# Supporting Information

# Crystal Structure and Luminescence Properties of Lead-Free Metal Halides: $(C_6H_5CH_2NH_3)_3MBr_6$ (M = Bi and Sb)

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**Table S1.** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1** at 100(2) K with estimated standard deviations in parentheses.

| Label | x | y | z | Occupancy | $U_{eq}$* |
|---|---|---|---|---|---|
| Bi(1) | 6391(1) | 4986(1) | 1470(1) | 1 | 65(1) |
| Br(1) | 7997(1) | 4257(2) | 1017(1) | 1 | 85(1) |
| Br(2) | 6737(1) | 2406(2) | 2242(1) | 1 | 86(1) |
| Br(3) | 5536(1) | 2786(2) | 656(1) | 1 | 88(1) |
| Br(4) | 6022(1) | 7709(2) | 695(1) | 1 | 81(1) |
| Br(5) | 7070(1) | 7436(2) | 2274(1) | 1 | 78(1) |
| Br(6) | 4705(1) | 5427(2) | 1774(1) | 1 | 91(1) |
| N(1) | 14978(8) | 9572(13) | 1784(5) | 1 | 118(4) |
| H(1A) | 15300 | 9764 | 1523 | 1 | 142 |
| H(1B) | 14865 | 8506 | 1796 | 1 | 142 |
| H (1C) | 15271 | 9895 | 2108 | 1 | 142 |
| C(1) | 14208(9) | 10415(16) | 1668(6) | 1 | 99(4) |
| H(1D) | 14344 | 11530 | 1577 | 1 | 119 |
| H(1E) | 13950 | 10459 | 2002 | 1 | 119 |
| C(2) | 13524(8) | 9771(11) | 1213(5) | 1 | 79(3) |
| C(3) | 12668(9) | 9521(15) | 1329(5) | 1 | 94(4) |
| C(4) | 12008(9) | 8975(14) | 911(5) | 1 | 104(4) |
| H(4) | 11443 | 8813 | 986 | 1 | 124 |
| C(5) | 12184(8) | 8672(12) | 390(5) | 1 | 90(3) |
| H(5) | 11740 | 8290 | 117 | 1 | 108 |
| C(6) | 13015(8) | 8932(11) | 269(4) | 1 | 80(3) |
| C(7) | 13693(8) | 9534(12) | 674(5) | 1 | 80(3) |
| N(2) | 13487(8) | 14974(11) | 383(5) | 1 | 100(3) |
| H(2A) | 13423 | 15865 | 581 | 1 | 120 |
| H(2B) | 13304 | 15185 | 28 | 1 | 120 |
| H (2C) | 14051 | 14685 | 435 | 1 | 120 |
| C(8) | 12961(9) | 13630(15) | 560(6) | 1 | 107(4) |
| H(8A) | 13332 | 13008 | 844 | 1 | 128 |
| H(8B) | 12789 | 12905 | 248 | 1 | 128 |
| C(9) | 12144(8) | 14135(13) | 778(5) | 1 | 85(3) |
| C(10) | 11348(9) | 14010(20) | 467(6) | 1 | 117(5) |
| H(10) | 11297 | 13644 | 105 | 1 | 141 |
| C(11) | 10607(10) | 14411(16) | 679(6) | 1 | 117(5) |

| | | | | | |
|---|---|---|---|---|---|
| C(12) | 10669(11) | 14960(13) | 1212(7) | 1 | 123(5) |
| H(12) | 10165 | 15236 | 1353 | 1 | 147 |
| C(13) | 11491(9) | 15098(14) | 1537(7) | 1 | 115(6) |
| H(13) | 11553 | 15463 | 1899 | 1 | 138 |
| C(14) | 12222(8) | 14672(15) | 1302(6) | 1 | 96(4) |
| H(14) | 12779 | 14760 | 1513 | 1 | 115 |
| N(3) | 7677(6) | 10103(10) | 1330(4) | 1 | 85(3) |
| H(3A) | 7173 | 9961 | 1100 | 1 | 102 |
| H(3B) | 7811 | 11163 | 1351 | 1 | 102 |
| H (3C) | 7619 | 9736 | 1663 | 1 | 102 |
| C(15) | 8365(7) | 9215(15) | 1133(4) | 1 | 86(3) |
| H(15A) | 8420 | 9615 | 769 | 1 | 103 |
| H(15B) | 8204 | 8068 | 1098 | 1 | 103 |
| C(16) | 9258(7) | 9372(13) | 1510(4) | 1 | 81(3) |
| C(17) | 9862(8) | 10650(15) | 1433(5) | 1 | 97(4) |
| H(17) | 9719 | 11395 | 1147 | 1 | 116 |
| C(18) | 10644(8) | 10772(17) | 1779(7) | 1 | 110(4) |
| H(18) | 11046 | 11579 | 1725 | 1 | 132 |
| C(19) | 10838(10) | 9670(16) | 2217(6) | 1 | 105(4) |
| H(19) | 11367 | 9759 | 2459 | 1 | 126 |
| C(20) | 10273(9) | 8501(18) | 2290(6) | 1 | 111(4) |
| H(20) | 10413 | 7785 | 2585 | 1 | 134 |
| C(21) | 9478(8) | 8316(15) | 1939(5) | 1 | 101(4) |
| H(21) | 9098 | 7474 | 1995 | 1 | 122 |

*$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

**Table S2.** Anisotropic displacement parameters ($Å^2 \times 10^3$) for **1** at 100(2) K with estimated standard deviations in parentheses.

| Label | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Bi(1) | 65(1) | 63(1) | 68(1) | -1(1) | 14(1) | -3(1) |
| Br(1) | 71(1) | 80(1) | 109(1) | 2(1) | 29(1) | 2(1) |
| Br(2) | 110(1) | 72(1) | 78(1) | -1(1) | 17(1) | 8(1) |
| Br(3) | 84(1) | 96(1) | 85(1) | -16(1) | 18(1) | -28(1) |
| Br(4) | 89(1) | 75(1) | 75(1) | 8(1) | 4(1) | 5(1) |
| Br(5) | 87(1) | 73(1) | 72(1) | -7(1) | 6(1) | -6(1) |
| Br(6) | 70(1) | 108(1) | 99(1) | -2(1) | 27(1) | -18(1) |
| N(1) | 103(8) | 95(6) | 144(9) | 18(6) | -18(7) | -46(6) |
| C(1) | 90(8) | 91(8) | 118(9) | 3(7) | 22(7) | -13(7) |
| C(2) | 83(7) | 63(6) | 91(7) | 13(5) | 11(6) | 6(5) |
| C(3) | 109(9) | 97(7) | 82(7) | -14(7) | 36(6) | -1(6) |
| C(4) | 82(7) | 132(11) | 97(8) | -12(8) | 16(6) | -1(8) |
| C(5) | 88(8) | 88(7) | 88(7) | -5(6) | -2(6) | 2(6) |
| C(6) | 86(7) | 71(6) | 83(6) | 15(5) | 16(5) | -4(5) |
| C(7) | 105(8) | 55(5) | 82(7) | -1(5) | 20(6) | 10(5) |
| N(2) | 109(7) | 89(7) | 110(7) | 20(5) | 43(6) | 20(5) |
| C(8) | 125(8) | 77(7) | 127(9) | 4(7) | 45(7) | 8(7) |
| C(9) | 98(7) | 71(6) | 87(7) | 1(6) | 22(6) | 10(6) |
| C(10) | 89(9) | 160(13) | 100(9) | -2(9) | 6(7) | 8(9) |
| C(11) | 102(10) | 141(11) | 100(9) | -4(9) | -9(8) | 30(9) |
| C(12) | 113(10) | 122(12) | 142(12) | 26(8) | 47(9) | 30(8) |
| C(13) | 86(9) | 128(13) | 130(12) | -14(8) | 15(9) | -15(8) |
| C(14) | 65(7) | 118(9) | 103(9) | -12(6) | 4(6) | 7(7) |
| N(3) | 68(5) | 85(6) | 99(6) | -7(4) | 7(5) | 1(5) |
| C(15) | 88(7) | 86(7) | 84(7) | -3(6) | 15(6) | -8(6) |
| C(16) | 70(6) | 72(6) | 103(7) | 1(5) | 18(6) | -13(6) |
| C(17) | 84(7) | 82(7) | 129(9) | 1(6) | 31(7) | 3(7) |
| C(18) | 74(7) | 88(8) | 168(12) | 2(7) | 23(8) | -12(9) |
| C(19) | 89(8) | 93(8) | 126(11) | 14(7) | 0(8) | -15(7) |
| C(20) | 95(9) | 114(10) | 123(10) | 2(8) | 11(8) | 38(8) |
| C(21) | 92(8) | 102(8) | 111(8) | -8(7) | 20(7) | 24(7) |

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

**Table S3.** Bond lengths [Å] for **1** at 100(2) K with estimated standard deviations in parentheses.

| Label | Distances |
|---|---|
| Bi(1)-Br(2) | 2.8284(11) |
| Bi(1)-Br(6) | 2.8465(12) |
| Bi(1)-Br(3) | 2.8480(11) |
| Bi(1)-Br(5) | 2.8866(10) |
| Bi(1)-Br(4) | 2.9246(11) |
| Bi(1)-Br(1) | 2.9408(11) |
| N(1)-C(1) | 1.362(16) |
| C(1)-C(2) | 1.502(17) |
| C(2)-C(7) | 1.407(16) |
| C(2)-C(3) | 1.411(17) |
| C(3)-C(4) | 1.395(17) |
| C(4)-C(5) | 1.377(16) |
| C(5)-C(6) | 1.379(16) |
| C(6)-C(7) | 1.408(15) |
| N(2)-C(8) | 1.473(16) |
| C(8)-C(9) | 1.508(17) |
| C(9)-C(10) | 1.339(17) |
| C(9)-C(14) | 1.348(17) |
| C(10)-C(11) | 1.37(2) |
| C(11)-C(12) | 1.38(2) |
| C(12)-C(13) | 1.39(2) |
| C(13)-C(14) | 1.392(19) |
| N(3)-C(15) | 1.436(14) |
| C(15)-C(16) | 1.534(15) |
| C(16)-C(21) | 1.361(16) |

| | |
|---|---|
| C(16)-C(17) | 1.433(16) |
| C(17)-C(18) | 1.360(18) |
| C(18)-C(19) | 1.40(2) |
| C(19)-C(20) | 1.326(19) |
| C(20)-C(21) | 1.386(17) |

**Table S4.** Bond angles [°] for **1** at 100(2) K with estimated standard deviations in parentheses.

| Label | Distances |
|---|---|
| Br(2)-Bi(1)-Br(6) | 89.78(4) |
| Br(2)-Bi(1)-Br(3) | 90.87(4) |
| Br(6)-Bi(1)-Br(3) | 85.88(4) |
| Br(2)-Bi(1)-Br(5) | 92.91(3) |
| Br(6)-Bi(1)-Br(5) | 88.57(3) |
| Br(3)-Bi(1)-Br(5) | 173.28(4) |
| Br(2)-Bi(1)-Br(4) | 178.50(3) |
| Br(6)-Bi(1)-Br(4) | 89.28(4) |
| Br(3)-Bi(1)-Br(4) | 90.24(3) |
| Br(5)-Bi(1)-Br(4) | 85.90(3) |
| Br(2)-Bi(1)-Br(1) | 91.55(4) |
| Br(6)-Bi(1)-Br(1) | 171.55(4) |
| Br(3)-Bi(1)-Br(1) | 85.75(3) |
| Br(5)-Bi(1)-Br(1) | 99.69(3) |
| Br(4)-Bi(1)-Br(1) | 89.54(3) |
| N(1)-C(1)-C(2) | 117.3(11) |
| C(7)-C(2)-C(3) | 119.8(11) |
| C(7)-C(2)-C(1) | 122.3(11) |
| C(3)-C(2)-C(1) | 117.6(11) |
| C(4)-C(3)-C(2) | 119.3(11) |
| C(5)-C(4)-C(3) | 120.8(12) |
| C(4)-C(5)-C(6) | 120.5(11) |
| C(5)-C(6)-C(7) | 120.6(10) |
| C(2)-C(7)-C(6) | 118.9(11) |
| N(2)-C(8)-C(9) | 115.7(10) |

| | |
|---|---|
| C(10)-C(9)-C(14) | 120.0(13) |
| C(10)-C(9)-C(8) | 121.0(12) |
| C(14)-C(9)-C(8) | 118.9(11) |
| C(9)-C(10)-C(11) | 120.4(13) |
| C(10)-C(11)-C(12) | 120.7(14) |
| C(11)-C(12)-C(13) | 119.2(15) |
| C(12)-C(13)-C(14) | 117.8(15) |
| C(9)-C(14)-C(13) | 121.9(12) |
| N(3)-C(15)-C(16) | 113.1(9) |
| C(21)-C(16)-C(17) | 118.7(10) |
| C(21)-C(16)-C(15) | 120.0(10) |
| C(17)-C(16)-C(15) | 121.2(10) |
| C(18)-C(17)-C(16) | 119.9(12) |
| C(17)-C(18)-C(19) | 119.3(13) |
| C(20)-C(19)-C(18) | 120.5(13) |
| C(19)-C(20)-C(21) | 121.9(13) |
| C(16)-C(21)-C(20) | 119.7(12) |

**Table S5.** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2** at 100(2) K with estimated standard deviations in parentheses.

| Label | x | y | z | Occupancy | $U_{eq}^*$ |
|---|---|---|---|---|---|
| Sb(1) | 6369(1) | 5031(1) | 6476(1) | 1 | 27(1) |
| Br(1) | 7050(1) | 2584(1) | 7273(1) | 1 | 38(1) |
| Br(2) | 5985(1) | 2336(1) | 5694(1) | 1 | 40(1) |
| Br(3) | 5536(1) | 7220(1) | 5682(1) | 1 | 44(1) |
| Br(4) | 7985(1) | 5769(1) | 6018(1) | 1 | 42(1) |
| Br(5) | 6711(1) | 7550(1) | 7240(1) | 1 | 45(1) |
| Br(6) | 4734(1) | 4603(1) | 6774(1) | 1 | 48(1) |
| N(1) | 3442(2) | 5031(4) | 5328(2) | 1 | 53(1) |
| H(1A) | 3089.8 | 4569.4 | 5037.87 | 1 | 64 |
| H(1B) | 3593.17 | 4274.93 | 5594.27 | 1 | 64 |
| H (1C) | 3931.79 | 5420.45 | 5219.39 | 1 | 64 |
| C(1) | 2964(3) | 6405(5) | 5547(2) | 1 | 59(2) |
| H(1D) | 2781.02 | 7197.29 | 5248.92 | 1 | 71 |
| H(1E) | 3373.19 | 6967.43 | 5838.47 | 1 | 71 |
| C(2) | 2150(2) | 5872(4) | 5782(2) | 1 | 42(1) |
| C(3) | 1338(3) | 6053(6) | 5456(2) | 1 | 65(2) |
| H(3) | 1278.3 | 6457.88 | 5093.11 | 1 | 78 |
| C(4) | 540(3) | 5570(6) | 5706(2) | 1 | 75(2) |
| H(4) | -34.47 | 5656.37 | 5501.38 | 1 | 90 |
| C(5) | 681(3) | 5017(6) | 6227(2) | 1 | 69(2) |
| H(5) | 194.29 | 4712.11 | 6388.11 | 1 | 83 |
| C(6) | 1498(3) | 4883(6) | 6528(2) | 1 | 66(2) |
| H(6) | 1568.67 | 4490.33 | 6893.02 | 1 | 80 |
| C(7) | 2220(3) | 5308(5) | 6312(2) | 1 | 54(1) |
| H(7) | 2782.3 | 5211.47 | 6531.82 | 1 | 65 |
| N(2) | 5021(2) | 433(5) | 6755(2) | 1 | 73(2) |
| H(2A) | 5240.04 | 479.44 | 6439.1 | 1 | 88 |
| H(2B) | 5407.18 | -83.93 | 7015.88 | 1 | 88 |
| H (2C) | 4927.98 | 1456.78 | 6869.24 | 1 | 88 |
| C(8) | 4197(3) | -455(5) | 6661(2) | 1 | 53(1) |
| H(8A) | 3957.5 | -466.25 | 7005.2 | 1 | 64 |
| H(8B) | 4317.01 | -1595.18 | 6569.92 | 1 | 64 |
| C(9) | 3500(2) | 232(4) | 6204(2) | 1 | 35(1) |

| | | | | | |
|---|---|---|---|---|---|
| C(10) | 3659(2) | 520(4) | 5667(2) | 1 | 38(1) |
| H(10) | 4225.47 | 346.85 | 5584.71 | 1 | 46 |
| C(11) | 2977(2) | 1064(4) | 5253(2) | 1 | 42(1) |
| H(11) | 3088.1 | 1246.86 | 4893.8 | 1 | 50 |
| C(12) | 2140(3) | 1335(5) | 5370(2) | 1 | 48(1) |
| H(12) | 1684.18 | 1706.72 | 5091.77 | 1 | 58 |
| C(13) | 1979(3) | 1051(5) | 5903(2) | 1 | 56(1) |
| H(13) | 1412.21 | 1231.48 | 5985.05 | 1 | 67 |
| C(14) | 2656(2) | 499(5) | 6318(2) | 1 | 47(1) |
| H(14) | 2540.38 | 305.76 | 6675.36 | 1 | 57 |
| N(3) | 7649(2) | -116(3) | 6330(2) | 1 | 43(1) |
| H(3A) | 7127.45 | 85.43 | 6110.67 | 1 | 51 |
| H(3B) | 7620.29 | 186.95 | 6678.14 | 1 | 51 |
| H (3C) | 7770.68 | -1194.29 | 6321.68 | 1 | 51 |
| C(15) | 8363(2) | 844(5) | 6126(2) | 1 | 45(1) |
| H(15A) | 8199.77 | 2007.58 | 6099.99 | 1 | 54 |
| H(15B) | 8416.93 | 463.66 | 5754.25 | 1 | 54 |
| C(16) | 9243(2) | 654(4) | 6505(2) | 1 | 39(1) |
| C(17) | 9470(3) | 1715(5) | 6950(2) | 1 | 56(2) |
| H(17) | 9077.85 | 2550.83 | 7012.9 | 1 | 68 |
| C(18) | 10282(3) | 1540(6) | 7307(2) | 1 | 65(2) |
| H(18) | 10427.87 | 2253.3 | 7610.05 | 1 | 78 |
| C(19) | 10864(3) | 338(5) | 7217(2) | 1 | 56(2) |
| H(19) | 11410.86 | 240.24 | 7454.25 | 1 | 67 |
| C(20) | 10645(3) | -726(5) | 6779(2) | 1 | 60(2) |
| H(20) | 11040.71 | -1560.7 | 6720.98 | 1 | 72 |
| C(21) | 9840(3) | -571(5) | 6422(2) | 1 | 50(1) |
| H(21) | 9698.74 | -1296.89 | 6122.7 | 1 | 60 |

*$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

**Table S6.** Anisotropic displacement parameters ($Å^2 \times 10^3$) for **2** at 100(2) K with estimated standard deviations in parentheses.

| Label | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Sb(1) | 25(1) | 27(1) | 29(1) | 1(1) | 7(1) | 3(1) |
| Br(1) | 42(1) | 37(1) | 33(1) | 6(1) | 1(1) | 3(1) |
| Br(2) | 46(1) | 39(1) | 34(1) | -6(1) | -1(1) | -2(1) |
| Br(3) | 37(1) | 54(1) | 42(1) | 11(1) | 10(1) | 21(1) |
| Br(4) | 30(1) | 39(1) | 59(1) | -1(1) | 13(1) | -2(1) |
| Br(5) | 62(1) | 35(1) | 39(1) | 0(1) | 8(1) | -7(1) |
| Br(6) | 31(1) | 63(1) | 54(1) | 3(1) | 17(1) | 16(1) |
| N(1) | 52(2) | 48(2) | 65(2) | -7(2) | 25(2) | -7(2) |
| C(1) | 68(3) | 36(2) | 78(3) | -6(2) | 29(2) | -6(2) |
| C(2) | 42(2) | 34(2) | 50(2) | 0(2) | 8(2) | -8(2) |
| C(3) | 65(3) | 79(3) | 49(2) | 10(3) | 4(2) | -9(2) |
| C(4) | 39(2) | 100(4) | 78(3) | 7(2) | -9(2) | -35(3) |
| C(5) | 53(3) | 82(3) | 77(3) | -4(2) | 23(2) | -23(3) |
| C(6) | 56(3) | 84(3) | 62(3) | 10(3) | 20(2) | 5(3) |
| C(7) | 40(2) | 67(3) | 55(3) | 4(2) | 5(2) | -4(2) |
| N(2) | 52(2) | 73(3) | 84(3) | -19(2) | -17(2) | 37(2) |
| C(8) | 47(2) | 55(2) | 53(2) | -14(2) | -2(2) | 11(2) |
| C(9) | 40(2) | 32(2) | 33(2) | -5(2) | 6(2) | -4(2) |
| C(10) | 37(2) | 36(2) | 44(2) | -4(2) | 14(2) | -1(2) |
| C(11) | 55(2) | 40(2) | 32(2) | -11(2) | 10(2) | -3(2) |
| C(12) | 46(2) | 46(2) | 48(2) | 0(2) | -4(2) | 0(2) |
| C(13) | 42(2) | 74(3) | 54(2) | 7(2) | 15(2) | -4(2) |
| C(14) | 48(2) | 63(2) | 34(2) | 0(2) | 15(2) | -2(2) |
| N(3) | 38(2) | 40(2) | 49(2) | 3(2) | 5(2) | -3(2) |
| C(15) | 43(2) | 43(2) | 48(2) | -2(2) | 7(2) | 6(2) |
| C(16) | 36(2) | 34(2) | 48(2) | -2(2) | 10(2) | 4(2) |
| C(17) | 43(2) | 59(3) | 68(3) | 8(2) | 8(2) | -18(2) |
| C(18) | 45(2) | 81(3) | 67(3) | -4(2) | 4(2) | -24(2) |
| C(19) | 33(2) | 64(3) | 69(3) | -1(2) | 5(2) | 13(2) |
| C(20) | 39(2) | 48(2) | 95(3) | 9(2) | 18(2) | 4(2) |
| C(21) | 45(2) | 43(2) | 65(3) | -3(2) | 15(2) | -10(2) |

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

**Table S7.** Bond lengths [Å] for **2** at 100(2) K with estimated standard deviations in parentheses.

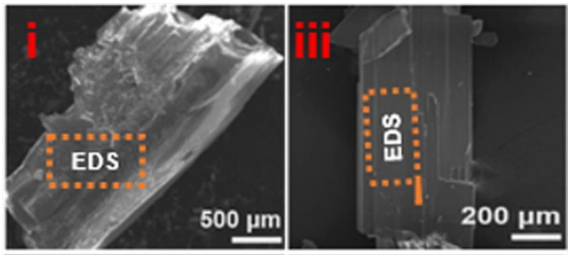
| Label | Distances |
|---|---|
| Sb(1)-Br(1) | 2.8324(4) |
| Sb(1)-Br(2) | 2.8784(4) |
| Sb(1)-Br(3) | 2.7563(4) |
| Sb(1)-Br(4) | 2.9319(4) |
| Sb(1)-Br(5) | 2.7401(4) |
| Sb(1)-Br(6) | 2.7323(4) |
| N(1)-C(1) | 1.475(5) |
| C(1)-C(2) | 1.516(5) |
| C(2)-C(3) | 1.355(5) |
| C(2)-C(7) | 1.352(5) |
| C(3)-C(4) | 1.501(6) |
| C(4)-C(5) | 1.325(7) |
| C(5)-C(6) | 1.334(6) |
| C(6)-C(7) | 1.343(5) |
| N(2)-C(8) | 1.427(5) |
| C(8)-C(9) | 1.503(5) |
| C(9)-C(10) | 1.386(5) |
| C(9)-C(14) | 1.378(5) |
| C(10)-C(11) | 1.385(5) |
| C(11)-C(12) | 1.370(5) |
| C(12)-C(13) | 1.380(5) |
| C(13)-C(14) | 1.383(5) |
| N(3)-C(15) | 1.488(4) |
| C(15)-C(16) | 1.496(5) |
| C(16)-C(17) | 1.375(5) |

| | |
|---|---|
| C(16)-C(21) | 1.382(5) |
| C(17)-C(18) | 1.388(6) |
| C(18)-C(19) | 1.356(5) |
| C(19)-C(20) | 1.363(6) |
| C(20)-C(21) | 1.379(5) |

**Table S8.** Bond angles [°] for **2** at 100(2) K with estimated standard deviations in parentheses.

| Label | Distances |
|---|---|
| Br(1)-Sb(1)-Br(2) | 86.201(11) |
| Br(1)-Sb(1)-Br(4) | 99.774(12) |
| Br(2)-Sb(1)-Br(4) | 89.442(11) |
| Br(3)-Sb(1)-Br(1) | 173.767(13) |
| Br(3)-Sb(1)-Br(2) | 90.299(12) |
| Br(3)-Sb(1)-Br(4) | 85.332(12) |
| Br(5)-Sb(1)-Br(1) | 92.801(12) |
| Br(5)-Sb(1)-Br(2) | 178.407(13) |
| Br(5)-Sb(1)-Br(3) | 90.581(13) |
| Br(5)-Sb(1)-Br(4) | 91.953(12) |
| Br(6)-Sb(1)-Br(1) | 88.425(12) |
| Br(6)-Sb(1)-Br(2) | 89.393(13) |
| Br(6)-Sb(1)-Br(3) | 86.380(12) |
| Br(6)-Sb(1)-Br(4) | 171.623(13) |
| Br(6)-Sb(1)-Br(5) | 89.338(13) |
| N(1)-C(1)-C(2) | 114.2(3) |
| C(3)-C(2)-C(1) | 118.1(4) |
| C(7)-C(2)-C(1) | 121.3(4) |
| C(7)-C(2)-C(3) | 120.5(4) |
| C(2)-C(3)-C(4) | 117.1(4) |
| C(5)-C(4)-C(3) | 117.7(4) |
| C(4)-C(5)-C(6) | 122.3(4) |
| C(5)-C(6)-C(7) | 120.9(4) |
| C(6)-C(7)-C(2) | 121.6(4) |
| N(2)-C(8)-C(9) | 114.9(3) |

| | |
|---|---|
| C(10)-C(9)-C(8) | 122.8(3) |
| C(14)-C(9)-C(8) | 118.2(3) |
| C(14)-C(9)-C(10) | 118.9(3) |
| C(9)-C(10)-C(11) | 120.4(3) |
| C(12)-C(11)-C(10) | 120.4(3) |
| C(11)-C(12)-C(13) | 119.4(4) |
| C(12)-C(13)-C(14) | 120.4(4) |
| C(9)-C(14)-C(13) | 120.5(3) |
| N(3)-C(15)-C(16) | 111.7(3) |
| C(17)-C(16)-C(15) | 119.8(3) |
| C(17)-C(16)-C(21) | 118.5(3) |
| C(21)-C(16)-C(15) | 121.7(3) |
| C(16)-C(17)-C(18) | 120.2(4) |
| C(19)-C(18)-C(17) | 120.5(4) |
| C(18)-C(19)-C(20) | 119.9(4) |
| C(19)-C(20)-C(21) | 120.3(4) |
| C(20)-C(21)-C(16) | 120.6(4) |




| ii | Bi | Br |
|---|---|---|
| Atom % | 2.7 | 15.2 |
| Ration | 1 | 5.6 |

| iv | Sb | Br |
|---|---|---|
| Atom % | 15.2 | 84.7 |
| Ration | 1 | 5.6 |

**Figure S1.** The SEM picture (i), (iii) and EDS results (ii)and (iv).

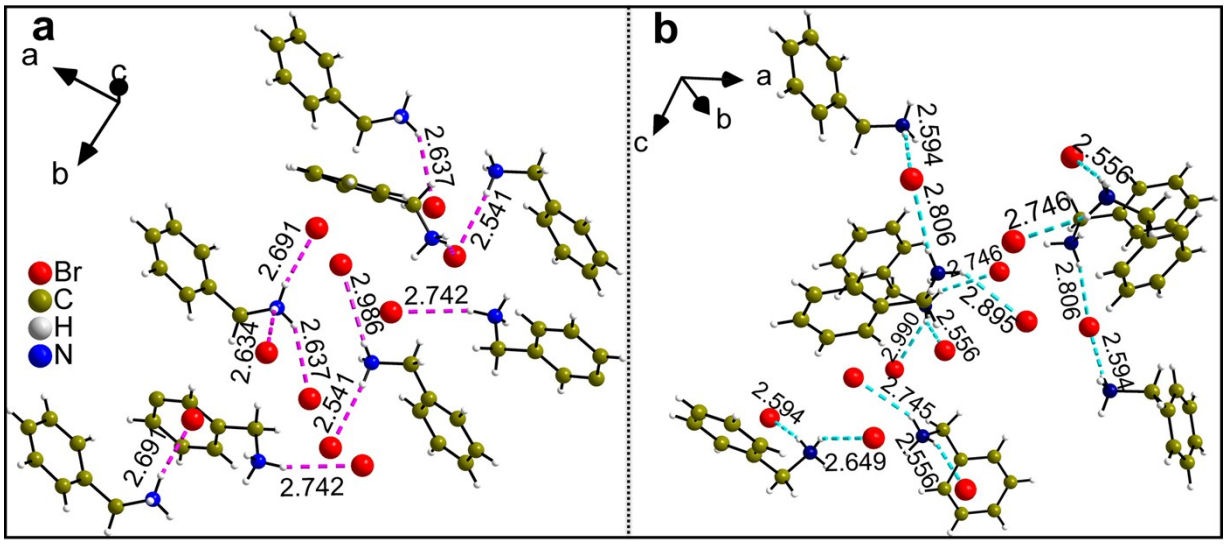



**Figure S2.** N–H···Br hydrogen bonding (dotted lines) of **1** (a) and **2** (b)

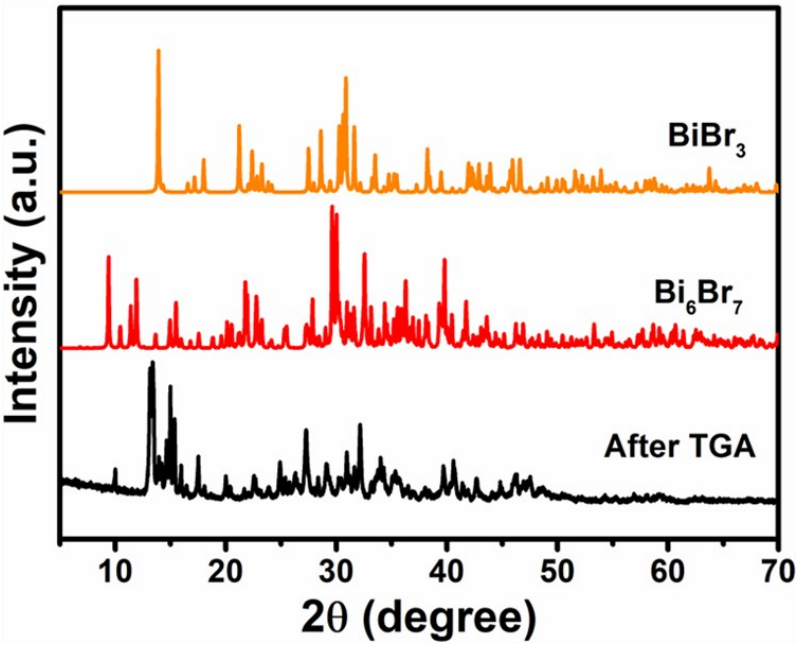



**Figure S3.** XRD analysis of **1** after the first step decomposition.

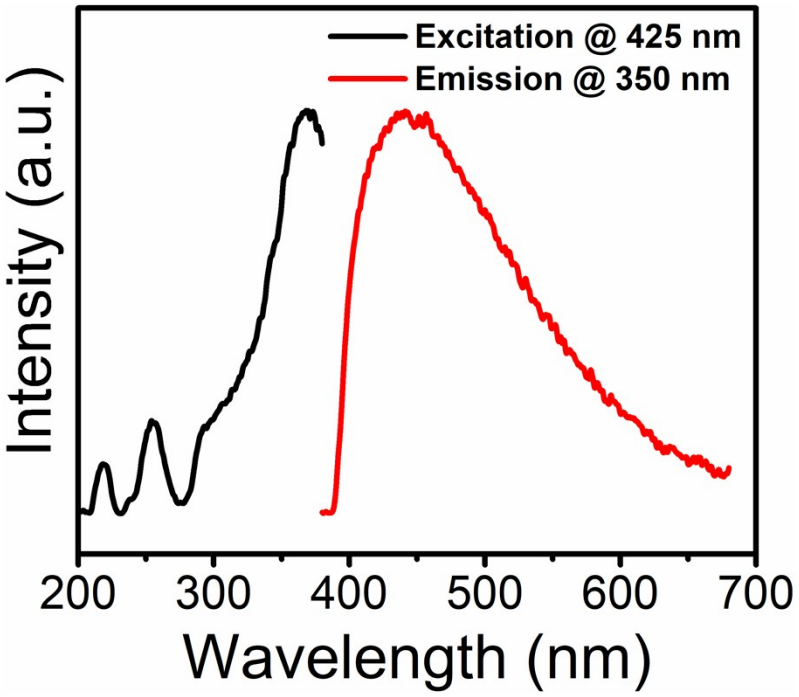



**Figure S4.** PLE and PL spectra of PMABr at room temperature.

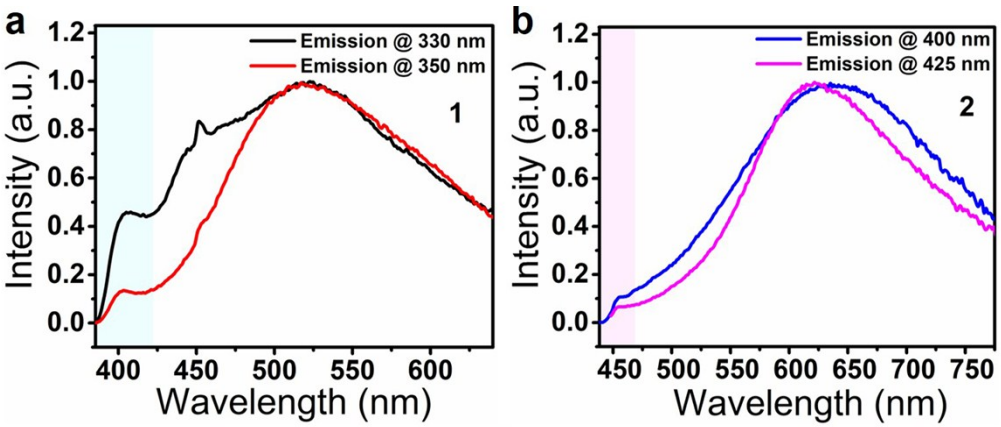



**Figure S5.** PL spectra excited by different excitation wavelengths for compounds **1** (a) and **2** (b).

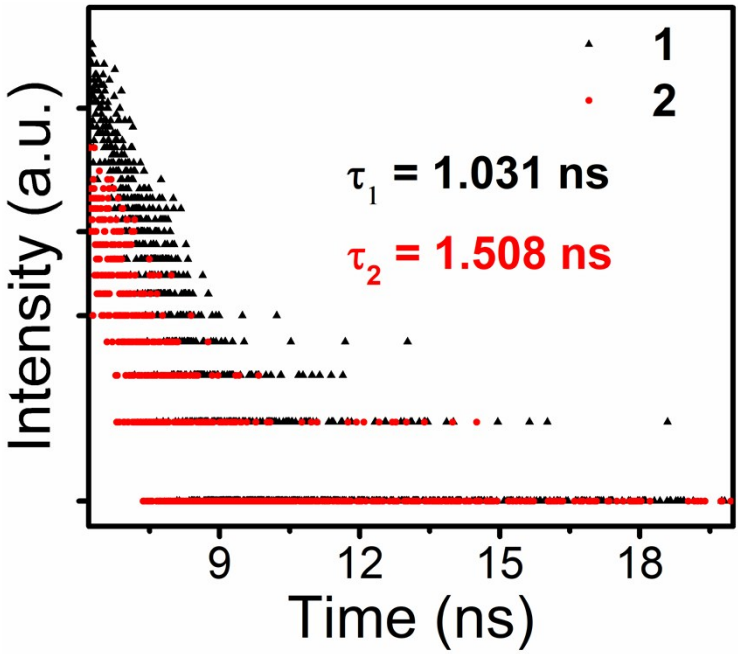



**Figure S6.** PL decay curves of compound **1** and **2** polycrystalline powder at room temperature.

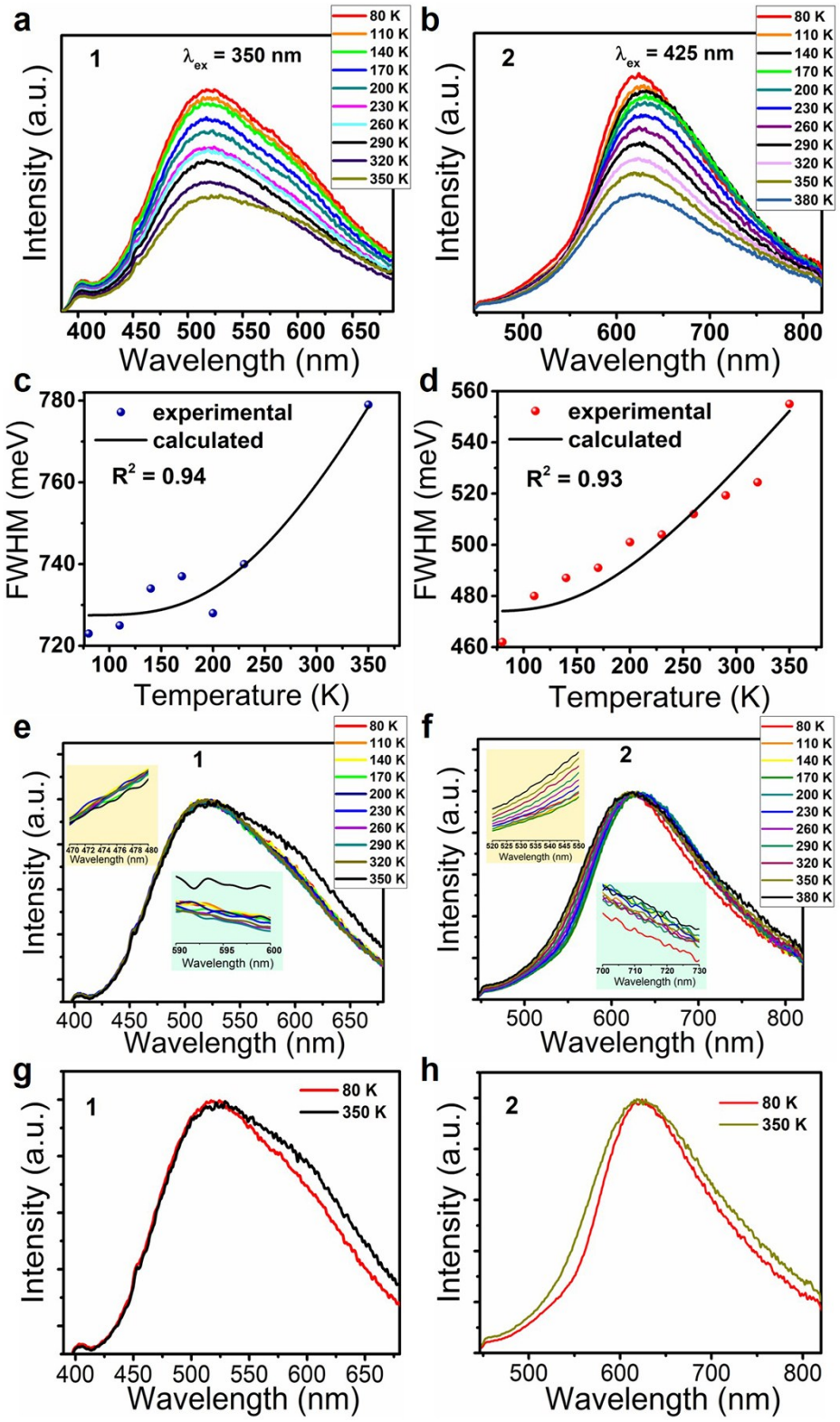



**Figure S7.** (a-b) temperature-dependent steady-state PL spectra of **1** and **2**. (c-d) Fitting of the FWHM for compound **1** and **2** as a function of temperature. (e-f) Temperature-dependent normalized steady-state PL spectra of **1** and **2**. (g-h) PL spectra of **1** and **2** at 350 K and 80 K.

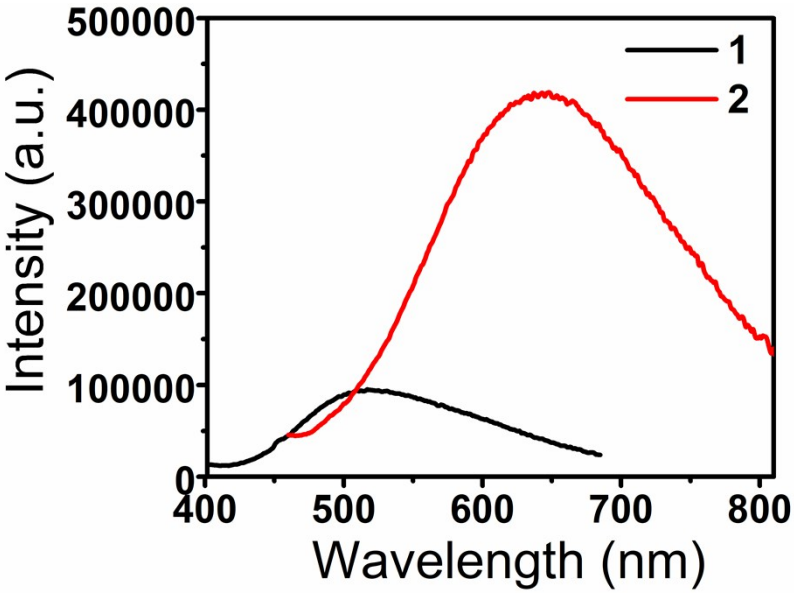



**Figure S8.** Comparison of PL spectra intensity of **1** and **2** under the same test conditions.