## Supplementary Information

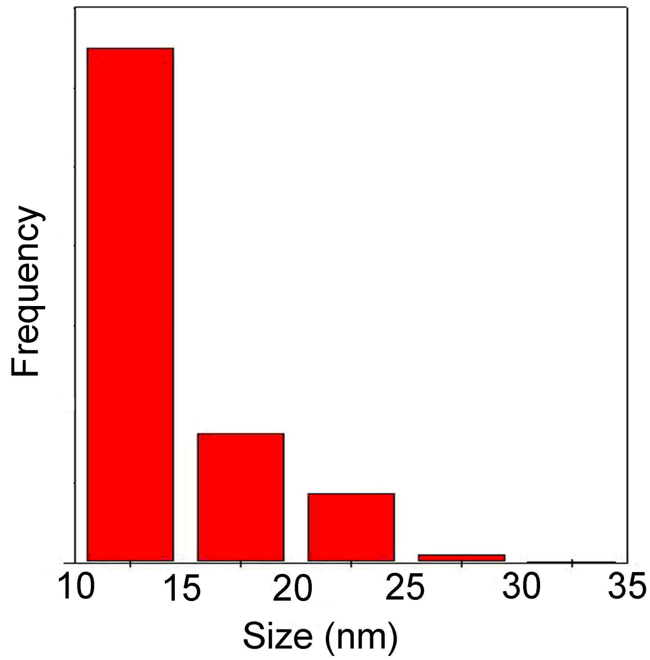


**Fig. S1.** Histogram showing a typical size distribution of the AuCl nanocubes synthesized by refluxing a mixture of 30 mg of $HAuCl_4.3H_2O$, 400 µl of oleylamine in 50 ml toluene at 120 °C.. The cube edge length is sensitive to the synthesis temperature, the initial Au salt and oleylamine concentrations.

**Particle size tuning**

The table below captures the effect of oleylamine amount and temperature on size of the AuCl cubes formed. Au(III) reduction to Au(I) is much faster at higher temperatures. For example, at 120 °C the yellow color characteristic of Au(III) ions disappears within 5-10 minutes, whereas it takes 5-6 hours at 60 °C.

| Experiment | Oleylamine amount (µL) | Temperature (°C) | Yield description |
|---|---|---|---|
| A | 400 | 120 | 20 nm |
| B | 400 | 60 | 20 nm and µm-size cubes |
| C | 200 | 60 | µm-sized cubes |

The cubes are capped by the amine as was shown by the XPS analysis. A higher concentration of amine leads to a reduction in the size of the cubes. Temperature also has a profound effect by altering the nucleation kinetics. A higher nucleation rate at higher temperatures leads to smaller cubes whereas lower temperatures lead to significant growth.

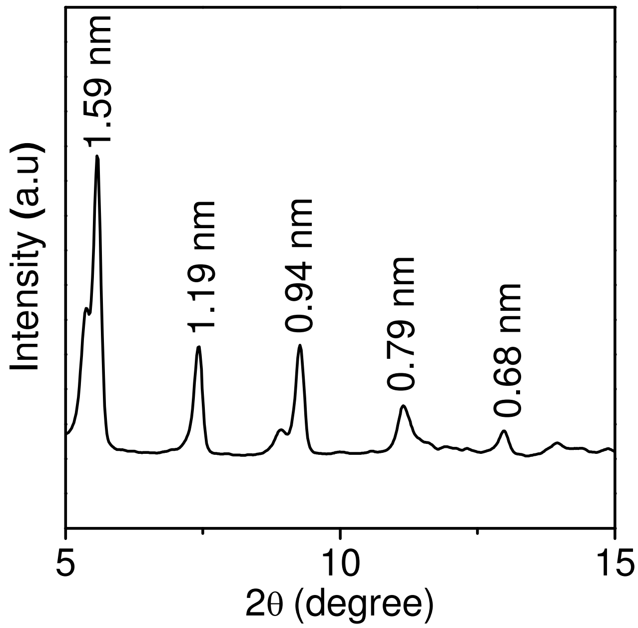


**Fig. S2.** Representative X-ray diffractogram from a nanocube sample drop-cast onto a glass slide showing low-angle peaks corresponding to the AuCl-oleylamine polymer strands. The cubes could be separated by centrifuging the solution followed by washing several times with toluene in which case the cubic AuCl was the only phase seen in the XRD patterns.

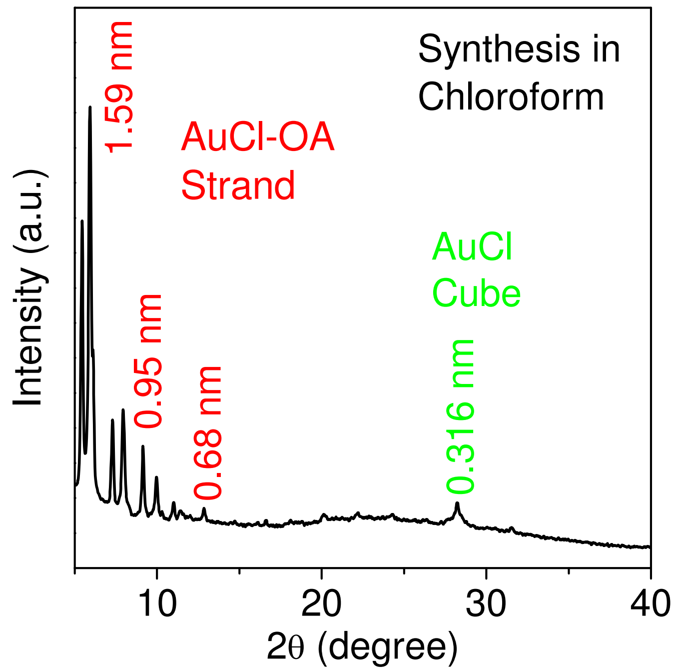


**Fig. S3.** X-ray diffractogram from the product synthesized in chloroform–which has a higher polarity than toluene—showing the formation of a small amount of rocksalt AuCl; the rest of the peaks corresponding to the AuCl-oleylamine strands which appears to be the major product. TEM studies confirmed that the rocksalt AuCl yield decreases when toluene is replaced with higher polarity solvents.