Electronic Supplementary Information

Polymorphism in nanoparticle-based crystals depending upon their single or poly-crystalline character

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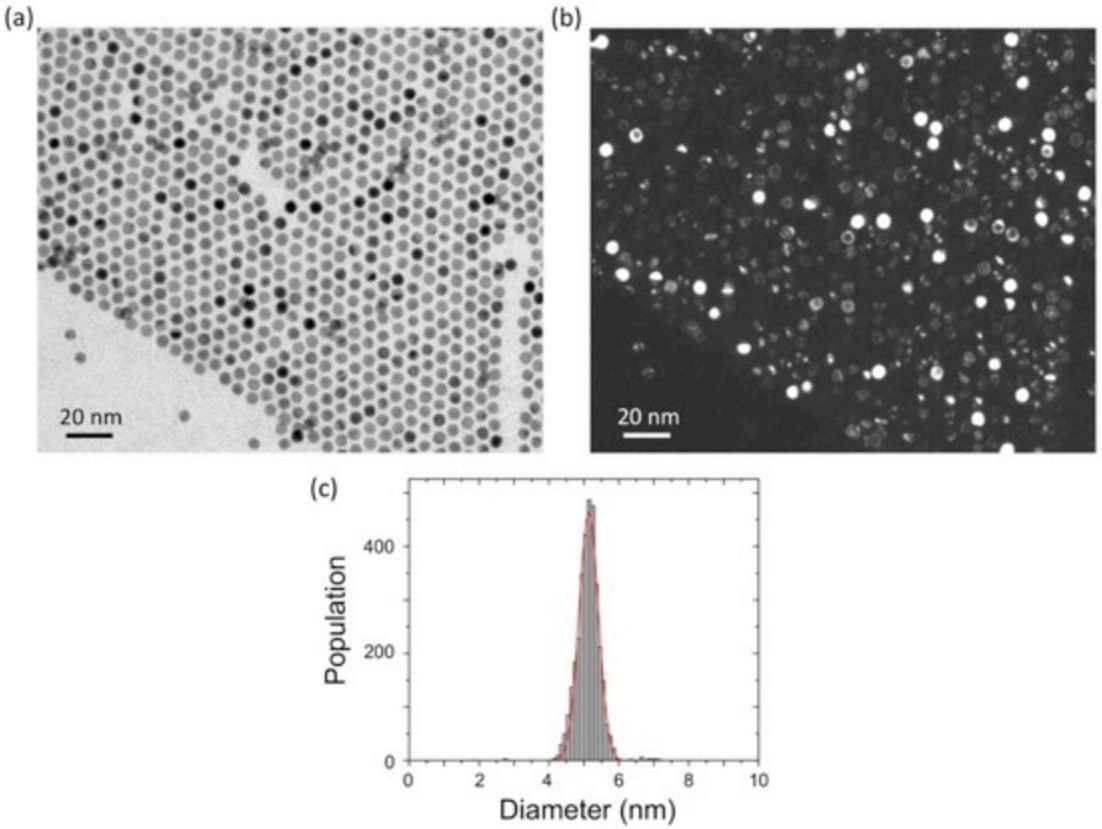

Figure S1. Bright (a) and dark (b) field TEM pictures of the as-synthesized gold nanocrystals with their size distribution (c).

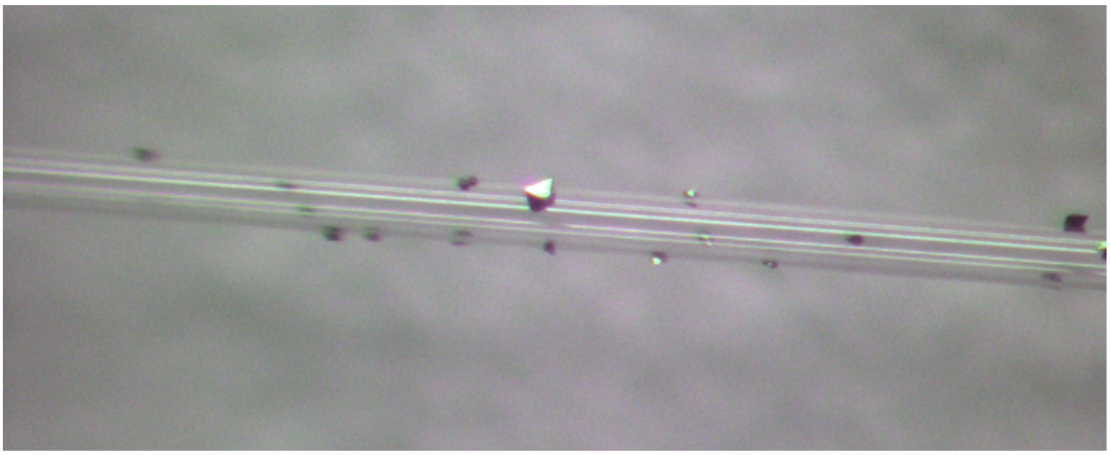

Figure S2. Optical micrograph of a capillary used to grow polyhedral superlattices.

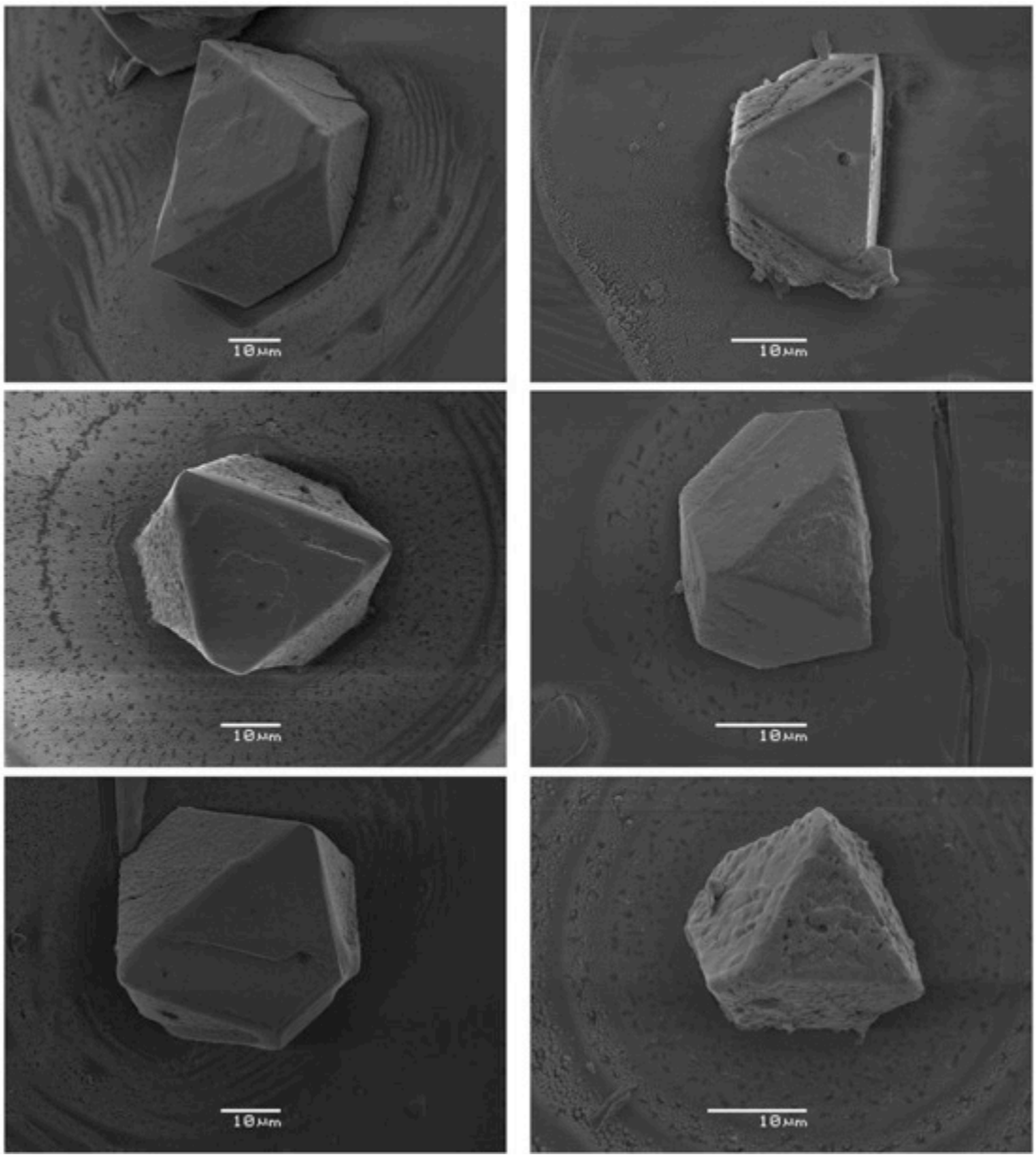

Figure S3. Typical polyhedral NC superlattice made of polycrystalline gold nanocrystals that are selected for the X-ray diffraction experiments.

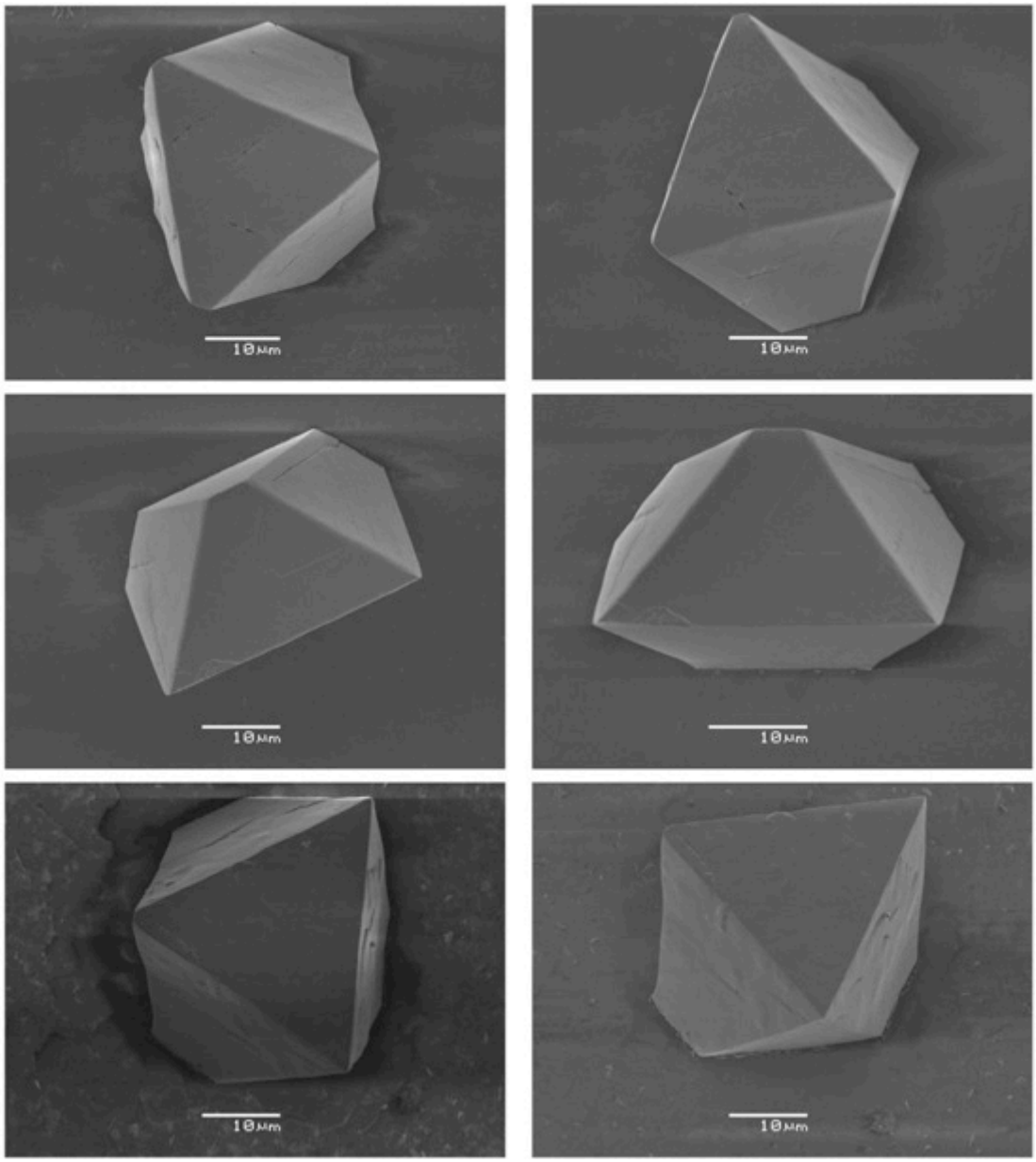

Figure S4. Typical polyhedral NC superlattice made of gold single crystals that are selected for the X-ray diffraction experiments.

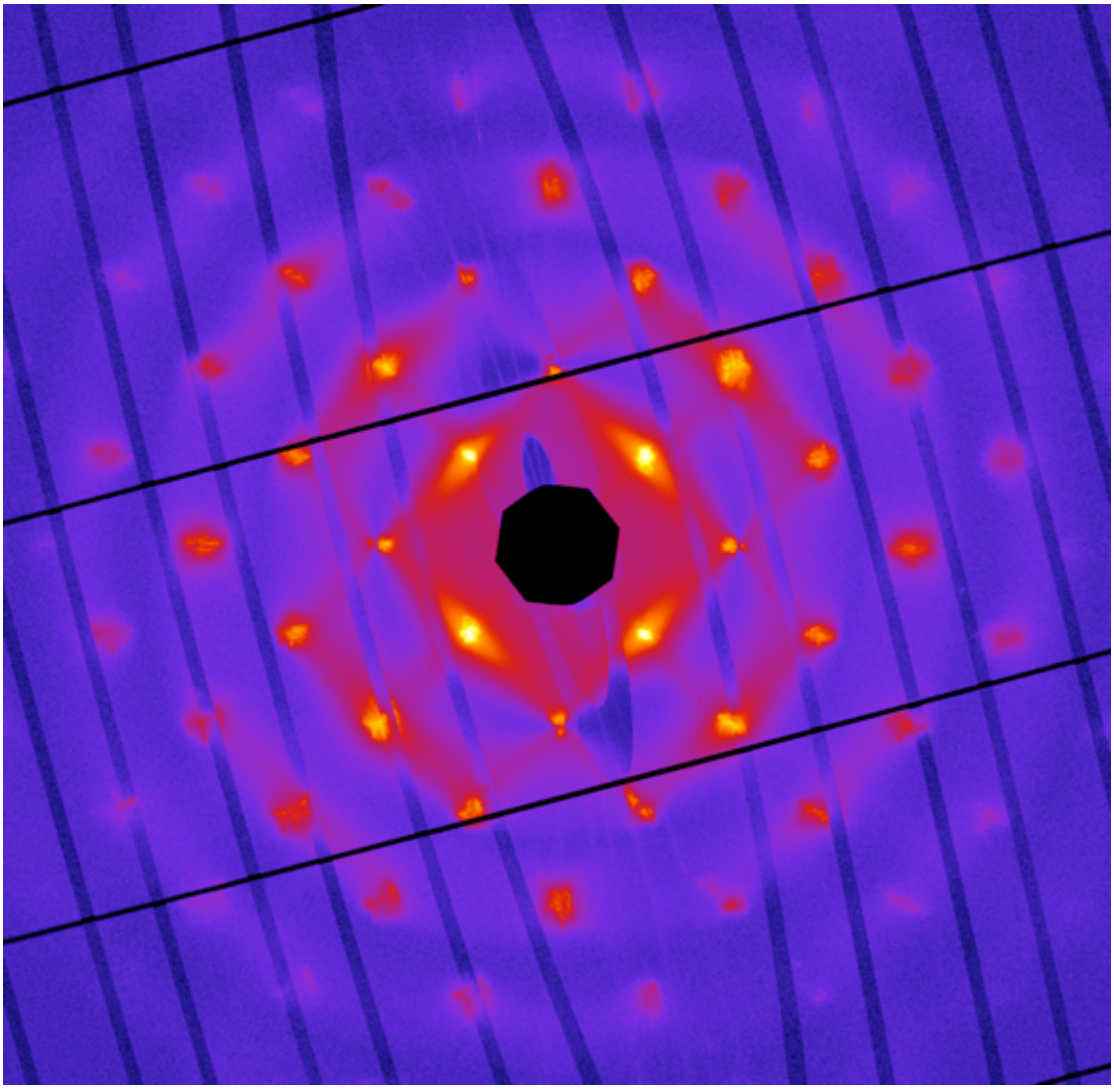

Figure S5. Reconstruction of reciprocal space planes of equation l=0 at small q value (q_{max}=7 nm^{-1}) of one polyhedral nanocrystal superlattice made of gold single crystals.

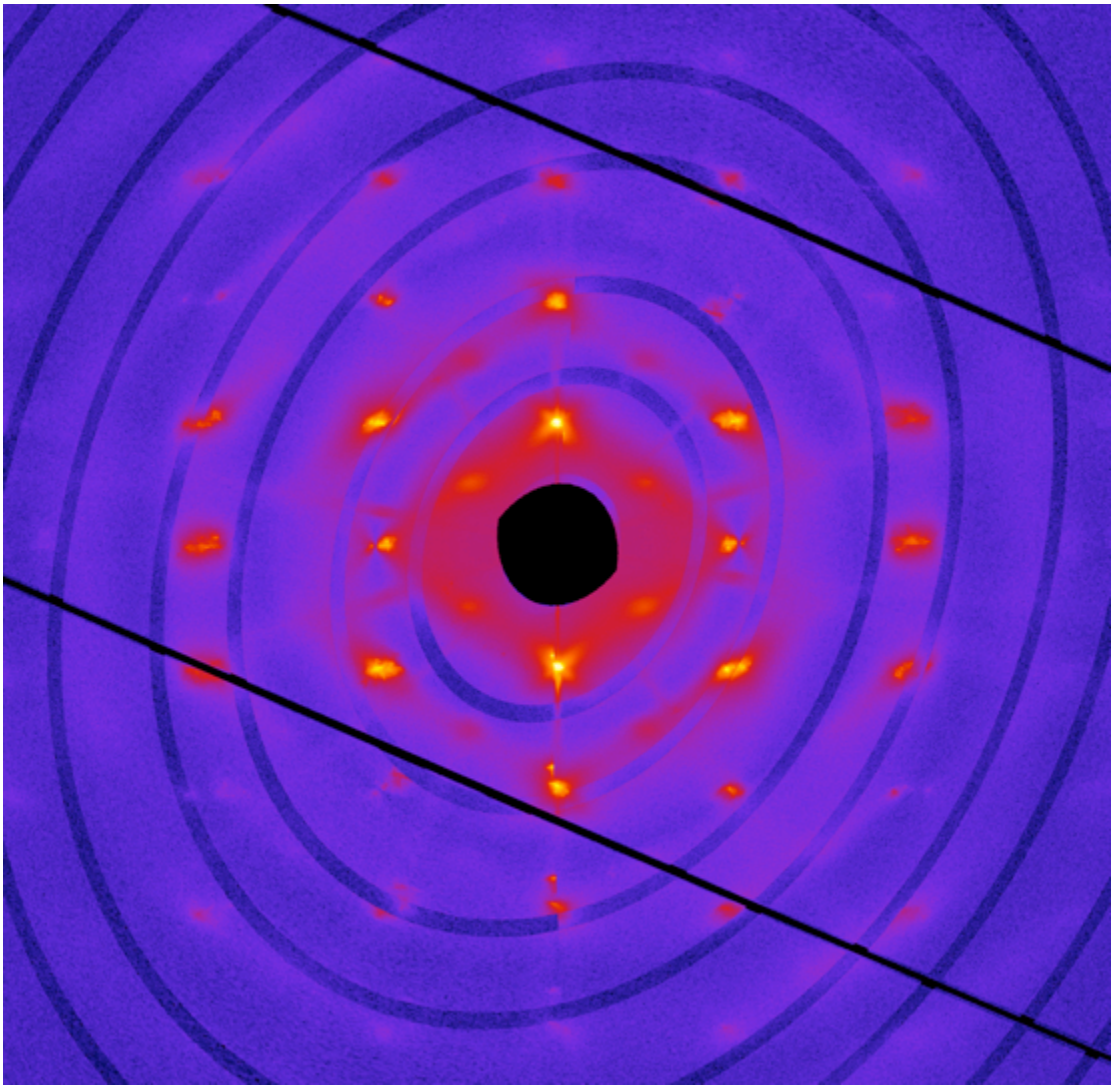

Figure S6. Reconstruction of reciprocal space planes of equation h+k=0 at small q value (q_{max}=7 nm^{-1}) of one polyhedral nanocrystal superlattice made of gold single crystals.

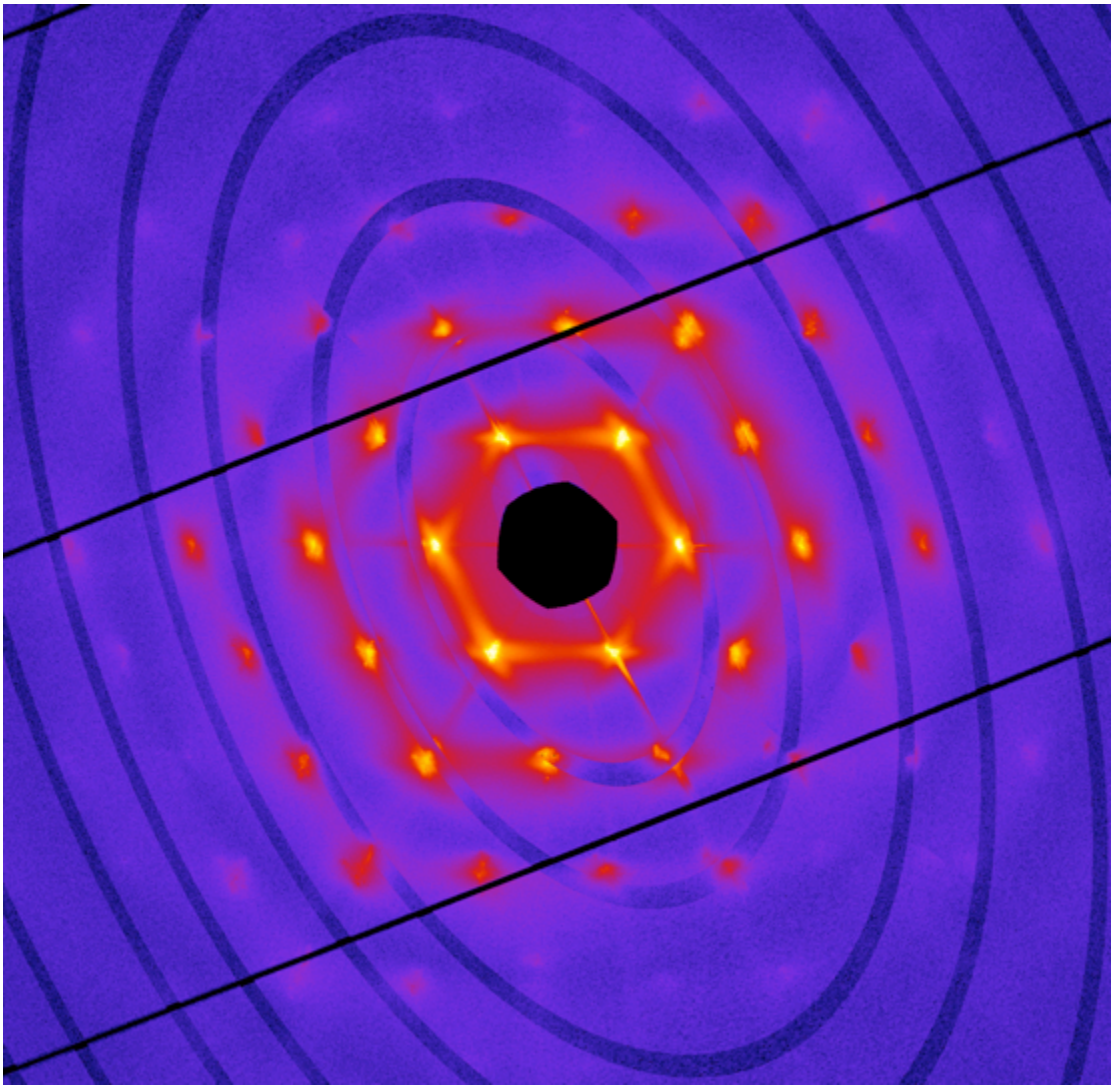

Figure S7. Reconstruction of reciprocal space planes of equation h+k+l=0 at small q value (q_{max}=7 nm^{-1}) of one polyhedral nanocrystal superlattice made of gold single crystals.

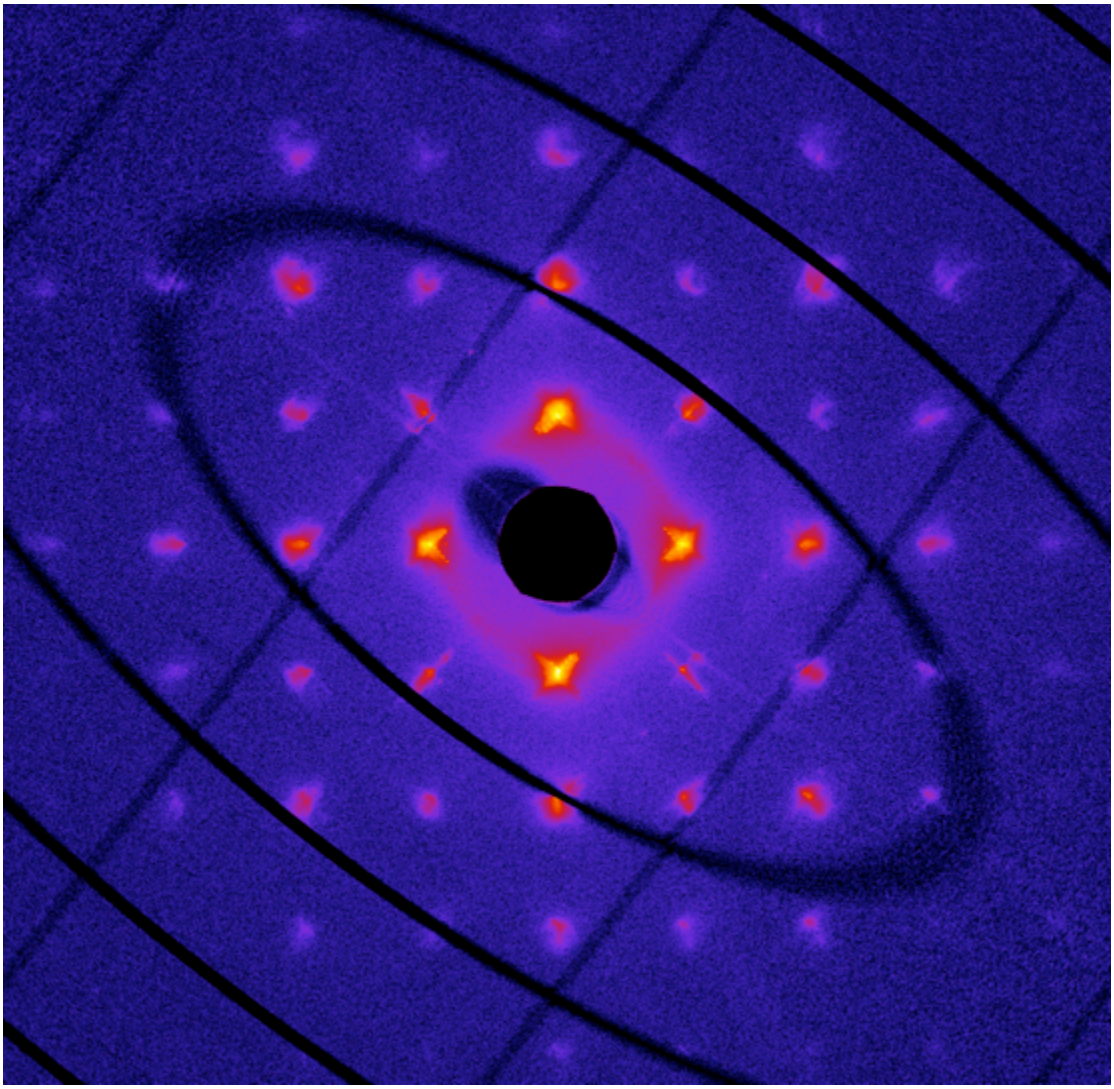

Figure S8. Reconstruction of reciprocal space planes of equation l=0 at small q value (q_{max}=7 nm^{-1}) of one polyhedral nanocrystal superlattice made of gold polycrystals.

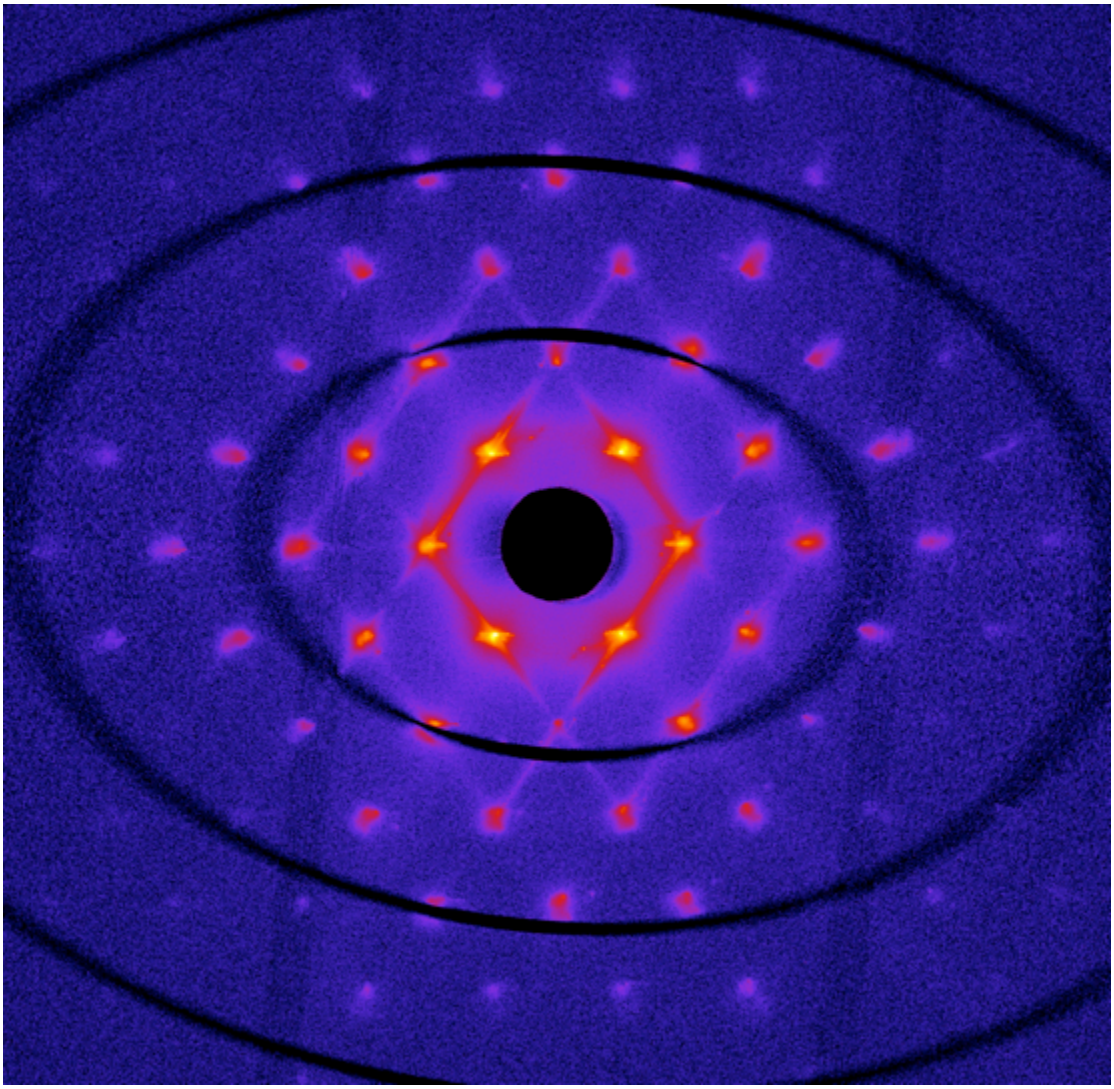

Figure S9. Reconstruction of reciprocal space planes of equation h+k=0 at small q value (q_{max}=7 nm^{-1}) of one polyhedral nanocrystal superlattice made of gold polycrystals.

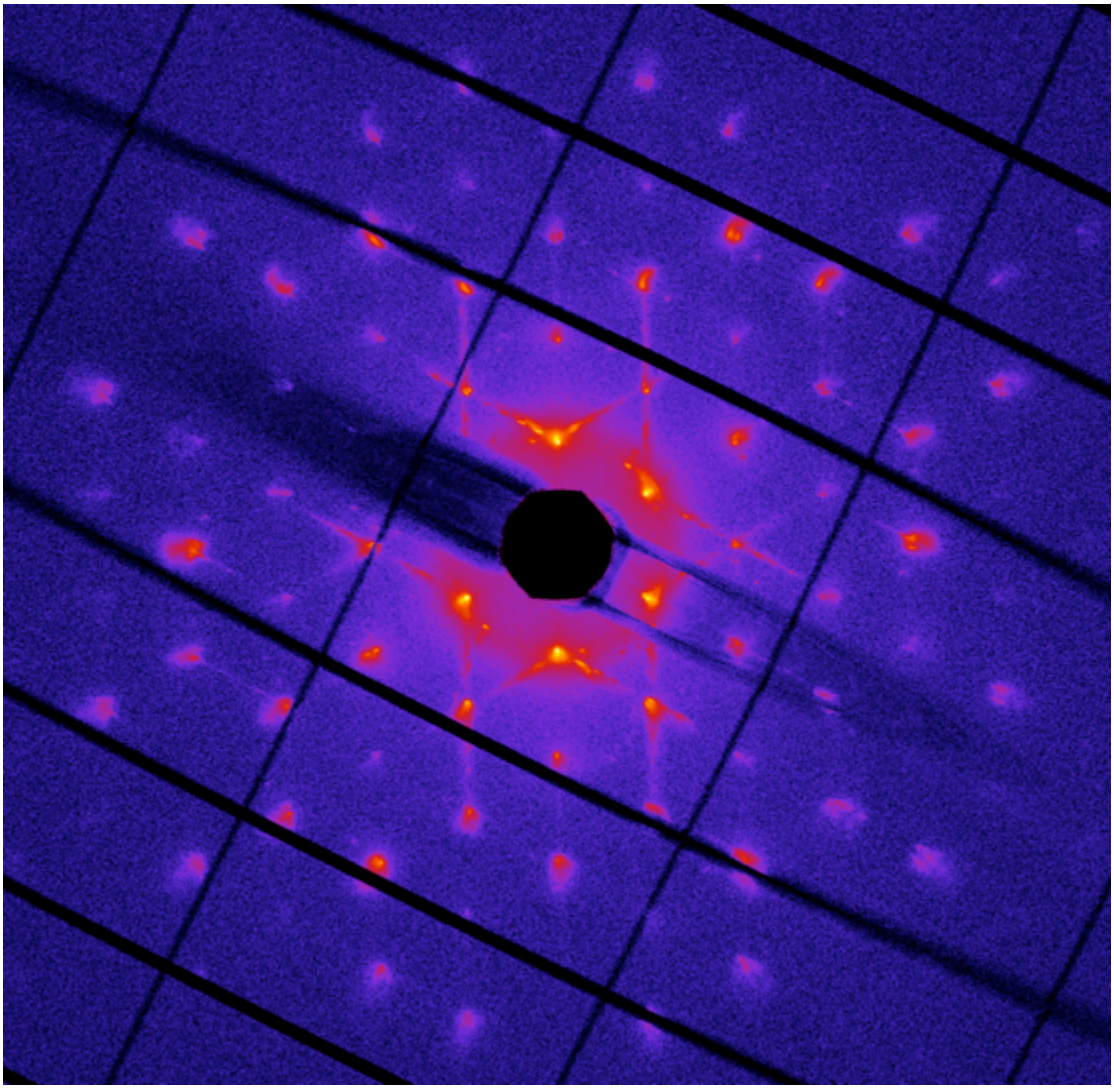

Figure S10. Reconstruction of reciprocal space planes of equation h+k+l=0 at small q value (q_{max}=7 nm^{-1}) of one polyhedral nanocrystal superlattice made of gold polycrystals.

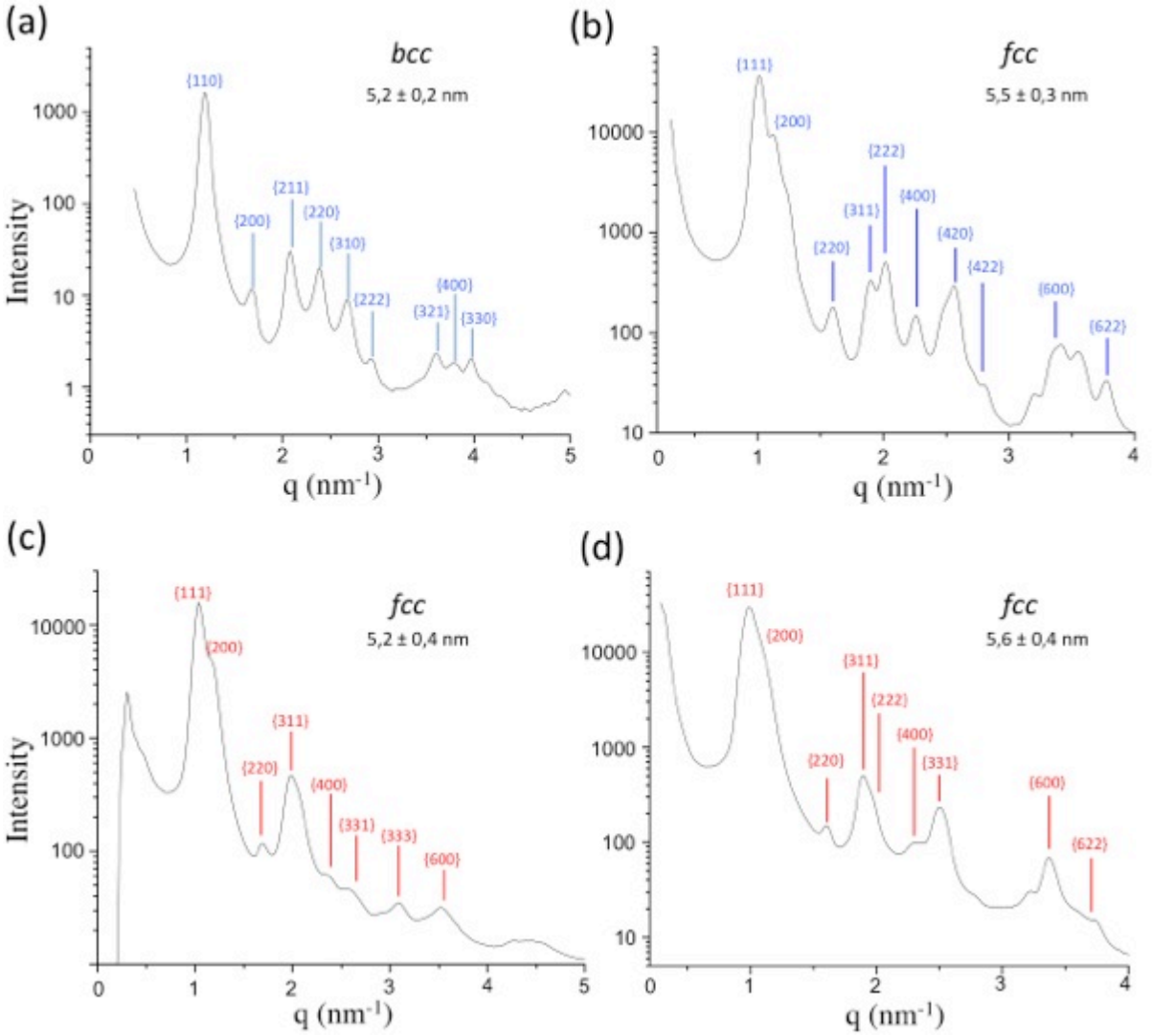

Figure S11. SAXS powder profiles for gold single (a-b) and polycrystals (c-d) with different size.

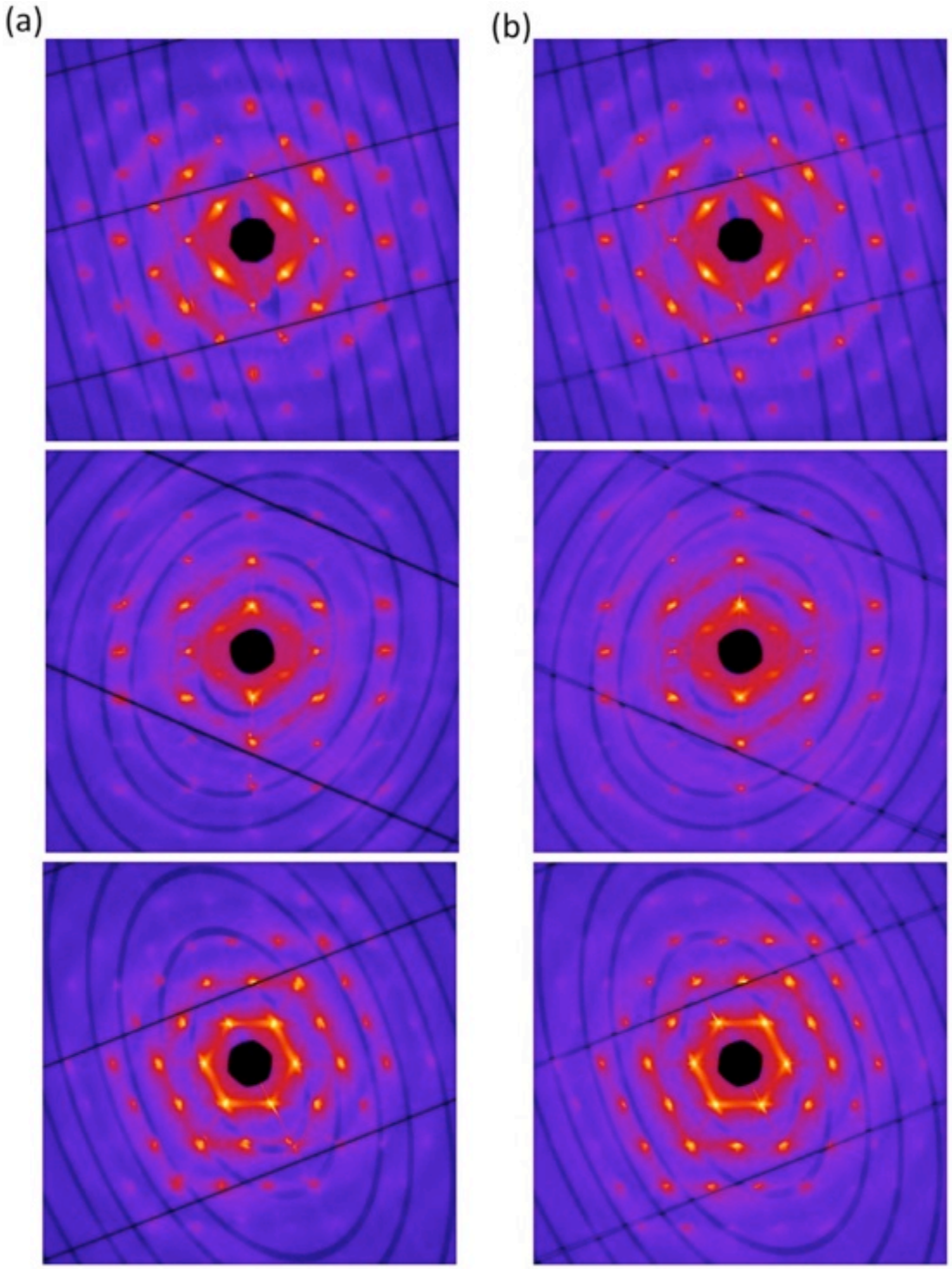

Figure S12. Reconstruction of reciprocal space planes of one polyhedral nanocrystal superlattice made of gold single crystals at 110K (a) and 290K (b).

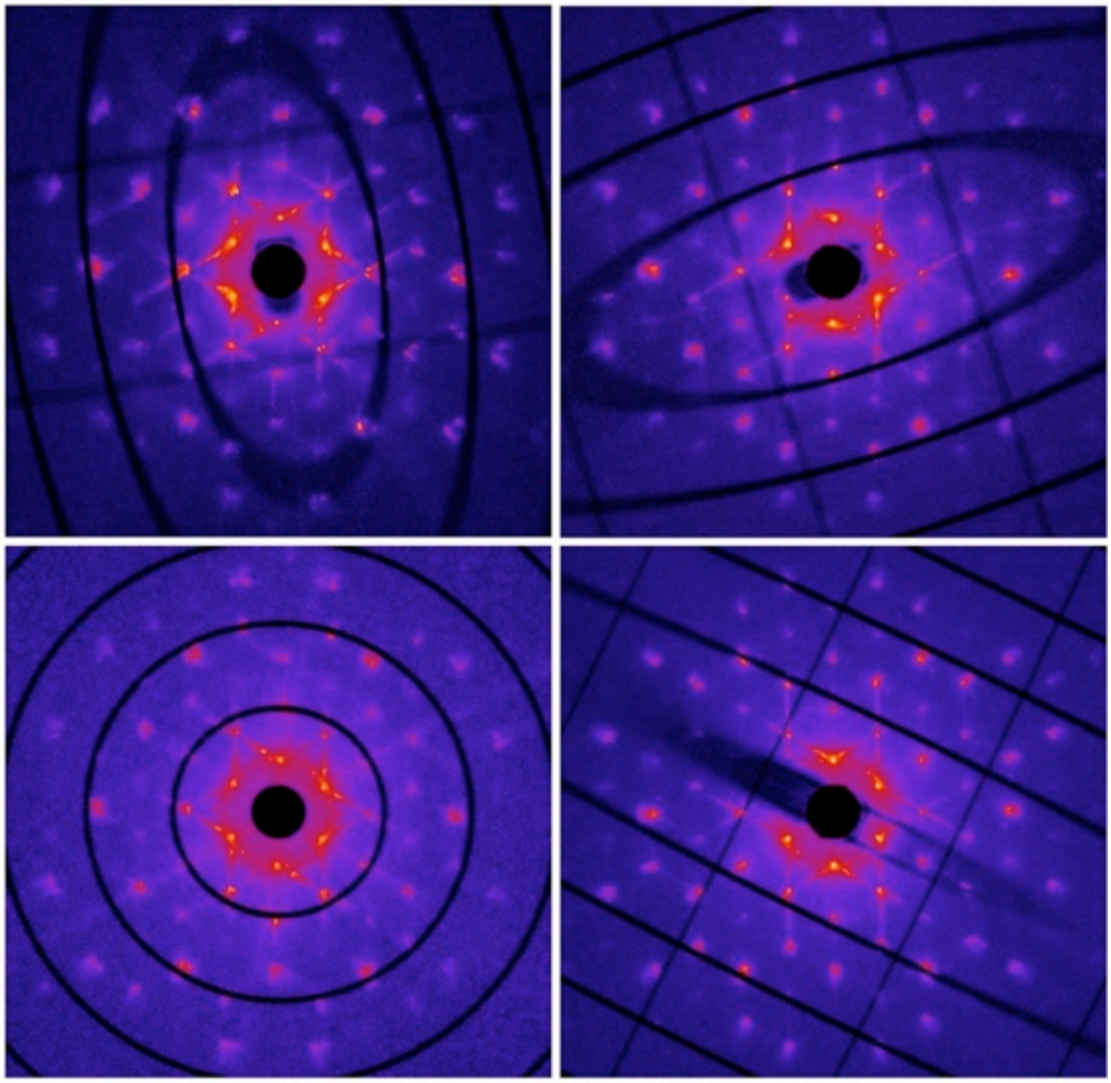

Figure S13. The 4 possible reconstructions of reciprocal space planes of equation h+k+l=0 of one polyhedral nanocrystal superlattice made of gold polycrystals.

Calculation of the inorganic core density in the colloidal crystal

In the case of BCC superlattice:

$$\Phi_{bcc} = \frac{2 \times 4/3 \times \pi \times \left(D_{TEM}/2 \right)^3}{a_{bcc}^3} = 29.5\%$$

where d_{inor} is the metallic NC diameter determined by TEM and a_{bcc} is the *bcc* unit cell.

In the case of FCC superlattice:

$$\Phi_{fcc} = \frac{4 \times 4/3 \times \pi \times \left(D_{TEM}/2 \right)^3}{a_{fcc}^3} = 29.5\%$$

where d_{inor} is the metallic NC diameter determined by TEM and a_{fcc} is the *fcc* unit cell.