Ensembles of nanoparticles possess collective properties that are dissimilar to those demonstrated by the individual particles and self-assembly has emerged as a powerful means by which the structure and properties of inorganic nanoparticle arrays can be manipulated. In order to aid in the resolution of the keenly contested debate between proponents of the fibrillation model and those of the electrostatic forces interaction model the structure formed by monolayers of PbS colloidal nanocrystals was investigated using high-resolution spherical aberration corrected TEM, high-resolution electron holography and energy filtered TEM [1,2]. By employing this suite of techniques it could be observed that the truncated octahedrally shaped nanoparticles form 2D close-packed layers interconnected by organic fibrils of oleic acid which are partially mineralised by PbS. These bridges, whose diameters are between 0.3 and 2 nm, keep the face to face orientation of the nanoparticles fixed, thus preventing them from assuming an arbitrary orientation. The complex and textured structure of the monolayer assembly is caused by the habit of the truncated octahedral PbS nanoparticles bearing angles close to ideal values of 54° and 71° between their {100} and {111} faces. By means of electron holography, approximately 10-15 fibrillar interconnections between neighbouring particles in the as-prepared films have been observed. Each nanoparticle is surrounded by six other individuals. At least two or three organic “linkages” are formed between the particles and connect to a nearest neighbour. Most of the organic connections can be mineralised successively by PbS during careful annealing. By using this bottom-up technique access to length scales of sub-nanometer dimensions, presently not accessible to top-down techniques can be attained. This type of isolated but yet interconnected structure formed by the inorganic bridges, represents an ideal “isolated but connected” structure that preserves the effects of quantum confinement present within the individual nanoparticles whilst at the same time having the potential to provide high electron mobility throughout the extended structure.

Fig. 1: 3D representation of the phase image retrieved from the electron hologram. Color code corresponds to 4 nm height from green to blue. The bridging organic fibrils appear yellow.

Fig. 2: 2D representation of phase image. The PbS nanoparticles and the interconnecting sub-nanometer oleic acid fibrils appear bright in the phase image.

Fig. 3: (a) Cs-corrected HR-TEM image of two nanoparticles interconnected by a PbS bridge. The PbS bridge (red arrow) has a diameter of 0.3 nm and a length of 1.5 nm. The periodicity along the bridge corresponds to 0.3 nm which is equivalent to the (200) lattice plane of PbS. (b) Digitally zoomed area.

Fig. 4: Idealized model of isolated but interconnected PbS nanoparticles.