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Electronic Supplementary Information

Multivalent bonds in self-assembled bundles of ultrathin gold nanowires

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1 Experimental Section:

Chemicals:

All chemicals were used without further purification: Oleylamine (technical grade, 70%) was purchased from Sigma-Aldrich (Germany). Triisopropylsilane (98%) was purchased ABCR (Germany). N-hexane (99%) was purchased from ABCR (Germany). Ethanol (99.8%) was purchased from Sigma-Aldrich (Germany). N-octane (98%) was purchased from Sigma-Aldrich (Germany). Cyclohexane (99%) was purchased from Sigma-Aldrich (Germany). Cyclooctane (99%) was purchased from Sigma-Aldrich (Germany). Benzene (99%) was purchased from Sigma-Aldrich (Germany). Toluene (99.5%) was purchased from Sigma-Aldrich (Germany).

Synthesis:

Ultrathin gold nanowires were synthesized using a protocol adapted from Feng and coworkers.¹ Briefly, HAuCl₄ (10 mM) was dissolved in a oleylamine:n-hexane mixture (8:27, v/v) to result in a dark yellow solution. Triisopropylsilane (1.2 M) was added and the solution was stirred vigorously for 30 s. Afterwards the reaction mixture was flushed with argon and kept undisturbed at 20°C for 16 h.

Variation of the OAm volume fraction of the dispersion:

As-synthesized AuNWs were mixed with n-hexane or oleylamine (OAm) to adjust the volume fraction from 5 to 73 vol.% (as-synthesized AuNWs: 18 vol.%). After mixing the resulting dispersions were immediately analyzed by SAXS and all SAXS patterns were normalized to the gold content of as-synthesized wires.

Washing and solvent exchange:

As-synthesized AuNWs were washed by repeated precipitation through the addition of ethanol. The supernatant was carefully removed and the wires were redispersed in the desired organic solvent. The washing step was repeated for a second time. All dispersions were kept at 4°C until further use.

Characterization:

TEM experiments:

1 µl of as-synthesized AuNWs was left to dry on a 400-mesh carbon coated copper grid (Plano, Germany) and then characterized by Transmission Electron Microscopy using a JEM 2010, JEOL, Germany, operating at 200 kV.

SAXS experiments:

We employed a laboratory scale SAXS setup, the XEUSS 2.0 from XENOCS SA (France) equipped with a CuK α X-ray source and a PILATUS3 R 1M (DECTRIS, Switzerland) X-ray area detector, to record the SAXS data. All measurements were performed at room temperature, 24 hours after solvent exchange, using capillaries with an inner diameter of 1 mm. Scattering patterns of regular superlattices exhibit peaks with spacing that corresponds to the distance between planes of the (super)lattice. Given the Miller indices h and k, the maxima's positions in q space and the distance between single scatterers of a 2D hexagonal lattice are related by²:

$$q(h,k) = \frac{4\pi}{\sqrt{3}*d} \sqrt{h^2 + k^2}$$
(1)

Further information extracted from SAXS data:

The SAXS pattern of AuNWs in cyclohexane (Fig S1) did not show any structure peaks, hence the pattern was dominated by the form factor of the wires. The minimum of scattered intensity was fit with the form factor of a cylinder³ using the ``SASfit'' software package⁴ and yielded a wire-radius of 0.85 ± 0.08 nm, which is in good agreement with TEM.



Figure S1. Small-angle X-ray scattering of AuNWs in cyclohexane

2 Supplementary figures:



Figure S2. Representative TEM images of AuNWs synthesized in n-hexane.



Figure S3. Representative TEM images of AuNWs synthesized in n-octane.



Figure S4. Representative TEM images of AuNWs synthesized in cyclohexane.



Figure S5. Representative TEM images of AuNWs synthesized in cyclooctane.



Figure S6. Representative TEM images of AuNWs synthesized in benzene.



Figure S7. Representative TEM images of AuNWs synthesized in toluene.

References:

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- 2 S. Förster, A. Timmann, M. Konrad, C. Schellbach, A. Meyer, S. S. Funari, P. Mulvaney and R. Knott, J. Phys. Chem. B, 2005, 109, 1347– 1360.
- 3 G. Fournet, Bull. la Société Française Minéralogie Crystallogr., 1951, **74**, 39.
- 4 I. Breßler, J. Kohlbrecher, and A. F. Thünemann. SASfit: A comprehensive tool for small-angle scattering data analysis. arXiv:1506.02958 [physics.data-an]. June 2015.