Tracking the Dimensional Conversion Process of Semiconducting Lead Bromide Perovskites by Mass Spectroscopy, Powder X-ray Diffraction, Microcalorimetry and Crystallography

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Table S1 Summary of crystal data and structural refinements for **1** and **2**.

	1	**2**
formula	$C_4H_{16}Br_5N_2OPbS_2$	$C_4H_{14}Br_4N_2PbS_2$
formula weight	779.05	681.12
crystal system	Monoclinic	Monoclinic
space group	$P2_1$	$C2/c$
T (K)	100(2) K	100(2) K
a (Å)	10.0824(3)	11.3898(3)
b (Å)	8.3838(2)	11.6104(3)
c (Å)	10.9546(4)	22.8884(6)
α (deg)	90	90
β (deg)	104.184(4)	90.983(2)
γ (deg)	90	90
V (Å^3)	913.81(17)	3026.32(14)
D_c (g cm^{-3})	2.882	2.990
F (000)	702	2448
Z	2	8
μ (mm^{-1})	20.739	21.956
Flack	-0.022(7)	/
reflns collected	9646	12759
unique reflns	3953	3766
R_{int}	0.051	0.026
data/parameters	3953/141	3766/121
GOF	0.994	1.028
R_1, wR_2 [$I > 2\sigma(I)$]	0.0254, 0.0461	0.0209, 0.0430
R_1, wR_2 (all data)	0.0298, 0.0471	0.0261, 0.0442

Table S2 Selected bond lengths (Å) and angles (°) for **1**and **2**.

1		**2**	
Pb(1)-Br(1)	2.8914(7)	Pb(1)-Br(2)	2.949(3)
Pb(1)-Br(4)	2.9468(8)	Pb(1)-Br(3)	2.956(2)
Pb(1)-Br(5)	2.9850(8)	Pb(1)-Br(1)[a]	3.012(3)
Pb(1)-Br(2)	3.0735(10)	Pb(1)-Br(5)	3.044(2)
Pb(1)-Br(2)[a]	3.0901(9)	Pb(1)-Br(1)	3.065(3)
Pb(1)-Br(3)	3.1151(7)	Pb(1)-Br(4)	3.177(3)
Br(1)-Pb(1)-Br(4)	83.86(2)	Br(1)-Pb(1)[b]	3.012(3)
Br(1)-Pb(1)-Br(5)	91.06(2)	Br(5)-Pb(1)[c]	3.044(2)
Br(4)-Pb(1)-Br(5)	88.49(2)	Br(3)-Pb(1)[d]	2.956(2)
Br(1)-Pb(1)-Br(2)	85.75(3)	Br(2)-Pb(1)-Br(3)	91.12(5)
Br(4)-Pb(1)-Br(2)	96.15(3)	Br(2)-Pb(1)-Br(1)[a]	87.85(7)
Br(5)-Pb(1)-Br(2)	174.05(3)	Br(3)-Pb(1)-Br(1)[a]	87.98(10)
Br(1)-Pb(1)-Br(2)[a]	96.64(3)	Br(2)-Pb(1)-Br(5)	85.71(5)
Br(4)-Pb(1)-Br(2)[a]	176.85(3)	Br(3)-Pb(1)-Br(5)	173.14(10)
Br(5)-Pb(1)-Br(2)[a]	88.40(3)	Br(1)[a]-Pb(1)-Br(5)	85.82(9)
Br(2)-Pb(1)-Br(2)[a]	86.991(10)	Br(2)-Pb(1)-Br(1)	89.06(7)
Br(1)-Pb(1)-Br(3)	170.69(3)	Br(3)-Pb(1)-Br(1)	95.46(10)
Br(4)-Pb(1)-Br(3)	88.76(3)	Br(1)[a]-Pb(1)-Br(1)	175.42(3)
Br(5)-Pb(1)-Br(3)	94.42(3)	Br(5)-Pb(1)-Br(1)	90.57(9)
Br(2)-Pb(1)-Br(3)	89.42(3)	Br(2)-Pb(1)-Br(4)	173.20(7)
Br(2)[a]-Pb(1)-Br(3)	91.05(3)	Br(3)-Pb(1)-Br(4)	90.17(5)
Pb(1)-Br(2)-Pb(1)[b]	169.75(3)	Br(1)[a]-Pb(1)-Br(4)	85.52(7)
		Br(5)-Pb(1)-Br(4)	92.29(5)
		Br(1)-Pb(1)-Br(4)	97.46(7)
		Pb(1)[b]-Br(1)-Pb(1)	151.33(10)
		Pb(1)[c]-Br(5)-Pb(1)	156.24(14)
		Pb(1)[d]-Br(3)-Pb(1)	143.88(16)
a = -x+1,y+1/2,-z+1; b = -x+1,y-1/2,-z+1.		a = -x+1/2,y+1/2,-z+1/2; b = -x+1/2,y-1/2,-z+1/2; c = -x+1,y,-z+1/2; d = -x,y,-z+1/2.	

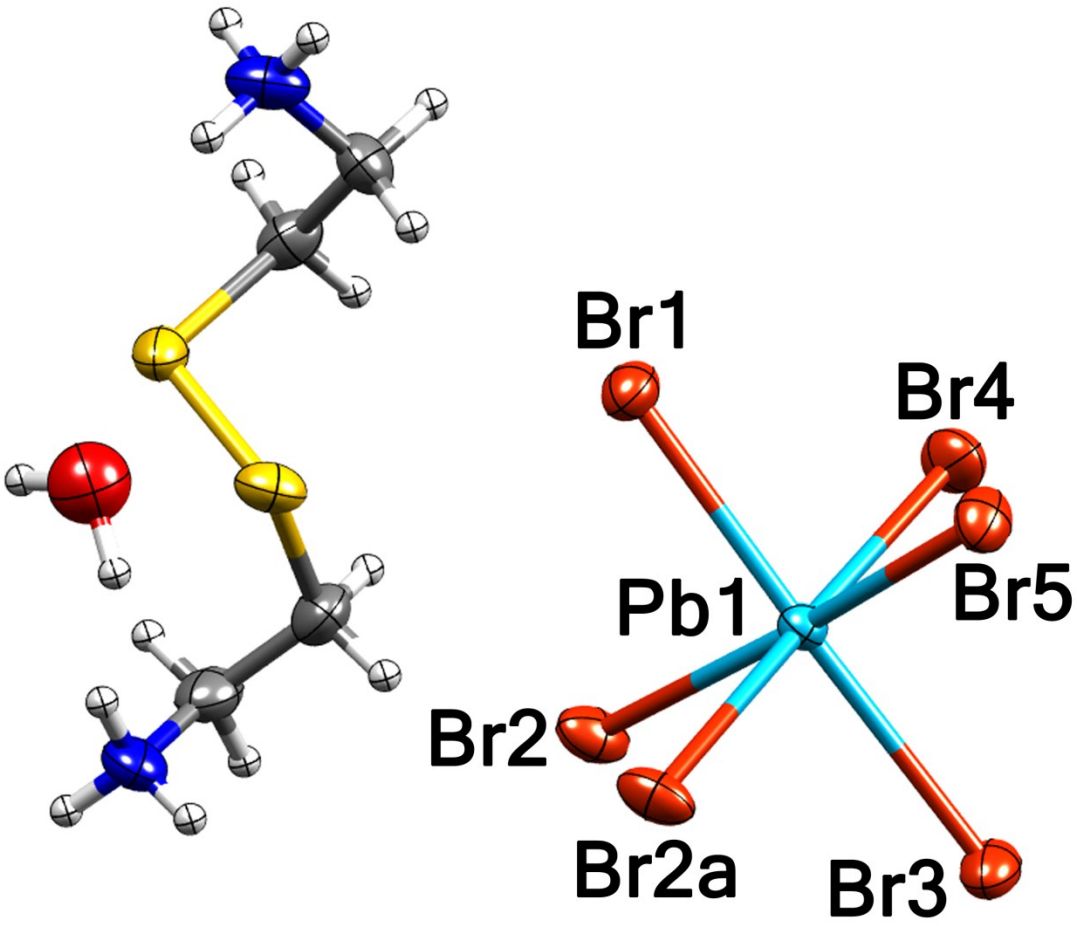

Figure S1. The asymmetric unit of **1**.

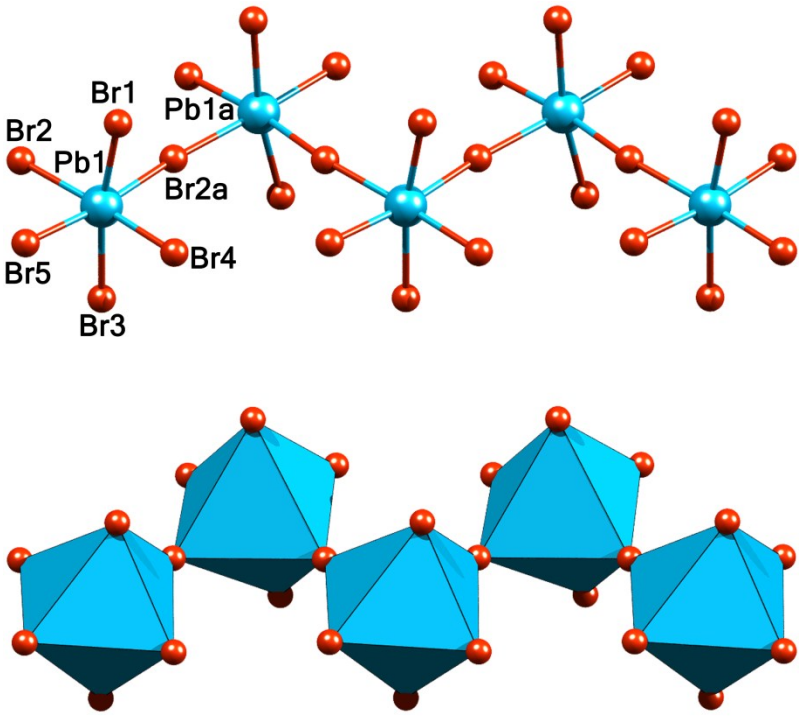

Figure S2. The 1D chain in **1**.

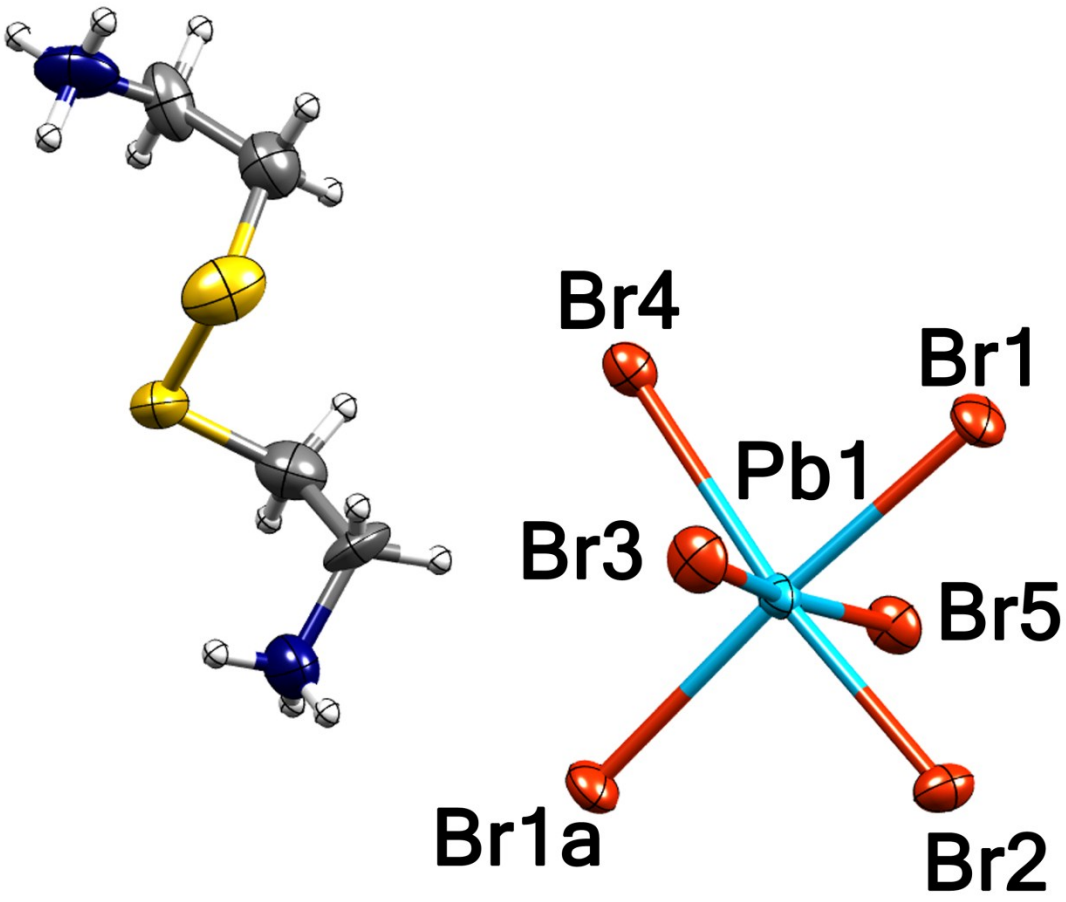

Figure S3. The asymmetric unit of **2**.

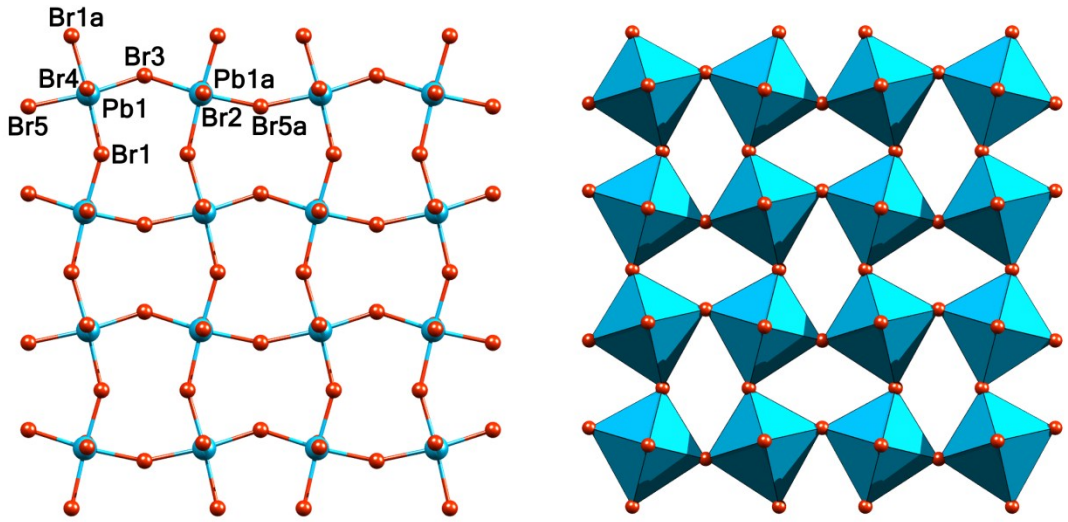

Figure S4. The 2D layer in **2**.

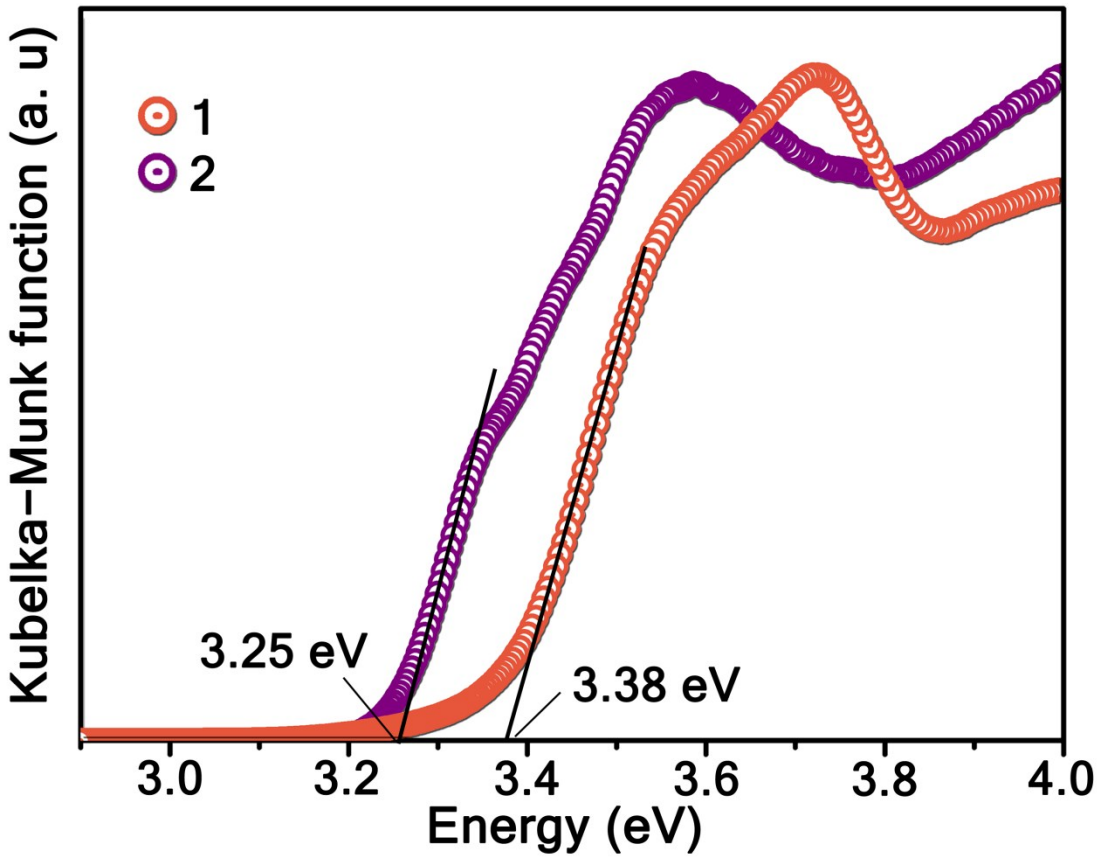

Figure S5. Optical absorption spectra of complexes **1** and **2**.

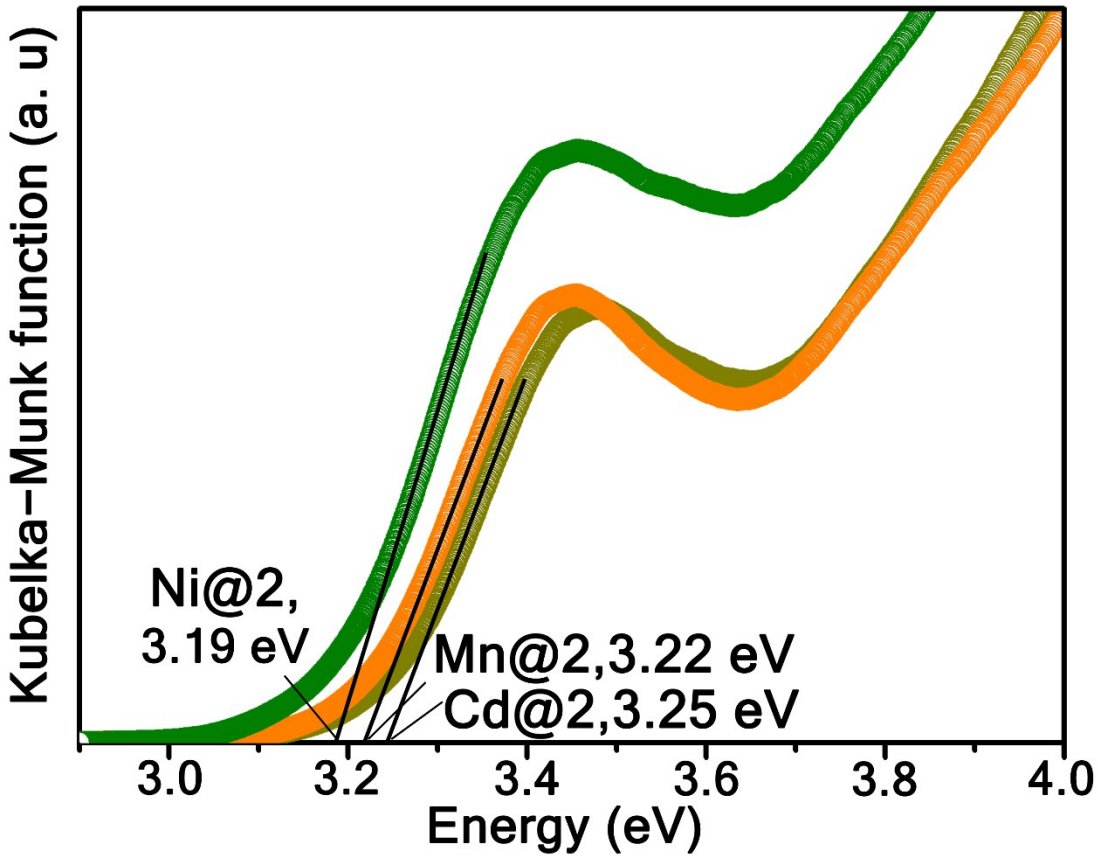

Figure S6. Optical absorption spectra of complexes Ni@**2**, Cd@**2** and Mn@**2**.

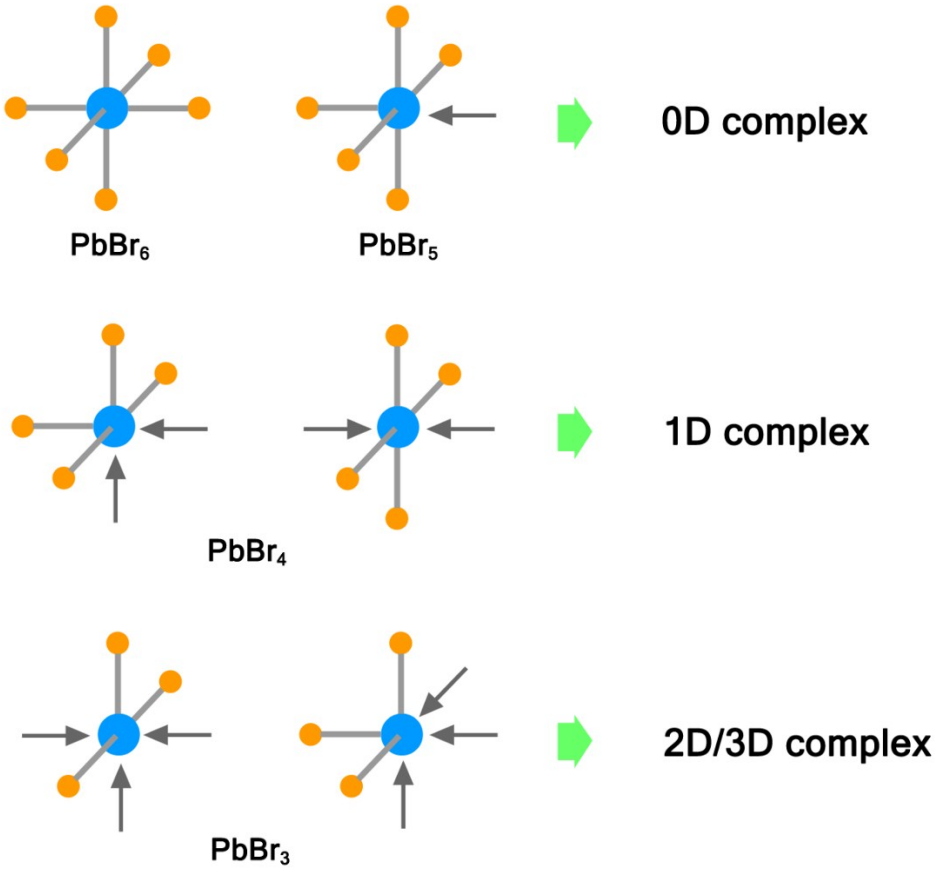

Fig. S7 Relation between the configuration of intermediate and dimension of products.

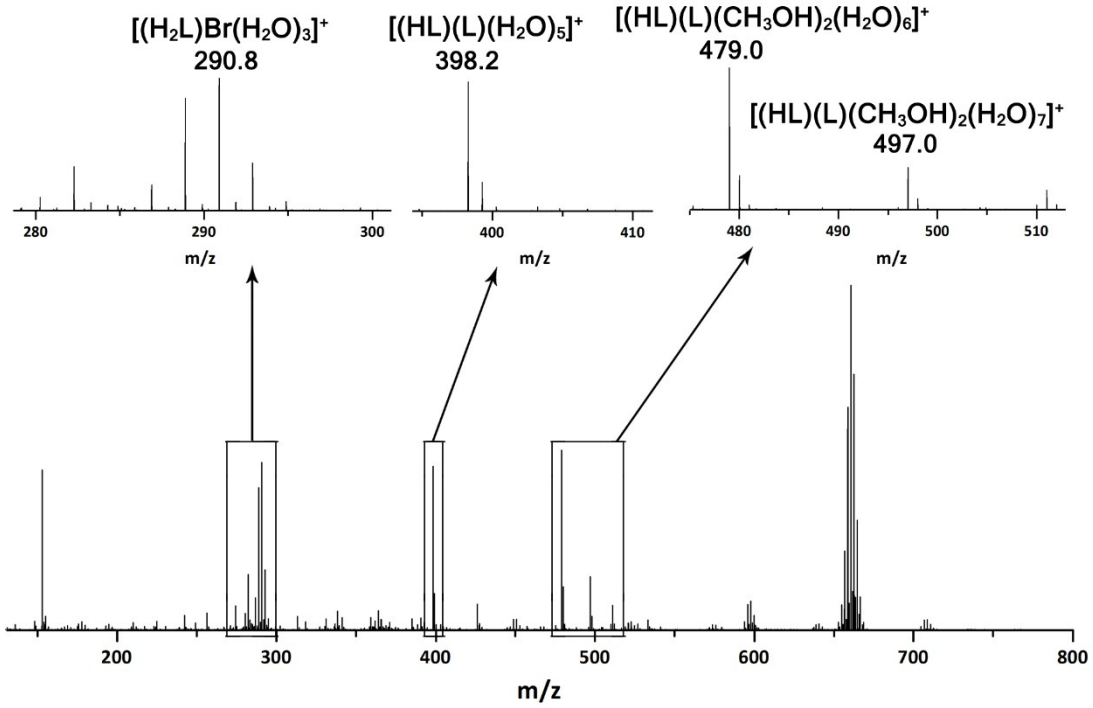

Fig S8. Positive-mode ESI-MS of the reaction solution 40 seconds of reaction. (L = $H_2NCH_2CH_2SSCH_2CH_2NH_2$).

Table S3 Fair evaluation of the MS spectra.

m/z	Fragments	Fitting data
153.1	$\{H[NH_2(CH_2)_2SS(CH_2)_2NH_2]\}^+$	153.05
600.8	$\{H_2[NH_2(CH_2)_2SS(CH_2)_2NH_2]PbBr_3\}^+$	600.79
660.7	$\{H_2[NH_2(CH_2)_2SS(CH_2)_2NH_2]PbBr_3(CH_3OH)_2\}^+$	664.82
708.7	$\{H_2[NH_2(CH_2)_2SS(CH_2)_2NH_2]PbBr_3(H_2O)_6\}^+$	708.84
449.8	$\{H_2[NH_2(CH_2)_2SS(CH_2)_2NH_2]MnBr_3\}^+$	447.73
450.8	$\{H_2[NH_2(CH_2)_2SS(CH_2)_2NH_2]NiBr_3\}^+$	450.73
508.8	$\{H_2[NH_2(CH_2)_2SS(CH_2)_2NH_2]CdBr_3\}^+$	504.70