Supporting Information

Solution-Processable Ultrathin Size- and Shape-Controlled Colloidal Cu$_{2-x}$S Nanosheets

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Methods

**Optical spectroscopy.** Samples for optical measurements were prepared by directly dissolving the crude reaction mixture in anhydrous toluene under nitrogen and stored in sealed cuvettes. Absorption spectra were measured on a double beam Perkin-Elmer Lambda 16 UV/Vis spectrometer. PL and PL excitation spectra were recorded by an Edinburgh Instruments FLS920 Spectrofluorimeter equipped with a 450 W Xenon lamp as excitation source and double grating monochromators. PL decay curves were obtained by time-correlated single-photon counting via time-to-amplitude conversion. A pulsed diode laser (EPL-445 Edinburgh Instruments, 441 nm, 55 ps pulse width, 0.2–20 MHz repetition rate) was used as the excitation source. Very low excitation fluences were used (<0.5 nJ/cm²) to avoid multiexciton formation, and to keep the ratio of stop to start pulses below 0.04.

**Transmission Electron Microscopy.** Transmission Electron Microscopy (TEM) and Energy Dispersive X-Ray Spectroscopy (EDS) were performed using a FEI Tecnai-12 microscope operating at 120 kV and a FEI Tecnai-20F microscope operating at 200 kV. Samples for TEM imaging were prepared by drop-casting a toluene solution of NSs onto a carbon-coated copper (400-mesh) TEM grid. The excess liquid was removed by blotting using filter paper. EDS measurements were performed using a dedicated low background holder and Cu-free Ni TEM grids. Acquisition time for EDS measurements was ~30 s – ~1 min. To ensure that the elemental concentrations were statistically valid and representative of the whole NS ensemble, EDS analyses were performed on wide areas (~10⁵–10⁶ nm²), encompassing several hundreds of NSs. We note here that even when taking the usual precautions (dedicated low background holder and Cu-free Ni TEM grids), there is always a background Cu signal contributing to the EDS spectrum. Although we could not determine the exact magnitude of this background, its upper limit is estimated to be of the order of a few percent with respect to the S signal, since Cu:S ratios as low as 0.03 could be measured in CdS NSs obtained from parent Cu₂₋ₓS NSs by Cu⁺ for Cd²⁺ cation exchange. Nevertheless, this introduces a larger uncertainty in the Cu content, with respect to the other elements. We have attempted to estimate the uncertainty in the composition of the NSs by averaging values obtained for different samples. Since the elemental ratios are defined with respect to S, standard deviation values are not provided for the S ratios.

**X-Ray Diffraction (XRD).** XRD diagrams were obtained by using a PW 1729 Philips diffractometer, equipped with a Cu Kα X-ray source (λ=1.5418 Å). Samples for XRD analysis were prepared by depositing a concentrated solution of purified NSs on a Si single crystalline substrate (100 orientation) under inert atmosphere.

**High-resolution (Scanning) Transmission Electron Microscopy and Energy Dispersive X-ray Spectroscopy mapping.** High-resolution TEM (Fig. 2c-d in the main text) was performed on a FEI Titan 50-80 cubed microscope equipped with an aberration-corrector for the image forming lens, operated at 120 kV. High-Angle Annular Dark-Field (HAADF) Scanning Transmission Electron Microscopy (STEM) and STEM Energy Dispersive X-ray Spectroscopy (EDS) mapping (Fig. S3) was performed on a FEI Titan 50-80 cubed microscope equipped with an aberration-corrector for the probe forming lens and a Super-X, large solid angle EDX detector. The microscope was operated at 120 kV and the STEM convergence semi-angle was ~21.4 mrad. The electron diffraction pattern shown in Fig. 2b in the main text was acquired using a FEI Tecnai microscope operating at 120 kV. It should be noted that the sample is highly beam sensitive and therefore does not allow a tilt series of a single nanosheet to be acquired for a thorough structural determination.
Figure S1: Low-angle X-ray diffraction (XRD) pattern of a sample of ultrathin colloidal Cu$_2$xS nanosheets deposited from a toluene solution on a silicon substrate. TEM images of this sample are shown in the main text (Fig. 1b,c), together with an XRD pattern extending to higher angles (Fig. 1d). The series of peaks can be ascribed to successive diffraction orders from a periodic superstructure formed by self-assembled nanosheet stacks. The peak separation (2.49°) corresponds to a periodicity of 36.7 Å, which indicates that the stacks consist of 2 nm thick nanosheets separated by one monolayer of DDT (the length of a fully extended DDT molecule is 17 Å, including the thiol headgroup).
Supporting Discussion: The crystal structure of the tetragonal Cu$_{2-x}$S phase

The binary Cu-S system has a very rich phase diagram [1], with several families of phases whereby many phases can be considered as polymorphs of each other. In the compositional range of Cu$_{2-x}$S with x = 0.0-0.2, the commonly observed phases are low-chalcocite, high-chalcocite, djurleite, and digenite. All these phases consist of a sub-lattice of S atoms, either in a (distorted) hexagonal close packed (HCP) or a (distorted) face-centered cubic (FCC) sub-lattice, with the Cu atoms occupying various interstitial sites within the S sub-lattice. In general, not all Cu positions allowed by the symmetry in the space group are occupied, leading to a partial occupation of the available Cu atomic sites. For the high-chalcocite phase, it was found both by experiment [2] and by means of quantum mechanical molecular dynamics simulations [3] that the Cu atoms are mobile on their partially occupied Cu sub-lattice, hopping from site to site with very low migration energies, whereby the Cu atoms are behaving as a liquid rather than as a solid [3]. This hybrid solid-liquid property, which likely applies to many more Cu-S phases, makes the structural determination very cumbersome, as the space group and the symmetry operations actually depend on the occupation and ordering of the Cu atoms on their sub-lattice.

Before discussing the structural properties of the nanosheets in detail below, we would like to emphasize that we could not perform a profound determination of the crystal structure, because the nanosheets are too beam-sensitive to acquire a tilt series of electron diffraction patterns. However when comparing our experimental results from XRD, electron diffraction (ED), and HRTEM data with the Cu-S phase diagram [1], the best correspondence is found with the metastable tetragonal phase. The XRD spectrum shows only one peak, which is not sufficient to determine the crystal structure. The ED pattern from a single, flat-lying nanosheet in Fig. 2b (Main text) reveals that the diffraction pattern of the crystal in this orientation is not hexagonal, but rectangular, with two lattice spacings of ~4.1 Å and ~5.3 Å that are perpendicular to each other. This agrees reasonably well with the tetragonal phase with tabulated lattice parameters $a=4.00$ Å, $c=11.3$ Å [1]. This suggests that the $a$-axis and the $c$-axis are in the plane of the nanosheets, while the $b$ axis (which is equivalent to the $a$ axis in the tetragonal structure) is perpendicular to the plane of the nanosheets. It also suggests that the experimentally found $c$-axis is compressed by ~5% with respect to the literature value ($c/2 = 5.3$ Å vs. $c/2 = 5.6$ Å, respectively). Considering that the lattice parameters in Cu$_{2-x}$S structures are dependent on the Cu content [1] and that in these very thin nanosheets the surfaces and surfactants will affect the ‘bulk’ properties, the tetragonal phase is a plausible structure to explain the experimental observations.

In the XRD pattern of Fig. 1d (main text), the peak at 47° corresponds to a spacing of 2.0 Å, which is equal to half the length of the $a$-axis (i.e., it corresponds to a (200) reflection). We mention here that the nanosheets have the tendency to lie flat on the substrate, and therefore the distribution of intensities in the X-ray diffraction pattern will differ from a reference pattern based on powder X-ray diffraction, whereby the crystals are in random orientations. The XRD pattern for digenite is included for comparison in Fig. 1d (main text). We mention here that digenite and the tetragonal phase are polymorphs of each other; they both have an FCC sub-lattice of S atoms and differ only in the ordering of the Cu atoms. The HRTEM image in Figure 2d (main text) shows the nanosheets edge-on, with a spacing of 3.9±0.2 Å perpendicular to the plane of the sheets. This spacing corresponds to the length of the $a$ lattice parameter and with the fact that in this stacking direction, buckled planes of
Cu atoms alternate with planes of S atoms. Because the S atoms are very light atoms in comparison with Cu, the Cu atoms are much better visible in HRTEM images.

Figure S2 below shows an atomic model of the tetragonal Cu$_2$S structure, based on the lattice parameters and a full occupation of atomic sites as provided in the original publication by Jánosi [4]. Figure S2a shows the buckled Cu atomic planes alternated with layers of S atoms. Five buckled planes of Cu atoms are shown, which corresponds to the actual thickness of the Cu$_2$S nanosheets. This image can be directly compared with the HRTEM image of Fig. 2d (main text). In Fig. S2b a [010] projection, corresponding to a flat-lying nanocrystal, is presented. The tetragonal $a$ and $c$ axes are in the plane of view. Now it becomes clear how the Cu$_2$S nanosheets can exhibit a hexagonal morphology: the facets of the hexagon follow the $\{111\}_{S,FCC}$ and $\{001\}_{S,FCC}$ lattice planes of the S sublattice. Compression of the tetragonal $c$-axis as discussed above brings the hexagon closer to a perfect hexagon with angles of 120° (a regular hexagon).

**Figure S2. Atomic model of the tetragonal Cu$_2$S structure.** The brown spheres depict Cu atoms, the yellow spheres S atoms. a) perspective view of the atomic structure with the $b$ axis pointing upward. The buckled Cu layers are visible, corresponding to the atomic layers with dark contrast in the HRTEM image shown in Figure 2d in the main text. b) Projection along the $b$-axis of the tetragonal structure. The tetragonal $a$ and $c$ axes are indicated. It now becomes clear why the outer morphology of the nanosheets can be hexagonal, whereas the crystal structure is tetragonal. The S atoms are on a stretched face-centered cubic (FCC) sub-lattice, and in the [010] projection of the tetragonal structure the S FCC sub-lattice is in a [110] projection, i.e., $[010]_{Cu2S,tetra}/[110]_{S,FCC}$. A hexagon (indicated in white) can then be constructed, following the $\{111\}_{S,FCC}$ and $\{001\}_{S,FCC}$ atomic planes of the S sub-lattice. The S and Cu atomic coordinates as determined by A. Jánosi [4] were used as input for the atomic model.
Figure S3. (a) High-Angle Annular Dark-Field (HAADF)- Scanning Transmission Electron Microscopy (STEM) image of colloidal Cu$_2$S NSs. The square indicates the region selected for elemental analysis. (b) Energy dispersive X-ray spectrum of that area. (c) STEM-EDS quantified chemical maps for Br, S, and Cu. It is clear that Br is present at lower concentrations than Cu and S, and is randomly distributed. The absence of the L$_\alpha$ line of Sn at 3.443 keV shows that the samples are devoid of Sn.
**Table S1.** Summary of the outcome of Cu$_{2-x}$S nanocrystal synthesis carried out under different conditions. In all cases the sulfur source (S-source, 2.1 mmol) was injected in a solution containing all other chemicals at 160 °C. The temperature was subsequently increased to 220 °C and maintained for 40 min. The reference synthesis is highlighted in yellow. Changes with respect to this reference synthesis are indicated in bold blue font. A cartoon representation of the observed shapes and the number of the Figure showing representative TEM images of the samples are given in column “Figure”.

<table>
<thead>
<tr>
<th>Cu-salt</th>
<th>S-source</th>
<th>Sn-salt</th>
<th>Halide source</th>
<th>[TOPO] M</th>
<th>Product</th>
<th>Figure</th>
</tr>
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<tbody>
<tr>
<td>Cu(Ac) 17 mM</td>
<td>DDT</td>
<td>Absent</td>
<td>SnBr$_4$ 5.8 mM</td>
<td>Absent</td>
<td>spherical NCs d= 9 nm</td>
<td>1a</td>
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<td>Sn(Ac)$_3$ 5.8 mM</td>
<td>SnBr$_4$ 0.1</td>
<td>ultrathin hexagonal NSs; w= 2 nm; L= 110 nm</td>
<td>1b, 3a, 4a</td>
<td></td>
</tr>
<tr>
<td>Cu(Ac) 17 mM</td>
<td>DDT</td>
<td>SnBr$_2$ 5.8 mM</td>
<td>SnBr$_4$ 0.1</td>
<td>spherical NCs d= 5 nm</td>
<td>3b</td>
<td></td>
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<tr>
<td>Cu(Ac) 17 mM</td>
<td>DDT</td>
<td>SnBr$_2$ 2.9 mM</td>
<td>SnBr$_4$ 0.1</td>
<td>Irregular and aggregated thin material</td>
<td>S4</td>
<td></td>
</tr>
<tr>
<td>Cu(Ac) 17 mM</td>
<td>DDT</td>
<td>SnBr$_4$ 1.45 mM</td>
<td>SnBr$_4$ 0.1</td>
<td>Nanodisks d= 8 nm; w= 4 nm</td>
<td>3d, S6</td>
<td></td>
</tr>
<tr>
<td>CuBr 17 mM</td>
<td>DDT</td>
<td>Absent</td>
<td>CuBr</td>
<td>ultrathin hexagonal NSs + irregularly shaped thin material</td>
<td>3e</td>
<td></td>
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<tr>
<td>CuBr 17 mM</td>
<td>DDT</td>
<td>Absent</td>
<td>CuBr + NaBr</td>
<td>ultrathin hexagonal NSs</td>
<td>3f</td>
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<td>DDT</td>
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<td>SnBr$_4$ 0.025</td>
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<td>4b</td>
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<td>DDT</td>
<td>SnBr$_4$ 2.9 mM</td>
<td>SnBr$_4$ 0.05</td>
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<td>S8</td>
<td></td>
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<td>DDT</td>
<td>SnBr$_4$ 5.8 mM</td>
<td>SnBr$_4$ 0.020</td>
<td>ultrathin hexagonal NSs; w= 2 nm; L= 2-3 µm</td>
<td>4d</td>
<td></td>
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<tr>
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<td>DDT</td>
<td>SnBr$_4$ 5.8 mM</td>
<td>SnBr$_4$ Absent</td>
<td>ultrathin triangular NSs; w= 2 nm; L= 3-4 µm</td>
<td>4c</td>
<td></td>
</tr>
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<td>Cu(Ac) 17 mM</td>
<td>DDT</td>
<td>SnCl$_4$ 5.8 mM</td>
<td>SnCl$_4$ 0.1</td>
<td>Nanodisks d= 8 nm; w= 4 nm</td>
<td>4e</td>
<td></td>
</tr>
<tr>
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<td>DDT</td>
<td>SnCl$_4$ 17.4 mM</td>
<td>SnCl$_4$ 0.1</td>
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<td>4f</td>
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<tr>
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<td>DDT</td>
<td>Absent</td>
<td>CuCl + NaCl</td>
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<td>S9</td>
<td></td>
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<tr>
<td>Cu(Ac) 17 mM</td>
<td>ODT</td>
<td>SnBr$_4$ 5.8 mM</td>
<td>SnBr$_4$ 0.1</td>
<td>ultrathin hexagonal NSs</td>
<td>S7b</td>
<td></td>
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<tr>
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<td>PET</td>
<td>SnBr$_4$ 5.8 mM</td>
<td>SnBr$_4$ 0.1</td>
<td>irregularly shaped and aggregated thin material</td>
<td>S7a</td>
<td></td>
</tr>
<tr>
<td>Cu(Ac) 17 mM</td>
<td>NDT</td>
<td>SnBr$_4$ 5.8 mM</td>
<td>SnBr$_4$ 0.1</td>
<td>nanoscrolls</td>
<td>S7c</td>
<td></td>
</tr>
<tr>
<td>Cu(Ac) 17 mM</td>
<td>sulfur</td>
<td>SnBr$_4$ 5.8 mM</td>
<td>SnBr$_4$ 0.1</td>
<td>Small and polydisperse spherical NCs</td>
<td>S7c</td>
<td></td>
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</table>

DDT= 1-dodecanethiol; ODT= 1-octadecanethiol; PET= phenylethanethiol; NDT: 1,9-nonanedithiol

[TOPO]= concentration of trioctylphosphine oxide

Ac= acetate
d= diameter; w= thickness; L= lateral dimension
Figure S4. TEM images of the reaction products obtained when SnBr₂ is used instead of SnBr₄. (a) after 10 min of reaction and (b) after 40 min of reaction. Scale bars correspond to 500 nm. These observations are summarized and compared with other syntheses in Table S1.

Figure S5: TEM images of (a) irregularly shaped thin material (EDS ratio Cu:S:Br= 1.41±0.14: 1.0: 0.03±0.01) and (b) well-defined hexagonal NSs (EDS ratio Cu: S: Br= 2.0±0.2: 1.0: 0.30±0.06) obtained when the concentration of SnBr₄ in the reaction medium is halved. Scale bars correspond to 500 nm. These observations are summarized and compared with other syntheses in Table S1.
Figure S6. TEM images of the products obtained when the concentration of SnBr₄ in the reaction is reduced to a quarter of that originally used. Large self-assembled corn cob superlattices, consisting of Cu₂₋ₓS nanodisks, are obtained. Scale bar in (a) corresponds to 200 nm, in (b) to 5 µm.
Figure S7. TEM images of the reaction products obtained using different sulfur sources. All other reaction parameters and chemicals are identical. (a) phenylethanethiol (a bulky and short thiol) yields irregularly shaped and aggregated thin material. (b) 1-octadecanethiol yields hexagonal NSs similar to those formed using 1-DDT, except for the inter-NS separation in the stacks (2 nm, see inset, scale bar corresponds to 50 nm). The longer inter-NS separation is consistent with the increase in length of the alkyl chain from 1.77 nm to 2.5 nm from DDT to ODT. (c) 1,9-nonanedithiol yields irregularly shaped thin material, often rolled up in nanoscrolls. (d) elemental sulfur yields small and polydisperse nanocrystals. These observations are summarized and compared with other syntheses in Table S1.
Figure S8. TEM images of Cu$_2$xS NSs obtained using different concentrations of reagents. (a) 34 mM Cu(acetate), 11.6 mM SnBr$_4$ and 0.2 M TOPO in ODE (total volume: 6.5 mL); injection of 2.1 mmol DDT (concentration 2C$_0$). (b) 8.5 mM Cu(acetate), 2.9 mM SnBr$_4$ and 0.05 M TOPO in ODE (total volume: 25.5 mL); injection of 2.1 mmol DDT (concentration ½ C$_0$). Scale bars correspond to 100 nm. Additional concentrations (C$_0$ and ¼ C$_0$) are given in the main text, Figure 4a,b. The lateral dimensions of the NSs are 110, 110, 210 and 370 nm for concentrations 2C$_0$, C$_0$, ½ C$_0$ and ¼ C$_0$, respectively. These observations are summarized and compared with other syntheses in Table S1.

Figure S9. Low-angle X-ray diffraction (XRD) pattern of a sample of large (~3 µm wide) ultrathin triangular Cu$_2$xS nanosheets deposited from a toluene solution on a silicon substrate. A representative TEM image of this sample is shown in the main text (Fig. 4c). The series of peaks can be ascribed to successive diffraction orders from a periodic superstructure formed by nanosheet stacks. The separation between the peaks (2.49°) corresponds to a periodicity of 36.7 Å, which is the same as that observed for the stacks of smaller (110 nm wide) hexagonal Cu$_2$xS nanosheets (Fig. S1). This shows that the large triangular Cu$_2$xS nanosheets are also 2 nm thick and are coated by DDT. The smaller number of successive diffraction peaks indicates that the coherence length of the stacks is shorter for larger nanosheets, possibly because they consist of just a few nanosheets lying flat on the silicon substrate.
Figure S10. TEM images of Cu$_{2-x}$S NSs obtained using CuCl (instead of Cu(acetate)) and NaCl (instead of SnCl$_4$). Scale bars correspond to 100 nm. These observations are summarized and compared with other syntheses in Table S1.

Figure S11. TEM image of Cu$_{2-x}$S NSs obtained using CuI (instead of Cu(acetate)) and KI (instead of SnCl$_4$). Scale bar correspond to 500 nm.
Figure S12. The reaction between Cu(I)-salts and thiols leads to Cu(I)-thiolates (1:1 stoichiometry) by thiol deprotonation. In the case of alkanethiols a metal-organic framework is formed which is stable as a lamellar solid up to 143.5°C (for Cu-Dodecanethiolate, Cu-DDT), when it undergoes a phase transition to a mesogenic liquid crystal [5]. This phase consists of a hierarchically self-assembled hexagonal columnar mesophase (a), in which each column is made of a stack of tetranuclear [Cu₄(DDT)₄] disks that are kept together by weaker Cu-S inter-disk interactions [5]. The inter-column and inter-disk interactions break at sufficiently high temperatures (205.6°C for Cu-DDT) leading to an isotropic liquid (b) [5]. Figure based on the data published by Espinet et al. [5].
Figure S13. (a-c) TEM images of samples prepared by dissolving metal salts in a solution of 1-DDT in ODE, followed by heating to 190 °C (scale bars correspond to 500 nm): (a) Cu(I)acetate only; (b) mixed Cu(I)acetate and SnBr₄; (c) SnBr₄ only. The samples were taken directly from the reaction mixture and diluted in toluene. The presence of Br clearly affects the long-range morphology and topology of the Cu-thiolate precursor complex at room temperature, converting it from a 3D gel network (a) to irregularly shaped thin sheets (b). It is interesting to note that SnBr₄ and DDT alone are not capable of forming polymeric frameworks (c). (d) Comparison between the absorption spectra of the three samples shown in (a-c) with that of a sample collected 1 min after DDT injection in a solution of Cu(I)acetate, SnBr₄ and TOPO in ODE at 190 °C. It is clear that the absorption peak observed at 375 nm in samples collected during the synthesis of ultrathin Cu₂₋ₓS NSs can be ascribed to a Br-modified Cu-thiolate precursor complex. This corresponds to a shift of 0.34 eV to lower energies with respect to the peak position of the Cu-thiolate precursor, which can be ascribed to the direct coordination of Br to Cu(I) atoms. The changes induced by Br in the optical spectra of the Cu-thiolate framework are discussed in more detail in the main text and below (Fig. S14).
Figure S14. (a) Absorption (Abs), photoluminescence (PL), PL excitation (PLE) spectra and (b) PL decay curve of a sample collected 1 min after DDT injection in a solution of Cu(I)acetate, SnBr<sub>4</sub> and TOPO in ODE at 190 °C. The red line in (b) is a bi-exponential fit to the decay curve. The PLE spectrum unambiguously shows that the PL band at 620 nm and the absorption peak at 375 nm originate from the same compound. As shown in Supporting Figure S12 and Figure 6 in the main text, these optical transitions can be ascribed to a Br-modified Cu-thiolate complex, and are shifted to lower energies with respect to those in the Cu-thiolate complex (viz., shifts of 0.34 eV and 0.48 eV for absorption and PL, respectively). The Stokes shift (1.3 eV) also increases with respect to that observed for the Cu-thiolate framework (1.17 eV). Multinuclear Cu(I) complexes with sulfur or halide donors typically show efficient PL at room temperature, peaking at wavelengths ranging from 500 - 700 nm, depending on the ligands and the structure of the complex or coordination polymer [6]. The PL is often characterized by two independent bands. The high energy PL peak originates from a Cu/halide-to-ligand charge transfer triplet state, while the low energy PL peak originates from a Cu<sub>4</sub>X<sub>4</sub> (X= donor atom, i.e. sulfur or halide) centered triplet state, which is a combination of X to Cu(I) charge-transfer and d-s transitions [6]. The low energy PL has larger Stokes shifts and longer lifetimes than the high energy PL. Moreover, the quantum yield of the high energy PL is lower, making it often absent at room temperature. The peak position, Stokes shift and lifetime (7.8 µs with a faster initial component of 1.8 µs) observed for the Br-modified Cu-thiolate precursor complex are consistent with emission from the low energy state. The large spectral shift can thus be interpreted as evidence that Br coordinates directly to Cu(I) atoms in the Cu-thiolate precursor framework. This is also supported by the dramatic increase observed in the PL QY after Br incorporation, since shorter Cu-Cu distances are known to lead to more efficient PL at RT [6].
Figure S15. Absorption, PL and PLE spectra of ultrathin colloidal CdS NSs obtained by Cu$^+$ for Cd$^{2+}$ exchange in Cu$_{2-x}$S NSs (see Figure 7a in the main text for TEM image). The cation exchange was not complete, leaving a small concentration of Cu in the NSs (ratio Cd: S: Cu: Br= 0.90±0.04: 1.0: 0.06±0.01: 0.03±0.01). The remaining Br is probably at the surface of the NSs. The absorption spectrum is in good agreement with that previously reported by Ithurria et al. [7] for CdS NSs with a thickness of 5 monolayers. This confirms the topotactic nature of the cation exchange, since the parent Cu$_{2-x}$S NSs also consisted of 5 monolayers (see Figures 1-2 and discussion in the main text). Interestingly, the PL of the CdS NSs obtained in the present work is very efficient, but is strongly red shifted with respect to the band edge absorption. This emission can be ascribed to radiative recombination of the exciton in the Cu$^+$ dopants [8]. The good correspondence between the PLE spectrum and the absorption spectrum shows that the Cu$^+$ dopants are populated by exciton transitions in the CdS NSs.
**Supporting References**


