

Supporting Information

Ligand-induced symmetry breaking, size and morphology in colloidal lead sulfide QDs: from classic to thiourea precursors.

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Supplementary Figures

Figure S1. DSE simulations (green solid curves vs synchrotron data, black dots) of PbS QDs (TMS-1 synthesis), 1040nm (a), 1359nm (b) and 1637nm (c), in the Porod (left) and WAXTS (right) angular regions.

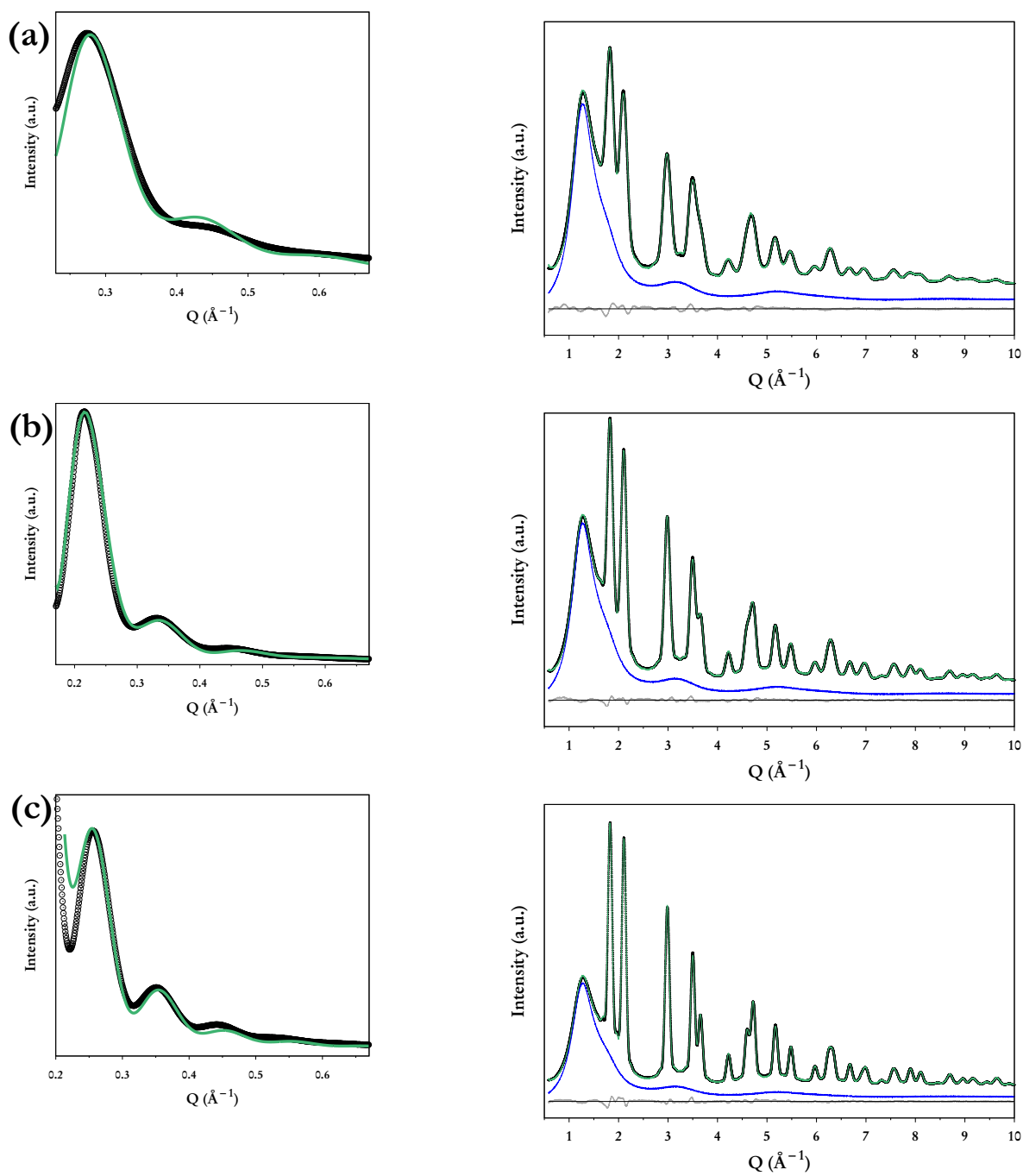


Figure S2. DSE simulations (blue and red solid curves vs synchrotron data, black dots) of PbS QDs, TMS-2 synthesis, 950nm (a) and 1300nm (b); Thiourea synthesis, 950nm (c), in the Porod (left) and WAXTS (right) angular regions.

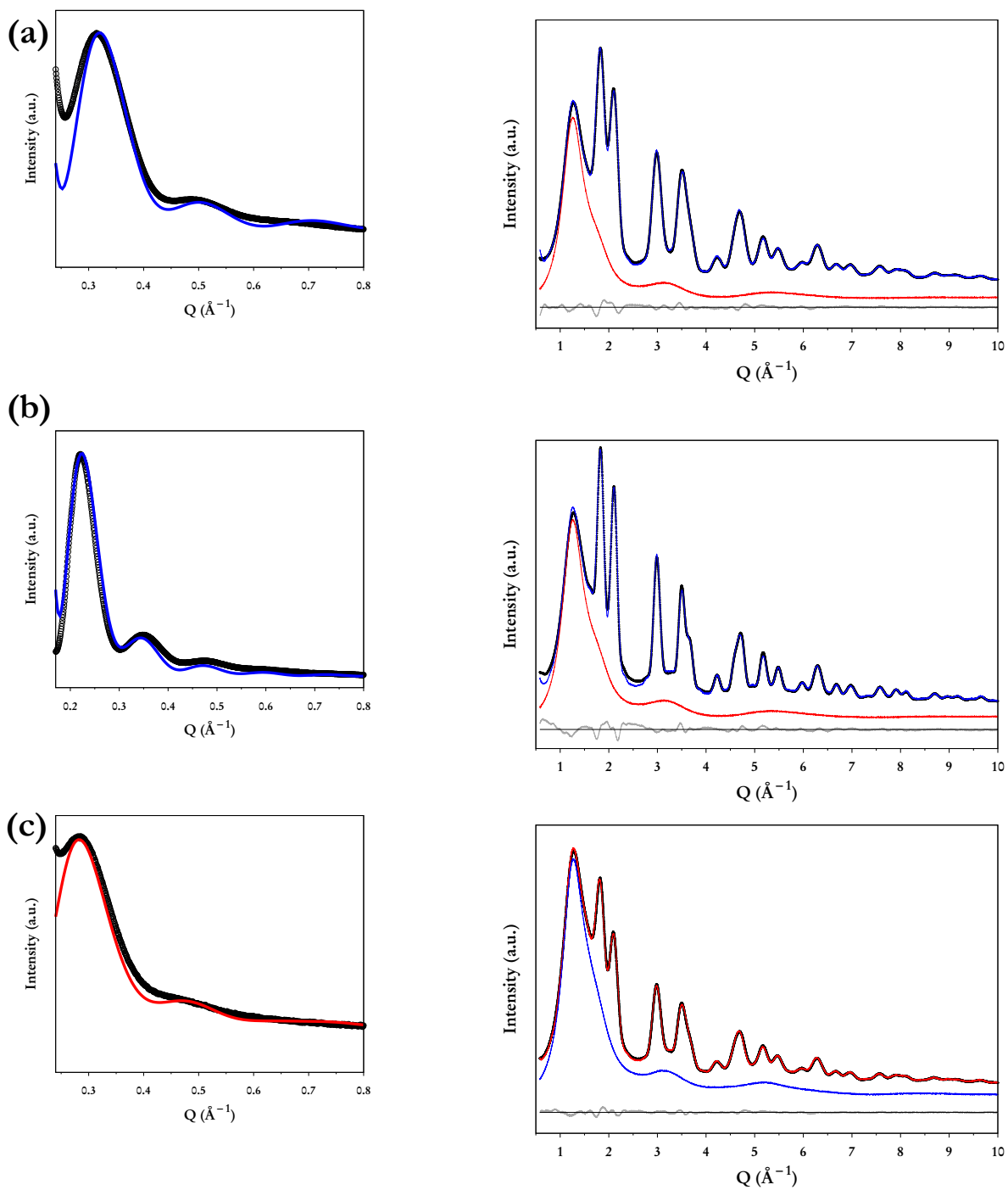
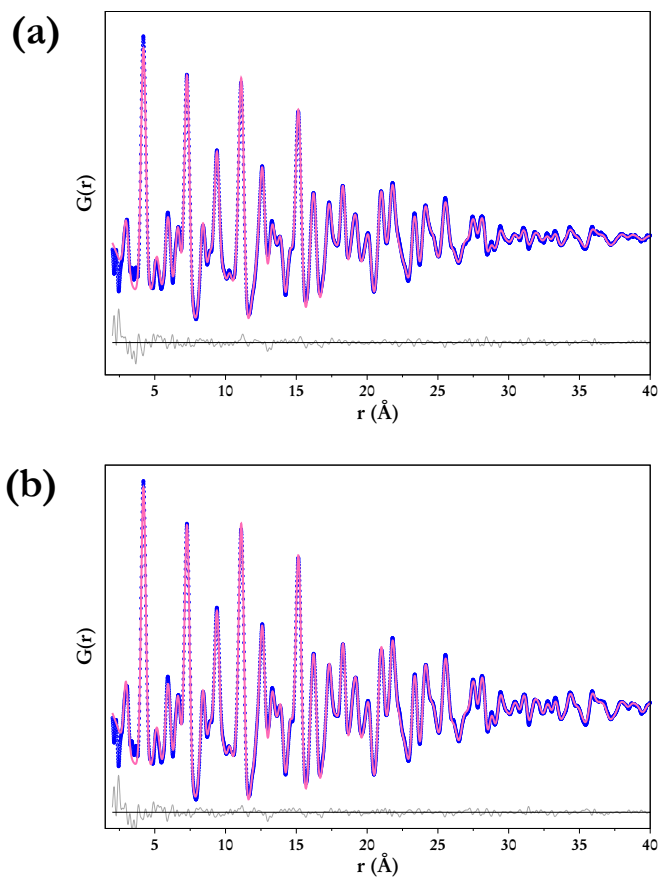


Figure S3. $G(r)$ best fits (magenta solid curves vs experimental data, blue dots) of PbS QDs 1359nm (a), 1637nm (b). Both samples have been prepared according to the TMS-1 synthesis.



Supplementary Tables

Table S1. Main structural and microstructural parameters derived through the DSE-based analysis on TMS-1, TMS-2 and Thiourea PbS QDs.

| Sample | α_{RH} (°) | $\Delta\eta_{[111]}/r_0^*$ | D (nm) ($D_{core} + D_{shell}$) | σ/D ($\sigma_{core}, \sigma_{shell}$) | $\Delta V/V_0^{\text{¥}}$ | Pb:S | Coverage (nm ⁻²) |
|------------------|-------------------|----------------------------|--|---|---------------------------|------|---------------------------------|
| TMS-1 1040 nm | 59.30 | 1.06% | 3.57 (2.54 + 1.04) | 8.4 % (0.23, 0.19) | 0.84% | 1.17 | 2.75 |
| TMS-1 1359 nm | 59.50 | 0.76% | 5.07 (4.00 + 1.07) | 7.3 % (0.30, 0.22) | 0.47% | 1.08 | 2.09 |
| TMS-1 1637 nm | 59.60 | 0.60% | 6.70 (5.67 + 1.04) | 6.8 % (0.40, 0.21) | 0.36% | 1.09 | 3.06 |
| TMS-2 950 nm | 59.10 | 1.46% | 3.10 (2.47 + 0.63) | 9.9 % (0.21, 0.22) | 1.01 % | 1.15 | 2.26 |
| TMS-2 950 nm | 59.00 | 1.44% | 3.11 (2.47 + 0.67) | 10.1 % (0.21, 0.22) | 0.82 % | 1.20 | 2.51 |
| TMS-2 1300 nm | 59.60 | 0.60% | 4.28 (3.49 + 0.79) | 8.7 % (0.30, 0.22) | 0.71% | 1.12 | 2.26 |
| Thiourea 950 nm | 59.10 | 1.38% | 3.31 (2.58 + 0.73) | 9.8 % (0.23, 0.23) | 0.98 % | 1.18 | 2.49 |
| Thiourea 950 nm | 59.10 | 1.37% | 3.16 (2.49 + 0.63) | 10.0 % (0.22, 0.23) | 1.09 % | 1.20 | 2.66 |
| Thiourea 1300 nm | 59.60 | 0.61% | 4.54 (3.71 + 0.82) | 8.3 % (0.30, 0.22) | 0.74% | 1.13 | 2.41 |

* r_0 is the diagonal of the undistorted cubic unit cell of equivalent volume.

¥ V_0 , unit cell volume of the bulk PbS (208.60 Å³).[1]

Table S2. Main structural and microstructural parameters derived through the PDF analysis on TMS-1 PbS QDs.

| Sample | α_{RH} (°) | $\Delta\eta_{[111]}/r_0^*$ | D (nm) | σ/D | $\Delta V/V_0^{\text{¥}}$ | Pb:S | B_{iso} Pb, S (Å ²) |
|---------------|-------------------|----------------------------|----------|------------|---------------------------|------|--------------------------------------|
| TMS-1 1040 nm | 59.38 | 0.94% | 3.48 | 17% | 1.31% | 1.41 | 1.52, 1.30 |
| TMS-1 1359 nm | 59.55 | 0.68% | 5.38 | 21% | 0.37% | 1.31 | 1.33, 1.33 |
| TMS-1 1637 nm | 59.63 | 0.56% | 6.84 | 10% | 0.22% | 1.28 | 1.36, 1.39 |

* r_0 is the diagonal of the undistorted cubic unit cell of equivalent volume.

¥ V_0 , unit cell volume of the bulk PbS (208.60 Å³).[1]

Table S3. Goodness of fits (GoF) of the best DSE models fitting the X-ray synchrotron data of PbS CQDs, corresponding to the $R\text{-}3m$ undistorted ($\alpha_{RH}=60^\circ$) and the distorted ($\alpha_{RH}<60^\circ$) structure. The α_{RH} values of the distorted model are reported in Table S1.

| Sample | GoF ($\alpha_{RH}=60^\circ$) | GoF ($\alpha_{RH}<60^\circ$) |
|------------------|-----------------------------------|-----------------------------------|
| TMS-1 1040 nm | 11.22 | 8.98 |
| TMS-1 1359 nm | 8.27 | 6.66 |
| TMS-1 1637 nm | 10.41 | 9.29 |
| TMS-2 950 nm | 5.92 | 4.99 |
| TMS-2 950 nm | 5.06 | 4.61 |
| TMS-2 1300 nm | 8.44 | 7.76 |
| Thiourea 950 nm | 5.36 | 4.50 |
| Thiourea 950 nm | 2.72 | 2.37 |
| Thiourea 1300 nm | 5.49 | 5.03 |

Table S4. Goodness of fits (GoF) obtained using the PDF analysis for the undistorted ($\alpha_{RH}=60^\circ$) and the distorted ($\alpha_{RH}<60^\circ$) $R\text{-}3m$ structure. The α_{RH} values of the distorted model are reported in Table S2.

| Sample | GoF ($\alpha_{RH}=60^\circ$) | GoF ($\alpha_{RH}<60^\circ$) |
|---------------|-----------------------------------|-----------------------------------|
| TMS-1 1040 nm | 7.87 | 3.80 |
| TMS-1 1359 nm | 3.16 | 3.01 |
| TMS-1 1637 nm | 2.98 | 2.96 |

References

- [1] Noda Y., Masumoto K., Ohba S., Sato Y., Toriumi K., Iwata Y., Shibuya I., *Acta Crystallogr. C*, **1987**, *43*, 1443-1445.