Electronic Supplementary Material (ESI) for CrystEngComm.


# Visualizing the Alignment of Lone Pair Electrons in $La_3AsS_5Br_2$ and $La_5As_2S_9Cl_3$ to Form an Acentric or Centrosymmetric Structure

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**Table S1**. Refined atomic coordinates and isotropic displacement parameters for $La_3AsS_5Br_2$ and $La_5As_2S_9Cl_3$

| Atoms | Wyckoff | *x* | *y* | *z* | Occupancy | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|---|---|
| | | | $La_3AsS_5Br_2$ | | | |
| La1 | *4a* | 0.1227(5) | 0.1977(12) | 0.3695(16) | 1 | 0.019(8) |
| La2 | *4a* | -0.0278(5) | 0.1974(13) | -0.1259(18) | 1 | 0.018(8) |
| La3 | *4a* | 0.2744(6) | 0.2081(15) | 0.013(2) | 1 | 0.019(8) |
| As1 | *4a* | 0.3189(10) | 0.309(2) | -0.425(4) | 1 | 0.023(10) |
| Br1 | *4a* | 0.1161(9) | 0.379(3) | -0.020(3) | 1 | 0.019(10) |
| Br2 | *4a* | -0.0165(7) | 0.387(3) | 0.257(3) | 1 | 0.034(10) |
| S1 | *4a* | -0.148(2) | 0.408(7) | -0.115(8) | 1 | 0.020(18) |
| S2 | *4a* | 0.201(2) | 0.055(6) | 0.693(9) | 1 | 0.002(16) |
| S3 | *4a* | -0.116(2) | -0.046(6) | 0.049(8) | 1 | 0.01(2) |
| S4 | *4a* | 0.2431(18) | 0.422(5) | 0.354(7) | 1 | 0.00(2) |
| S5 | *4a* | 0.047(3) | 0.052(5) | 0.615(8) | 1 | 0.024(18) |
| | | | $La_5As_2S_9Cl_3$ | | | |
| La1 | *4d* | 0.79282(15) | 0.19329(15) | 0.75 | 1 | 0.0030(4) |
| La2 | *8e* | 1.20520(11) | 0.27459(11) | 0.83927(2) | 1 | 0.0044(4) |
| La3 | *8e* | 0.71453(11) | 0.04165(10) | 0.95753(2) | 1 | 0.0036(4) |
| As1 | *8e* | 0.6919(2) | 0.3080(2) | 0.86781(4) | 1 | 0.0064(5) |
| S1 | *8e* | 0.9173(5) | 0.1059(4) | 0.88787(8) | 1 | 0.0059(8) |
| S2 | *8e* | 1.4525(5) | 0.2479(4) | 0.90716(8) | 1 | 0.0052(8) |
| S3 | *8e* | 0.5801(4) | 0.1247(5) | 0.67708(8) | 1 | 0.0060(8) |
| S4 | *8e* | 0.6137(7) | -0.1684(7) | 0.75 | 1 | 0.0114(12) |
| S5 | *4d* | 1.1120(5) | -0.0903(5) | 0.96471(8) | 1 | 0.0087(8) |
| Cl1 | *4c* | 0.5538(7) | -0.25 | 1 | 1 | 0.0067(11) |
| Cl2 | *8e* | 1.0579(5) | -0.0207(4) | 0.70333(8) | 1 | 0.0078(8) |

**Table S2**. Selected interatomic distances for $La_3AsS_5Br_2$ and $La_5As_2S_9Cl_3$

| Atom Pairs | | Distances (Å) | Atom Pairs | | Distances (Å) |
|---|---|---|---|---|---|
| | | | $La_3AsS_5Br_2$ | | |
| La1 | S5 | 2.81(7) | La3 | S2 | 2.83(6) |
| | S2 | 2.88(7) | | S2 | 2.92(5) |
| | S5 | 2.91(6) | | S4 | 2.92(4) |
| | S2 | 2.92(5) | | S1 | 2.98(6) |
| | S4 | 3.14(4) | | S3 | 2.98(5) |
| | Br1 | 3.06(2) | | S4 | 3.05(5) |
| | Br1 | 3.13(2) | | S1 | 3.08(5) |
| | Br2 | 3.37(2) | As1 | S3 | 2.25(5) |
| La2 | S5 | 2.84(5) | | S1 | 2.26(5) |
| | S5 | 2.86(7) | | S4 | 2.28(5) |
| | S3 | 3.02(6) | | | |
| | S3 | 3.04(4) | | | |
| | S1 | 3.08(5) | | | |
| | Br2 | 3.04(3) | | | |
| | Br2 | 3.10(2) | | | |
| | Br1 | 3.44(3) | | | |
| | | | $La_5As_2S_9Cl_3$ | | |
| La1 | S4 | 2.867(5) | La3 | Cl1 | 2.841(2) |
| | S4 | 3.029(5) | | Cl1 | 2.874(3) |
| | S3 | 3.132(3) | | S5 | 2.902(4) |
| | S3 | 3.132(3) | | S5 | 2.966(4) |
| | Cl2 | 2.872(3) | | S1 | 2.989(3) |
| | Cl2 | 2.872(3) | | S2 | 3.010(3) |
| | Cl2 | 2.968(3) | | S2 | 3.041(3) |
| | Cl2 | 2.968(3) | | S5 | 3.153(3) |
| La2 | Cl2 | 2.827(3) | As1 | S3 | 2.258(3) |
| | Cl2 | 2.839(3) | | S1 | 2.269(3) |

| | | | |
|---|---|---|---|
| S3 | 2.913(3) | S2 | 2.272(4) |
| S1 | 2.968(3) | | |
| S3 | 2.977(3) | | |
| S2 | 3.069(3) | | |
| S1 | 3.091(3) | | |
| As1 | 3.5592(16) | | |

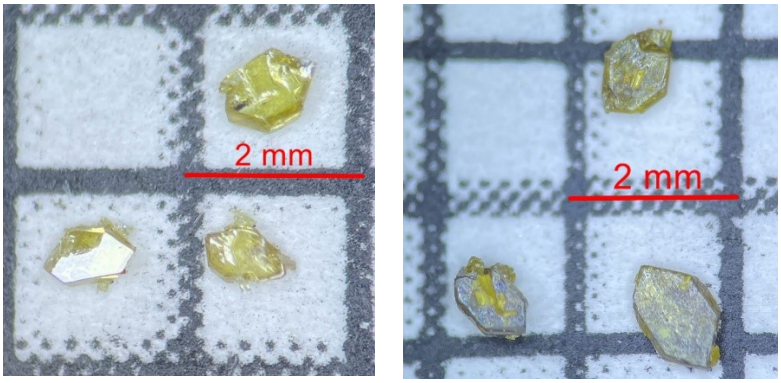


**Figure S1.** Optical microscope images of selected crystals of $La_3AsS_5Br_2$ (left) and $La_5As_2S_9Cl_3$ (right).

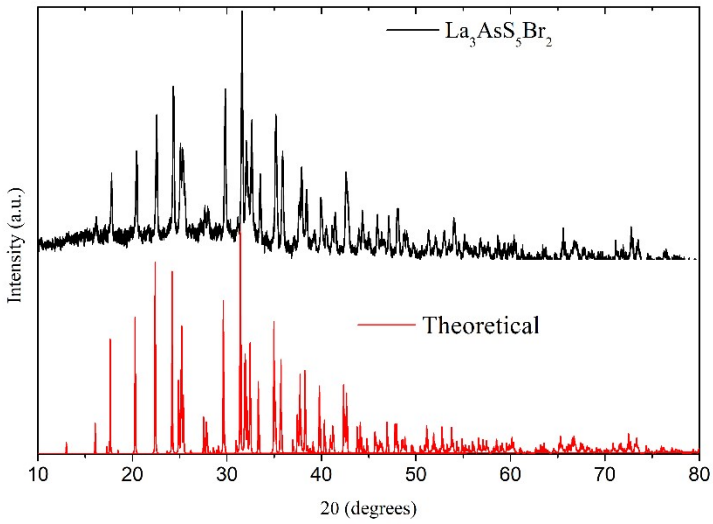


**Figure S2**. The calculated and experimental X-ray diffraction patterns of $La_3AsS_5Br_2$.

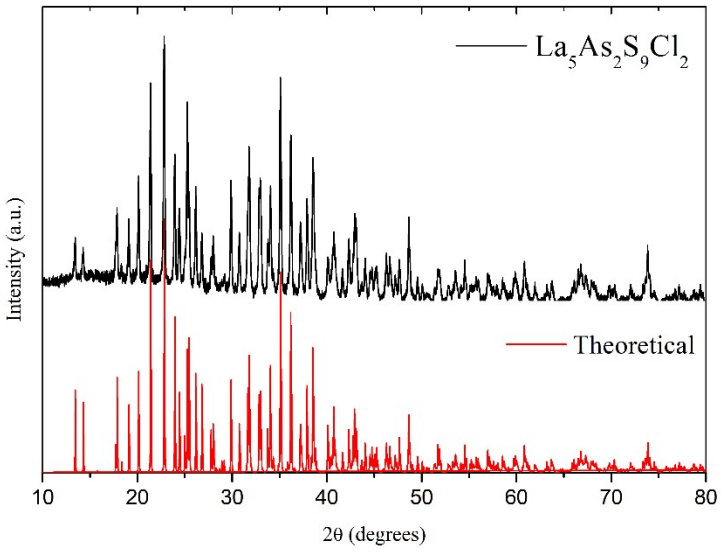


**Figure S3**. The calculated and experimental X-ray diffraction patterns of $La_5As_2S_9Cl_3$.

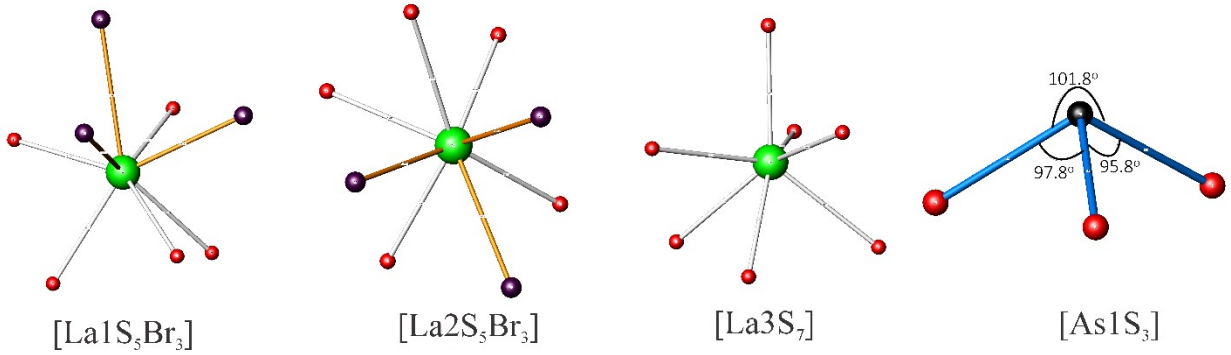


**Figure S4**. Basic building units (BBU) of $La_3AsS_5Br_2$.

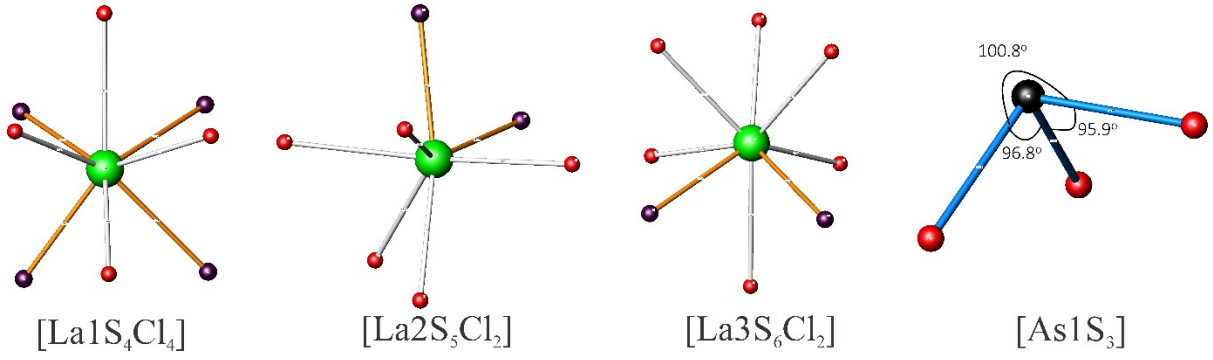


**Figure S5**. Basic building units (BBU) of $La_5As_2S_9Cl_3$.

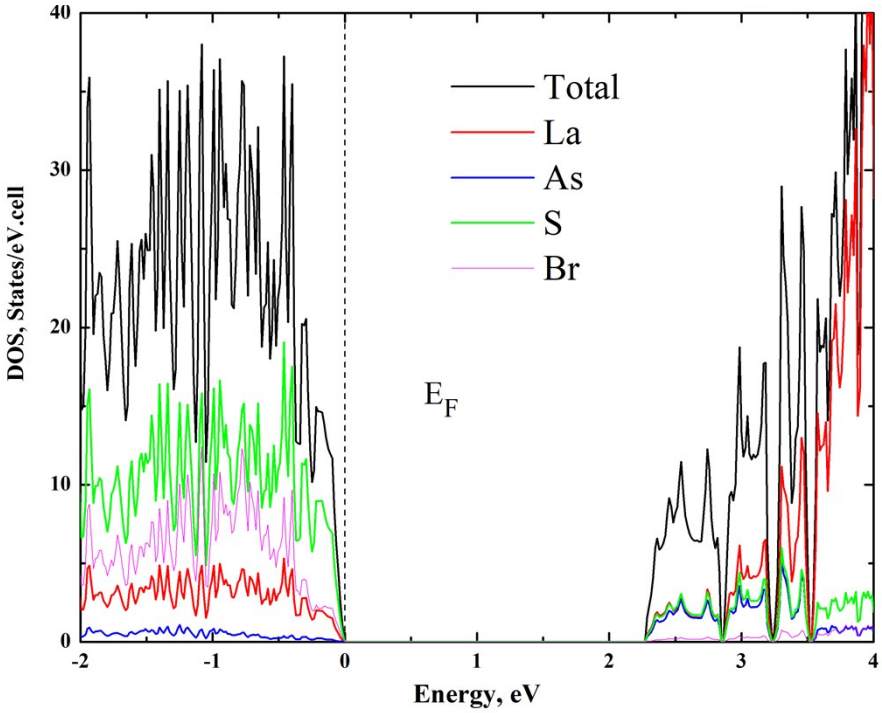


**Figure S6**. Density of states (DOS) of $La_3AsS_5Br_2$.