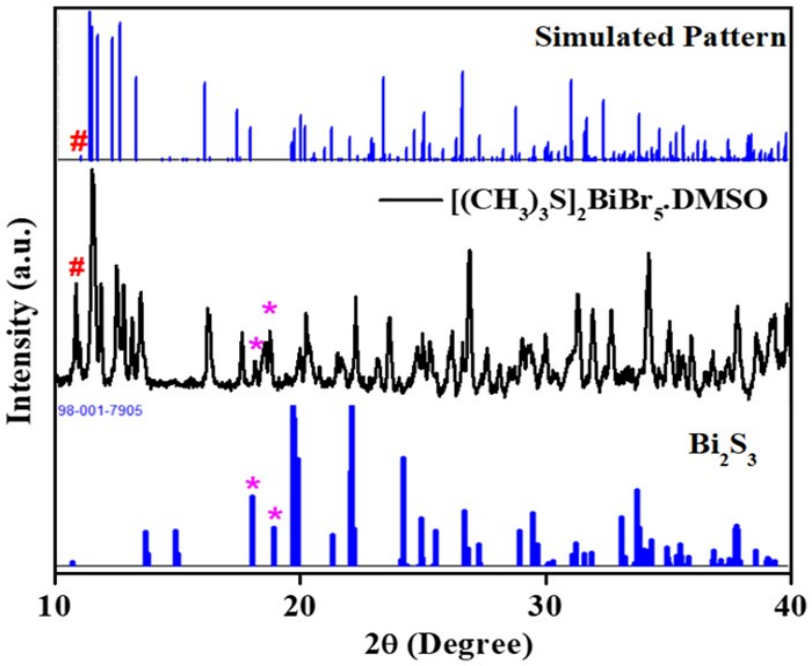

Figure S1. PXRD pattern of $[(CH_3)_3S]_2BiBr_5$.DMSO (black). The upper blue PXRD shows the simulated pattern obtained from the single crystal data and the lower one shows the Bi_2S_3 reference pattern.

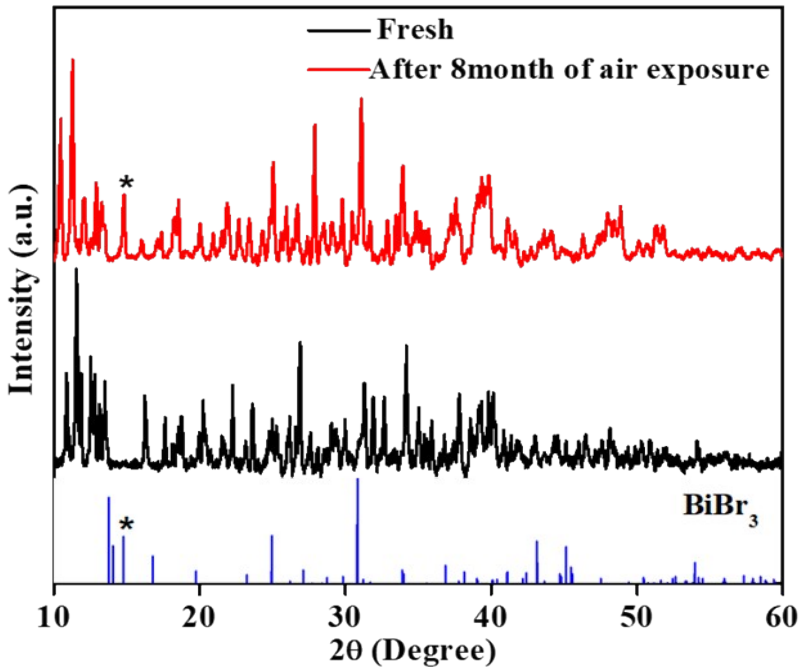

Figure S2. PXRD pattern of fresh $[(CH_3)_3S]_2BiBr_5$.DMSO (black) and after eight month of air exposure. The lower blue PXRD shows the $BiBr_3$ reference pattern.

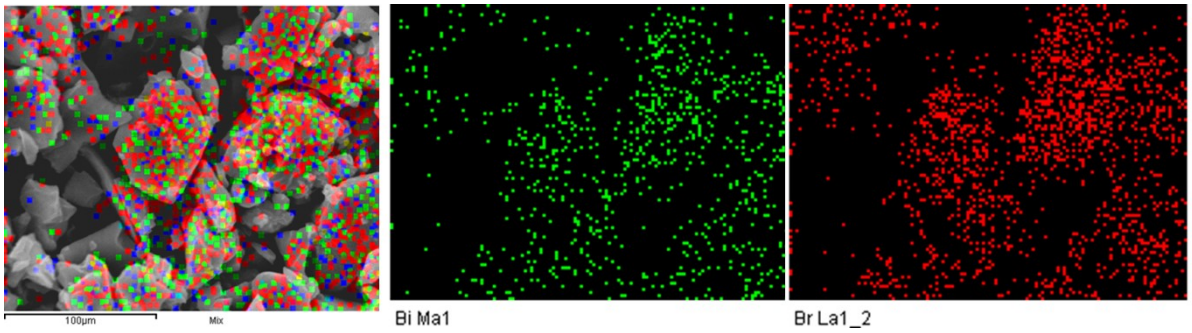

Figure S3: Elemental mapping of $(TMS)_2BiBr_5$.DMSO.