A Stepwise Reaction Achieves Emissive, Ultra-Small Ag₂ZnSnS₄ Nanocrystals

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Abstract

Pirquitasite Ag$_2$ZnSnS$_4$ (AZTS) nanocrystals (NCs) are emergent, lead-free emissive materials in the coinage chalcogenide family with applications in optoelectronic technologies. Like many multinary nanomaterials, their phase-pure synthesis is complicated by the generation of e.g. binary/ternary chalcogenide and metallic impurities. Here, we develop a stepwise synthetic procedure that controls the size, morphology, and transformations of acanthite ($\alpha$-Ag$_2$S) and canfieldite (Ag$_8$SnS$_6$) intermediates. This reaction scheme improves size-dispersity and grants the production of small AZTS NCs ($d$: 2.1-4.0 nm) that have not been achieved through established single-injection procedures—expanding the accessible range of quantum-confined AZTS emission to shorter wavelengths ($\lambda$: 650-740 nm). We show that the initial sulfur stoichiometry is the key handle for template-size tunability and reveal that temporally separating transformation steps is crucial to obtaining AZTS NCs with emission $\lambda<740$ nm. We then use NMR and optical spectroscopies to demonstrate that the installation of thiol ligands improves colloidal stability and photoluminescence, while carboxylate ligands do not. Finally, facilitated by this enhanced synthetic control, we show that our ultra-small AZTS NCs can act as effective, less-toxic sensitizers for red-to-blue triplet fusion upconversion. Our results highlight transferrable insights for the synthesis and post-synthetic treatment of complex less-toxic quaternary nanocrystalline systems.

Key words: kesterite, AZTS, nanocrystals, quantum dots, colloidal synthesis, NMR, triplet fusion
Introduction

The current synthetic control and the understanding of the photophysics of nanocrystals (NCs) has enabled their use in myriad applications including bioimaging, light-emitting devices, and sensing.1–4 Many reports have featured established binary (PbS, CdS/Se, In/GaAs) and, more recently, ternary (CuInS2, halide perovskite) NCs.5 However, these heavily studied systems involve chemical elements where sustainability is a concern, due to questions regarding toxicity or terrestrial abundance.5–6 Consequently, there is a desire to develop new and environmentally friendly alternatives.

For example, quaternary kesterite-Cu2ZnSnS4 (k-CZTS) NCs have been extensively explored as candidate material for photovoltaic and photocatalytic applications due to the earth-abundance and low toxicity of the constituent atoms.7 Unfortunately, k-CZTS can be challenging to employ in optoelectronic applications because of a susceptibility to antisite defects that trap carriers and suppress photoluminescence. These defects form when Cu and Zn switch positions in the lattice, which occurs with a low energy barrier due to their similar ionic radii.8–10 To overcome these drawbacks, NCs composed of the underexplored quaternary silver analog Ag2ZnSnS4 (AZTS) have been recently investigated because of its decreased predisposition to antisite defects.11 Initial reports have confirmed red/near-infrared emission that can be improved through the growth of a ZnS shell, and tuned between 740–850 nm via size-controlled synthesis that exploit quantum confinement.12 This red/near-infrared wavelength range is of particular interest for application such as thin-film photodetectors and NC-sensitized triplet fusion upconversion, where Pb-based NCs have been dominant.1,3,13–15 Thus, AZTS NCs stand as an intriguing candidate for a new generation of greener optoelectronic devices.

Reported synthetic procedures for AZTS NCs vary considerably. For example, current syntheses make use of various temperatures (140–240 °C), different solvents [octadecene,11 oleylamine (OLA),16–17 oleic acid (OA)11], and a number of tin sources [Sn(II) vs. Sn(IV)],11,16,18 each with differing reactivities. The properties and emissivity of AZTS NCs from these various reactions range widely, but the diversity of precursors and solvents blurs a general understanding on the formation mechanism. Such mechanistic understanding is paramount for the controlled growth of high-quality multinary NCs where the larger combinatorial space can allow the formation of undesired phases.19–21 For instance, metallic (e.g. Ag0), binary (Ag2S, SnS, SnS2, ZnS) and ternary (Ag8SnS6, Ag2SnS3) phases could plausibly form during reactions targeting AZTS NCs. Such species can both serve as synthetic intermediates—regulating/complicating the reaction kinetics—as well as unwelcome impurities in the final AZTS product. Therefore, it is important to attain a unified understanding of the effects of solvents, precursors, and intermediate phases to control and direct the formation of phase-pure AZTS NCs.

We recently demonstrated that the synthesis of quaternary CZTS NC polymorphs can be guided by the intentional formation of selected, binary Cu2–xS templates21—in essence achieving a cleaner reaction pathway through a complex material system by removing degrees of synthetic freedom. An advantage to the controlled generation of intermediates is the separation of conversion steps in time to prevent the unintended generation of undesired phases. Further, conversion mechanisms that preserve the size of the parent/templating NC can expand the accessible range of sizes/shapes beyond those easily obtainable directly through a heat-up or hot-injection route.22–23 However, the existence and relevance of intermediates in the synthesis of AZTS is not yet clear, even though some binary/ternary phases have been reported as impurities in the final product.17 Particularly, no
Ag₂S intermediates have yet been identified, though Ag₂S impurities have been detected in the mechanochemical synthesis of Ag₂FeGeS₄, a similar crystalline system. These observations raise the possibility to implementing a template-guided synthesis of AZTS NCs, particularly considering the well-established cation exchange procedures in the copper analog system.

In addition to the advantages provided through synthetic control by templated reactions, post-synthetic processing is essential to the use of NCs in many optoelectronic technologies because many photophysical properties are strongly correlated to the surface chemistry. Then, the development of strategies for post-synthetic modification is aided by an understanding of ligand binding motifs through which ligands interact with the surface of NCs. However, experimental explorations of the surface chemistry of AZTS NCs have not been reported. Indeed, this surface is expected to be complex. For instance, we and others have shown that the binding motifs of simpler binary NCs are already heterogeneous. In addition, the Hens group has reported that the surface chemistry of ternary nanocrystals of In(As,P) and CuInS₂ show increased complexity that depends on multiple parameters (e.g. stoichiometry, shape, and local variation in binding/ligation at facet-edges and apices). Quaternary NC systems bring further complications as every additional metal element combinatorically expands the accessible multi-metallic co-ordination environments. Thus, the surface chemistry of AZTS NCs is expected to be rich, so improved understanding can guide the development of tailored ligand exchange reactions to support their implementation in technologies.

Nuclear magnetic resonance (NMR) spectroscopy is particularly useful to probe the surface chemistry of NCs. We summarize key techniques that we employ in our experiments, and refer the reader to established texts for comprehensive discussion. For example, the linewidth broadening of features in ¹H NMR can differentiate ligands that are anchored to the surface of NCs from those free in solution. Then, diffusion-ordered spectroscopy (DOSY) can corroborate and extend this understanding, allowing a distinction between rapidly diffusing ligands that are free in solution, and the slowly diffusing ligands that are bound to the surface. Other techniques that are particularly useful in our studies are nuclear Overhauser effect spectroscopy (NOESY) and rotating-frame nuclear Overhauser effect spectroscopy (ROESY). Through NOESY, the interaction of ligands with the surface of NCs can also be inferred. The nature of the measurement (i.e. the NOE) stems from a transfer of magnetization between spin pairs that are in close physical proximity to one another. That is, if the magnetization of one such spin is perturbed from equilibrium, it will have a detectable effect on the other. This magnetization transfer selectively gives rise to off-diagonal cross-peaks in the 2D NOESY spectrum with frequencies that correspond to interacting on-diagonal resonances. Particular NOE enhancements depend on the dipolar relaxation pathways, which operate to a different extent for free and bound ligands. Specifically, two types of relaxation are considered, the double- and the zero-quantum transitions. These relaxation pathways have a molecular tumbling dependence, so one will dominate over the other depending on (among other parameters) the viscosity of the solvent and the effective solvodynamic size of system containing the relevant paired spins. The double-quantum transition (W₂) is favoured in fast-tumbling molecules (i.e. those free in solution at ambient temperatures), and it will generate a positive NOE enhancement. Conversely, the zero-quantum transition (W₀) is preferred in slow-tumbling molecules (e.g. ligands anchored to the NC surface) and will result in negative NOE enhancements. In principle, the overall sign and magnitude of the resulting cross-
peak broadly depends on which effect dominates, and the latter cross-peaks arising from zero-quantum processes are referred to as negative cross-peaks by convention, even though they exhibit the same sign as the on-diagonal peaks.\textsuperscript{39}

However, unambiguous interpretation of NOE experiments benefits from an additional step. This is first because the build-up time of the double-quantum transition under usual conditions is much longer relative to the zero-quantum transition, so the former enhancements are generally overpowered by the zero-quantum signal when both fast and slow tumbling molecules are present. Additionally, molecules undergoing chemical exchange (\textit{e.g.} ligands binding to/detaching from the NC surface) can also give rise to overlapping negative cross-peaks. The practical consequence is that it is challenging to distinguish between bound ligands (negative NOEs) and those undergoing chemical exchange using NOESY alone.

To ease the interpretation, ROESY is used to distinguish negative NOESY cross-peaks that arise from ligands interacting with the surface of the NC from those signals stemming from chemical exchange.\textsuperscript{37} In ROESY experiments all NOE-type cross-relaxation rates between homonuclear spins remain positive for all tumbling rates (\(\tau_c\)), while chemical exchange-type processes continue to show as a negative cross-peaks. This is achieved by working in the rotating frame where the effective field is decreased to a few kilohertz (\textit{vs.} megahertz in NOESY). These conditions significantly diminish the spectrometer observation frequency (\(\omega_0\)), making the ROE variation with the molecular tumbling rate (\(\omega_0\tau_c\)) in the same regime (\textit{i.e.} giving positive enhancements) for all realistic tumbling rates.\textsuperscript{39, 41} Essentially, fast and slow-tumbling species will both behave as if they were rapidly rotating, allowing transitions associated with both NOE-type quantum cross-relaxations to build up comparably.\textsuperscript{42-43} Hence, overall, cross-peaks that have signs that change phase between ROESY and NOESY spectra from a system reflect molecular ligands that are indeed interacting with the surface of a slowly-tumbling NC, while signals with same (positive) sign in both measurements reflect moieties that are interacting by other mechanisms, such as chemical exchange.

Surface chemistry studies are particularly useful to improve the performance of technologies that rely on tailored surface functionalization. For instance, triplet-fusion upconversion is an approach to generate high-energy photons from longer-wavelength light.\textsuperscript{44} It is based on the coalescence of two spin-triplet molecular excitons to create one higher-energy singlet, which can then fluoresce. Effective performance at modest excitation intensities is possible because molecular triplets can be very long-lived (\(>>\mu\text{s}\)), allowing a large concentration of triplets to build up such that bimolecular fusion outcompetes monomolecular triplet decay. Triplet-fusion upconversion is of interest for applications including bioimaging and \textit{in situ} photochemistry, exploiting the superior penetration of \textit{e.g.} biological tissue by longer-wavelength light.\textsuperscript{1, 3, 45-48} However, because direct triplet photoexcitation is spin-forbidden in relevant molecular systems, leading upconversion systems use external sensitizers that can efficiently generate triplet states.\textsuperscript{49} NCs can be used as triplet-sensitizers,\textsuperscript{3, 50-51} taking advantage of their large molar absorption coefficients, spin-mixed band-edge states, and functionalizable surface.\textsuperscript{52} Leading strategies further improve upconversion performance \textit{via} the extraction of photoexcitations from the NC to the surface ligands.\textsuperscript{53} Examples of such upconversion systems employ PbSe,\textsuperscript{50} PbS,\textsuperscript{3, 54} CdSe,\textsuperscript{51} and CuInS\textsubscript{2} NCs,\textsuperscript{55} each of which contains chemical elements that are either toxic or poorly abundant. Thus, more-sustainable
alternatives could advance the implementation of NC-sensitized triplet fusion upconversion technologies.

Here, we report a synthetic approach that yields Ag$_2$ZnSnS$_4$ NCs with improved control of size, morphology, and phase purity. Supported by our mechanistic investigations, we designed a synthetic procedure that controllably forms the key reaction intermediates in situ in a stepwise fashion, passing through acanthite ($\alpha$-Ag$_2$S) and canfieldite (Ag$_6$SnS$_8$) phases that template the ultimate phase-pure pirquitasite (Ag$_2$ZnSnS$_4$) product. Purity of the AZTS product is also aided by rapid heating and a low reaction temperature (<80 °C) to avoid the unwanted reduction of the silver precursor. Vitally, our stepwise synthetic route ensures sulfur-poor conditions during the formation of the $\alpha$-Ag$_2$S intermediate, favouring the morphology that is then a superior template for AZTS NCs. We substantiate this approach and confirm the key intermediates by mapping the stepwise evolution of the reaction using X-ray diffraction, Raman measurements, optical spectroscopy, and electron microscopy. Taken together, our experiments reveal that separating the conversion steps in time is crucial to obtaining small AZTS NCs with emission < 740 nm.

We then gain insight into the surface chemistry of AZTS nanoparticles and are able to modify their surface to improve their photophysical performance. Through surface and optical studies, we demonstrate that thiols are an effective post-synthetic additive that can enhance both the colloidal stability and the optical properties of AZTS NCs by displacing native OLA ligands in an L-for-L exchange. Conversely, through 1 and 2D $^1$H NMR, we show that the introduction of carboxylic acids indirectly pulls dynamically bound OLA ligands from the surface of the NCs, inducing significant aggregation. Finally, in a demonstration of the significantly improved size control and photophysical properties these less-toxic/earth-abundant AZTS NCs, we show the capability of our NCs to act as sensitizers for red-to-blue triplet-fusion upconversion.
Results/Discussion

Ag NPs at the early stages of the reaction affect the resulting phase purity of AZTS NCs

With the overall goal of understanding the synthesis of AZTS NCs, we first sought to identify any significant transformations that might take place prior to sulfur injection. Particularly, amine solvents are known to reduce metal precursors, and can result in the generation of metallic nanoparticles.\textsuperscript{21,56} Then, metallic silver NPs are known to form readily in reducing conditions,\textsuperscript{57-59} and Ag\textsuperscript{+} has the lowest reduction potential of the three metals used in the AZTS reaction. Accordingly, we studied the interaction between the silver precursor and OLA in isolation. A solution of Ag(OAc) in OLA was gradually heated (5 °C/min) to 180 °C and aliquots were withdrawn at 10 °C increments and placed in vials at room temperature (Figure S1a, See Methods for details on materials and procedures). We observed that the colour of the reaction changed from pale yellow to dark red/brown, consistent with the formation of Ag NPs, and in agreement with previous comparable reports. We confirmed the nature and size of the metallic Ag NPs using UV-Vis, PXRD, and TEM (Figure S1). Our experiments showed that Ag\textsuperscript{0} can form under conditions similar to AZTS reactions at temperatures as low as 50 °C.

Then, we investigated the implications of the presence of Ag NPs in the formation of AZTS NCs by designing a AZTS synthesis that would enhance the pre-injection formation of Ag NPs. This was inspired by the demonstration by Ning and Zou that Ag NPs promote the formation of Ag\textsubscript{3}SnSe/Ag\textsubscript{2}S heterostructures.\textsuperscript{60} Specifically, we brought a solution of Ag(OAc) in OLA to 100 °C, and held it at this temperature for 3 minutes. This extended heating caused a pronounced colour change (Figure S1a), consistent with reduced silver, and we identified large (~15 nm) nanoparticles in TEM images taken subsequently (Figure S1b). The temperature was then decreased to 80 °C, and the remaining precursors needed to synthesize AZTS (i.e. TMS-S, SnCl\textsubscript{4}, and Zn(OAc)\textsubscript{2}⋅2 H\textsubscript{2}O, See Methods) were injected to this mixture. Aliquots were taken periodically for 180 minutes following the injection and were placed in vials for further characterization.

We observed considerable evidence that AZTS NCs are produced in this reaction, but that the presence of Ag NPs affects the formation of AZTS NCs. Optical spectra from aliquots include the characteristic emission of AZTS NCs,\textsuperscript{11} and progressively red-shift as the particles grow (Figure S2c and d). From the aliquot taken 10s post-injection, the emission peak is at 660 nm. This is a shorter wavelength than achieved in previous reports. Thus, these data highlight that reaction quenching at early times is a route to generating ultra-small AZTS NCs. However, at these early times in the Ag NP-containing reaction (e.g. 10 s aliquot), we noticed a red-shifted shoulder that correlates with the emission of α-Ag\textsubscript{2}S NCs.\textsuperscript{61} This indicated a mixed composition, and prompted further characterization to identify impurities. For example, Raman measurements from the 10s aliquot show a pronounced peak at 309 cm\textsuperscript{-1} that is absent in the control reaction where the formation of Ag NPs is repressed (Figure S2a). This peak indicates the presence of canfieldite Ag\textsubscript{3}SnSe\textsubscript{6} (ATS) in the reaction products at this time.\textsuperscript{62} Additional features are observed at (91 cm\textsuperscript{-1}), a known mode in α-Ag\textsubscript{2}S, which is also consistent with partial conversion. TEM images of these early-time products show worsened size-dispersity compared to the control reaction and the presence of larger, high-contrast particles (Figure S2b). Thus, though these data highlight that reaction quenching at early times is a route to generating ultra-small AZTS NCs, they indicates
that the suppression of Ag NPs. Thus, for reactions that seek to make small particles by quenching shortly after sulfur injection, it is desirable to suppress the (pre-injection) formation of metallic Ag NPs to yield AZTS with improved phase purity and size dispersity.

**Sulfur stoichiometry modulates α-Ag$_2$S template morphology, which impacts AZTS phase-purity**

Continuing our efforts to design a synthesis of ultra-small AZTS with high phase purity, we next explored the influence of sulfur stoichiometry on the formation and nature of α-Ag$_2$S intermediate species. We drew insight from previous studies of related materials with anisotropic intermediates and a final cation-exchange step, where it was shown that uneven diffusion of cations from reactions that proceed from a facet or edge can lead to incomplete, morphology-dependent exchange. A particularly relevant example in the silver chalcogenide family is the formation of Ag$_3$SnSe$_6$ crystals, where large Ag$_2$Se networks have been observed to prevent the full incorporation of Sn$^{4+}$. Analogous α-Ag$_2$S networks have been identified in the synthesis of α-Ag$_2$S NCs. Thus, in the synthesis of AZTS, we suspected that the formation of α-Ag$_2$S networks could lead to an inhomogeneous conversion upon Sn$^{4+}$ and Zn$^{2+}$ injection, and hypothesized that their suppression can be beneficial to the synthetic quality of the final multinary product. Notably, the stoichiometric precursor ratios for the overall synthesis of AZTS are very sulfur-rich with respect to the initial formation of binary α-Ag$_2$S particles. These conditions enhance network formation in the targeted synthesis α-Ag$_2$S NCs, so we expected that single-injection syntheses of AZTS would be prone to form intermediate α-Ag$_2$S networks.

To test this hypothesis, we synthesized α-Ag$_2$S networks in situ using sulfur-rich conditions (1:2 Ag:S, stoichiometric ratio in the Ag$_2$ZnSnS$_4$ system) and contrasted this with a reaction with 1:0.41 Ag:S designed to generate a sulfur-poor environment in the initial nucleation period. To gain insight into the dynamic reaction conditions and evaluate the size and morphology of prompt α-Ag$_2$S intermediates, we used a syringe pre-filled with cold EtOH to withdraw an aliquot from each reaction immediately following TMS-S injection (See Methods). These aliquots were dispensed into a vial, centrifuged, and the pellet was re-dispersed in toluene for TEM and PXRD analysis. TEM images from the sulfur-rich synthesis show large, irregular networks (20-100 nm, Figure 1a), while the PXRD diffractogram displays sharp reflections that match the α-Ag$_2$S pattern (Figure S3a). Thus, we concluded that the traditional reaction stoichiometry for AZTS forms large α-Ag$_2$S networks in situ at 80 °C. In sharp contrast, comparable TEM imaging of the sulfur-poor reaction (Figure 1d) did not detect large α-Ag$_2$S networks, suggesting that their formation had been effectively restrained. Instead, we observed the formation of smaller, well-separated NCs with a well-defined average size of 3.4 ± 0.6 nm (Figure 1d). PXRD on these samples reveals broadened reflections that are consistent with small α-Ag$_2$S crystallites (Figure S3a). As discussed above, we expect that small crystallites would be superior templates (relative to large networks) for the formation of phase-pure ultra-small AZTS NCs, so we pursued this strategy.

Then, to assess the effect of α-Ag$_2$S networks on the overall synthesis of AZTS, we carried on with the two syntheses described above (sulfur-rich and -poor) by injecting the Sn$^{4+}$ and Zn$^{2+}$ precursors. We monitored the progress of the reactions by taking further aliquots (See Methods).
These mixtures were emissive, so optical spectroscopy gave immediate insight (Figure S3b). Upon the injection of the Sn and Zn sources into the sulfur-rich reaction, we noticed a broad emission feature in the 700–900 nm range that evolved over the course of the reaction (Figure S3b). Emission from both AZTS and α-Ag$_2$S NCs has been reported in this general range. This differed from our observations in the sulfur-poor reaction (Figure 2d), where the emission was narrower, with a clear peak that evolved from 650 to 790 nm as the reaction progressed. TEM images of the sulfur-rich reaction show a range of structures (*i.e.* pseudo-spherical particles with surrounding residues and larger irregular structures) where the familiar α-Ag$_2$S networks appear to be breaking apart (Figure S4). This indicates mediocre size dispersity and elevated phase impurities in the final product. Raman measurements from either synthesis confirm the formation of AZTS via the signal at 365 cm$^{-1}$ and the strong signal at 345 cm$^{-1}$, assigned to the A$_1$ mode stemming from the symmetric motion of S atoms (Figure 1b,c) in AZTS. However, the spectra from the sulfur-rich synthesis (where α-Ag$_2$S are prominent) show additional features that correspond to the expected impurities. For instance, we recognize a prominent mode at 93 cm$^{-1}$ in the sulfur-rich reaction that corresponds to α-Ag$_2$S. This implies slowed conversion to the pure quaternary phase, consistent with our hypothesis that large networks hinder cation diffusion and inconveniently provoke an anisotropic conversion. Further, even 30 minutes into the sulfur-rich reaction, we observe modes at 230, 265, and ~309 cm$^{-1}$ that are associated with ATS, indicating that Zn incorporation is hindered, and that persistent ternary impurities form when α-Ag$_2$S networks are present. Taken together our observations link the presence of large α-Ag$_2$S networks during the initial nucleation of binary templates and poor phase-purity of the desired AZTS product.
A stepwise reaction achieves ultra-small AZTS NCs

Building from these results, we considered strategies to mitigate the effect of large α-Ag$_2$S networks to achieve the synthesis of phase-pure, ultra-small AZTS NC. For instance, increasing the temperature has been shown to speed the digestion of α-Ag$_2$S networks.$^{66}$ Indeed, we note that previous syntheses of AZTS use elevated reaction temperatures (150-200 °C), which approach the polymorphic transition to argentite (β-Ag$_2$S) in the bulk system.$^{72}$ However, as we demonstrated above, reaction temperatures above 80 °C trigger the appreciable reduction of the silver precursor. Alternatively, prior work on the intentional synthesis of α-Ag$_2$S NCs showed that an extended reaction time can remove large networks.$^{67}$ We tested this, and confirmed that allowing the sulfur-rich, α-Ag$_2$S-network-forming reaction to proceed at 80 °C for 30 minutes eliminates networks and forms large α-Ag$_2$S NCs (Average size: 4.4 ± 0.5 nm, Figure S5a), likely through a non-classical growth mechanism.$^{68}$ However, when we subsequently converted these large, ripened templates to AZTS, we could only obtain NCs that emit at wavelengths longer than 725 nm, consistent with large particles (Figure S5b). This aligns with the slow reaction kinetics that we observe in single-injection reactions to form AZTS NC, where infrared emission spectra at early times (e.g., 10s) prominently indicate the presence of α-Ag$_2$S, but do not yet exhibit significant emission from quaternary AZTS (Figure S6a and b). Indeed, in single-injection reactions it took >15 minutes for the emission spectrum to predominantly resemble AZTS—with a peak at 780 nm that again pointed to large NC products (>4.5 nm) with relaxed quantum confinement (Figures 2a, b, and S6c). Therefore, we concluded that an extended growth period can improve phase-purity, but it is counterproductive to achieving a small α-Ag$_2$S NCs template (<~3.5 nm) for the subsequent conversion to strongly confined AZTS NCs.

Instead, inspired on our study of the formation mechanism of quaternary Cu$_2$ZnSnS$_4$ NCs$^{21}$ and the reported morphologies of Ag$_2$S templates,$^{67-68,73}$ we designed a synthetic route to yield smaller AZTS NCs with improve phase purity and better size and morphological control. Our approach was to manage the stepwise progression through the key intermediates—binary (α-Ag$_2$S) and ternary (ATS)—while suppressing both the formation of metallic Ag NPs as well as large α-Ag$_2$S networks. With this aim, we developed and explored a synthetic route based on a non-conventional quadruple injection approach (Scheme 1, Figure S7). In the first step, we exploit sulfur-poor reaction conditions to access optimal α-Ag$_2$S templates. In the second step, we then supply Sn and additional S to form the canfieldite phase (ATS), targeting a clean transformation. As a final step, we add Zn to induce the complete conversion from ATS to pirquitasite (AZTS). We provide full details in Methods, but summarize the approach and results here.

Broadly, the Ag precursor in OLA is placed and heated in a flask before additional precursors are added via four consecutive injections within ~4 seconds. Rapid heating (12 °C/min) from the start of the reaction is essential to lessen the unwanted reduction of Ag$^+$. The first injection introduces a fifth of the total equivalents of sulfur in the form of TMS-S in toluene. As discussed previously, this has the advantage of allowing the α-Ag$_2$S template to form under sulfur-poor conditions at 80 °C. The next two injections (Sn$^{4+}$-OLA and additional TMS-S in toluene respectively) form the ATS phase and supply enough sulfur to satisfy the stoichiometry of the final AZTS product. The precursors for these effectively successive injections are kept separate to avoid the formation of
We found that this injection approach.

Characterizing the synthesis at this point, we establish the formation of ATS via the strong Raman signal at 309 cm\(^{-1}\) (Figure S8a) and PXRD measurements that match the reference pattern for canfieldite (ATS, Figure S8b).\(^{74-75}\) Further, we confirm that the conversion is blocked if no additional TMS-S is added alongside the Sn (Figure S9). Thus, we consider that Sn\(^{4+}\) ions are added into the lattice along with at least two S\(^{2-}\) ions in order to meet the tetrahedral geometry of the ternary and quaternary phases, in a similar mechanism to that of Cu\(_2\)ZnSnS\(_4\) NCs.\(^{76-77}\) The last injection of Zn\(^{2+}\)-OLA generates the final quaternary AZTS product, which we confirm via Raman (Figure 1d, S10a) and PXRD (Figure S10b). We found that a separate injection is needed, because injections of pre-mixed Sn and Zn precursors yield \(\alpha\)-Ag\(_2\)S only, with no signs of AZTS emission (Figure S11). Lastly, we tested our strategy by performing the reverse quadruple injection, where the Zn precursor is injected before the Sn. We found that this only yields poorly emissive species that are not consistent with AZTS (Figure S12). This can also be understood by analogy to Cu\(_2\)ZnSnS\(_4\) NCs\(^{76-77}\) due to the similar role of Sn\(^{4+}\), facilitating the subsequent integration of Zn\(^{2+}\) through the addition of S\(^{2-}\) into the lattice.

To evaluate whether this quadruple-injection approach permitted the synthesis of ultra-small, phase-pure particles, we first focussed on reactions that were quenched 10 seconds after the final precursor injection. (See Methods) Following two-step size-selective centrifugation with ethanol antisolvent, TEM of the product revealed ultra-small NCs (2.1 \(\pm\) 0.3 nm diameter \(\lambda_{\text{em}} = 650\ nm\), Figure 2a, c, and d). Despite the smaller particles, this relative size dispersity compares favourably to previous reports.\(^{11}\) Raman measurements of the final product match AZTS, showing a strong signal at 345 cm\(^{-1}\), associated to the A\(_1\) mode (Figure 1).\(^{78}\) This signal is relatively broad, consistent with phonon confinement effects, and contributions from other known modes for this phase 298 cm\(^{-1}\) (A\(_1\), very weak), 270 (B\(_1\), medium), and 216 cm\(^{-1}\) (E, weak).\(^{78}\) No prominent impurity modes from ternary (ATS, 309 cm\(^{-1}\))\(^{62}\) or binary (Ag\(_2\)S 91, Sn\(_2\)S 218/318, ZnS 278/351 cm\(^{-1}\))\(^{79}\) species are observed, indicating a phase-pure product. PXRD diffractograms of the AZTS product are broadly consistent with the reference pattern for the tetragonal phase (Figure S10b). However, disambiguation from ternary ATS (309 cm\(^{-1}\)) is challenging due to the considerable breadth of reflections from these NCs (which comprise 16 unit cells on average, unit cell parameters: \(a\sim1.1\) and \(b=c\sim0.5\ nm\)),\(^{11}\) and the possibility of nano-scale strain. Taken together, these data confirm that we can obtain phase-pure, ultra-small AZTS NCs with improved size-dispersity via the quadruple-injection approach.

**Scheme 1.** Cartoon depicting the quadruple-injection sequence designed for the one-pot synthesis of Ag\(_2\)ZnSnS\(_4\) nanocrystals to achieve sulfur-poor conditions for the initial formation of binary \(\alpha\)-Ag\(_2\)S intermediates. Sn\(_x\)S impurities.
We then characterized the optical properties of the AZTS NCs synthesized through our quadruple-injection method. Optical absorption spectra show shoulders consistent with a excitonic feature with a peak wavelength that is <600 nm initially (i.e. 10 s after injection) and then progressively red-shifts towards λ: 700 nm over the reaction. (Figure 2c) This matches expectations for the growth of quantum-confined particles. Most notably, photoluminescence spectra from AZTS NCs obtained 10s after injection exhibit a prominent feature centered at 650 nm (Figure 2d). This is a considerably shorter emission wavelength than previous reports (cf. 740 nm),11-12 and is consistent with strong quantum confinement in ultra-small particles. The emission spectra also show a slight shoulder near 800 nm (consistent with α-Ag2S, vide supra) that is observable in the 10s aliquot,
but is no longer observed 5 minutes after injection. This agrees with the rapid formation of phase-pure AZTS from $\alpha$-Ag$_2$S NCs, which is corroborated by Raman spectra that show the growth of an intense AZTS peak (345 cm$^{-1}$) over this period. The shape and evolution of the optical spectra following the quadruple injection differ strongly from the single-injection reaction (Figure 2b). There, the feature near 650 nm is absent in the aliquot at 5 minutes (as well as earlier times when overall emission is very weak Figure S6a), and we instead see considerable photoluminescence beyond 800 nm. These observations match the expected effects of persistent, large $\alpha$-Ag$_2$S networks (vide supra), and demonstrate an advantage of the quadruple-injection approach.

Further, we find that the quadruple-injection strategy for AZTS NCs achieves phase and morphological purity at significantly lower reaction temperatures compared to the 140–220 °C used in previous reports.\textsuperscript{11,16-17,70,80} Indeed, we found that 80 °C was an optimal temperature to avoid the formation of impurity phases (e.g. Figure 1d, S13) while controllably obtaining small AZTS NCs e.g. average sizes between 2.1 ± 0.2 (Figure 2a) and 4.5 ± 0.6 nm (Figure S14), corresponding to peak emission wavelengths between 650–790 nm (Figure 2d). We could controllably obtain larger NCs (e.g. 6.7 ± 0.8 nm, $\lambda_{\text{PL}}$: 820 nm) by injecting at 80 °C, and then increasing the temperature to 120 °C (Figure S15). In contrast, temperatures lower than 80 °C results in a much slower growth (Figure S16.) While we could detect the formation of ultra-small AZTS NCs at temperatures as low as 40 °C (Figure S16), Raman data shows that ATS impurities are already noticeable in the early time aliquots at 70 °C (Figure S17). Thus, when seeking the smallest particles via reactions quenched shortly after injection, we find that a temperature of 80 °C is optimal to ensure rapid, complete full conversion to the AZTS phase. Interestingly, a previous study on the solvothermal synthesis of macroscopic Ag$_8$SnS$_6$ crystals found that this related reaction also does not proceed at temperatures below 80 °C.\textsuperscript{81} Taken as a whole, our data confirms that a quadruple-injection procedure allows access to smaller particles than previous reports, moving the short-wavelength bound of the emission range from 740 to 650 nm. We also show that this informed reaction design yields improved size-control and dispersity relative to single-injection syntheses, by efficiently guiding the conversion from $\alpha$-Ag$_2$S to AZTS NCs through intermediate phases.

\textit{Understanding surface chemistry to improve the colloidal stability of AZTS NCs}

We observe that the surface of AZTS NCs synthesized in OLA is highly sensitive to purification. For example, during washing, we find that the addition of ethanol antisolvent beyond the minimum required to form a pellet yields a precipitate that is not directly redispersible in toluene (See Methods). We interpret this as evidence for induced aggregation, which is consistent with a dynamic surface due to ligand self-exchange, as seen in other NCs with OLA passivation.\textsuperscript{82-83} We sought information to aid the design of a surface passivation procedure that would better colloidally stabilize the small AZTS NCs (2.7 ± 0.4 nm, Figure S18) while enhancing their optical properties. Therefore, we used NMR experiments to understand the types of ligand binding at the surface. As we discuss in the introduction, a key aspect of NMR experiments on NCs is that they can distinguish between bound and free-floating ligands because e.g. the limited mobility and
slower tumbling of surface-anchored molecules leads to significant broadening of their $^1$H NMR features relative to the same molecules in free solution.\textsuperscript{37,84}

We first explored the surface of as-synthesized AZTS NCs with their native OLA ligands, dispersed in toluene-$d_8$.\textsuperscript{1}H NMR experiments (Figure 3a) show the broadening of $\alpha$-H (3 ppm), aliphatic protons ($\sim$1.4 ppm), and olefinic protons (5.55 ppm), relative to the same features in well-solvated (free) OLA. This indicates a degree of binding. Nonetheless, these features appear at lower ppm (e.g. olefinic at 5.55 ppm) compared to other NC systems where OLA and oleic acid (OA) are tightly bound (>5.60 ppm).\textsuperscript{36,85} This is additional circumstantial evidence that OLA on as-synthesized AZTS NCs is in a dynamic absorption/desorption exchange. Further evidence for the dynamic binding of OLA species on AZTS NCs was provided by 2D NMR techniques. We first used diffusion-ordered spectroscopy (DOSY) to monitor the $^1$H resonances associated with OLA (Figure 3b). Then, we used the Stokes-Einstein equation to extract a diffusion coefficient, D

\textbf{Figure 3.} $^1$H NMR characterization for as-synthesized AZTS NCs. a) 1D spectra of native NCs (blue trace) display resonances that correspond to the OLA reference spectrum (red trace), but are broadened. This is consistent with ligands bound to the surface of slowly-tumbling NCs, indicating that as-synthesized AZTS are passivated with OLA. †This feature arises from residual ethanol from purification. b) Corresponding DOSY spectrum for native NCs show that OLA molecules diffuse more slowly than e.g. solvent molecules, corroborating OLA binding to the NC surface.
(230 \mu m^2 \cdot s^{-1}), which in turn equates to a solvodynamic diameter of 3.3 nm in toluene (See Section S2). This is smaller than the predicted size of the particles with OLA ligands (5.7-6.7 nm), taking the chain length as 1.5-2 nm.\footnote{35} However, these ostensibly counterintuitive results are in line with previous reports on dynamic surface passivation, where the measured diffusion coefficient of amine ligands is an average over the exchanging populations of free and bound species.\textsuperscript{35,37} Then, we identified negative cross-peaks in the NOESY spectrum of native OLA AZTS NCs for the olefinic and aliphatic protons, indicating that the broadened resonances observed through \(^1\)H NMR have negative NOE enhancements (Figure S19a). These peaks change sign in the ROESY spectrum, confirming that some ligands are indeed interacting with the surface (Figure S19b). We also find weak, negative cross-peaks along the diagonal of the ROESY spectrum, showing that a portion of ligands are also undergoing an adsorption/desorption exchange.\textsuperscript{39,42-43} Taken together, our suite of NMR measurements corroborate our qualitative observations on the sensitivity of the NCs to purification, and we thus we conclude that the binding of OLA ligands to the surface of AZTS NCs is dynamic.

Our first attempt to understand the dynamic binding of OLA in as-synthesized AZTS NCs and ultimately generate tighter binding motifs was inspired by recent work on related materials. Specifically, while L-type binding for OLA is a common motif on semiconductor NCs, it was shown by Dierick (Hens) and co-workers that binding on the surface of CuInS\(_2\) NCs is heterogeneous, and that shorter-chain, anionic impurities from the OLA solvent (\textit{e.g.} OH\_) can bind to the surface.\textsuperscript{87} These X-type impurity species could be removed via exchange with a different X-type ligand, such as a long-chained carboxylic acid, and this improved the colloidal stability of CuInS\(_2\) NCs.

For AZTS NCs, we hypothesized that such short, molecular impurities, in addition to Cl\(^-\) ions from the Sn precursor, could be bound to the surface of as-synthesized AZTS NCs and contribute to their poor colloidal stability. A heterogeneous binding environment would reflect the complexity of such a quaternary system, particularly where the structure of the surface is unclear—including the identities and oxidation states of atoms at any terminal facets and edges. Thus, we investigated an X-for-X exchange procedure on the surface of AZTS NCs, targeting increased colloidal stability. Experimentally, we titrated OLA-passivated AZTS NCs with undec-10-enoic acid (UDA). This ligand was used instead of more-common OA additive because, while UDA and OA have the same head-groups and similar aliphatic tails, UDA has a distinct vinylic NMR resonance that allows it to be readily distinguished from OLA.\textsuperscript{30}

We first observe through DOSY experiments that overall ligand binding of UDA-titrated NCs remains dynamic (Figure S20c). For instance, the effective solvodynamic diameter that we extract for bound UDA is smaller than measured previously for bound OLA features in as-synthesized NCs (1.3 vs. 3.3 nm, where the NC core is 2.7 nm and the expected diameter with extended UDA ligands would be ~5 nm). This indicates that UDA is not providing a stronger binding motif through the replacement of X-impurities, but that it is instead involved in a dynamic interaction with the surface. We then identify that UDA can protonate OLA and form OLA\(^+\) species that can interact with the surface (See Figure S20 and S21). This is consistent with the binding of X-type ligands as overall-neutral, ion pair ligands (\textit{e.g.} OLA\(^+\) UDA\(^-\)).\textsuperscript{88-89} Further, we recognize
clear evidence of NC aggregation at high UDA concentrations (Figure S23). A plausible passivation scheme that rationalizes this aggregation is the net depletion of the neutral OLA available for (dynamic) L-type binding via the formation of OLA\textsuperscript{−}−UDA\textsuperscript{−} adducts—which themselves only loosely bind to the heterogeneous surface motifs of AZTS NCs. Still, we cannot rule out some minimal X-type (UDA\textsuperscript{−}) exchange with impurity-type ligands, and we discuss possible alternative exchange mechanisms in Supporting Section A. In sum, our experiments show that the addition of carboxylic acids has overall-negative repercussions on the colloidal stability, perturbing the binding equilibrium and inducing the aggregation of AZTS NCs.

Seeking a less-disruptive ligand exchange procedure to enhance the colloidal stability of as-synthesized (OLA-passivated) AZTS NCs, we pursued an exchange with thiols. This choice of ligand was guided by previous reports on L-type interactions with Ag in metallic, Ag\textsubscript{2}Se NCs.\textsuperscript{90-92} These studies demonstrated that thiols bound preferentially to amines, so long-chained thiols could replace dynamically bound OLA and increase the colloidal stability. In addition, long-chain alkylthiols have a much higher pK\textsubscript{a} (~10.6)\textsuperscript{93} compared to carboxylic acids (~4.5), which we expected would reduce the troublesome formation of the ion-pair adducts (e.g. OLA\textsuperscript{−}-thiolate) that promote the aggregation of AZTS NCs titrated with UDA (vide supra).

We explored the binding of thiols to AZTS NCs via titration of 2-phenylethanethiol (PET), because its recognizable \textsuperscript{1}H NMR signals allow it to be distinguished from OLA (Figure S24). The introduction of PET into the ligand shell can be seen through the broadening of both the signal in the aromatic region (7.2-7.8 ppm) and that of the alkyl protons (2.8 and 4.0 ppm, Figure 4a/b, S24). Similar to UDA, titrations using PET also provoked a narrowing of the olefinic proton signal of OLA at ~5.6 ppm (from 46 to 27 Hz, Figure 4a) and emergence of clear signatures for free/dynamic OLA at 1.15 ppm (Figure S24). These observations are evidence of the displacement of OLA from the NC surface. NOESY measurements on these samples show negative cross peaks for PET while ROESY inverts their sign, confirming an interaction of PET with the NC surface (Figure S25a and b). Thus, we conclude that PET replaces OLA on the surface of AZTS NCs. Practically, PET exchanges significantly increased the colloidal stability of AZTS NCs compared to the as-synthesized product (with OLA-only passivation). For instance, the addition of PET permitted as many purification cycles with ethanol as desired, each generating highly dispersible and oily pellets (Figure S26b). This contrasted to the behaviour of as-synthesized AZTS NCs, where precipitation with ethanol results in a dryer pellet (Figure S26a) that was no longer redispersible (without additives) after two cycles. We also tested the addition of 1-dodecanethiol (DDT), a common NC ligand with a thiol head-group that lacks a \textsuperscript{1}H NMR resonance distinct from e.g. OLA. We showed that DDT also displaces OLA from AZTS NCs while avoiding aggregation (Figure S27). This is consistent with our expectations that thiol ligands are an attractive general motif to improve the colloidal stability of these NCs.

Despite the markedly improved colloidal stability of AZTS NCs treated with thiols, we found that these exchanges were partial and that thiol ligands displayed some residual dynamism in binding. For instance, even at the endpoint of our PET titrations (1.2:1.0 PET:OLA), DOSY spectra detect bound PET ligands (i.e. that exhibit effective diffusion coefficients of D= 320 μm\textsuperscript{2}·s\textsuperscript{−1}) but continue to display signatures of OLA with comparable diffusivity. This implies that populations of both
molecules continue to interact with the (slowly diffusing) NCs. Further, the corresponding solvodynamic diameters for both ligands are only 2.3 nm (where the AZTS core diameter alone is 2.7 nm), again consistent with a degree of dynamic exchange between bound and free ligands.

Thus, knowing that this partial exchange of OLA with thiols already improved the colloidal stability of AZTS NCs, we attempted to drive the exchange to completion. We first tried to wash OLA-passivated NCs with excess PET and then to re-precipitate them by adding EtOH (see Methods). After five washes, the olefinic signal for OLA remained visible in the $^1$H NMR spectrum (~5.5 ppm, Figure S28a), showing that this method does not fully remove OLA. Second, we tested a more aggressive procedure that was reported to replace tightly bound OLA with thiols on the surface of CuInS$_2$ NCs. In brief, we dispersed OLA-passivated AZTS NCs in a mixture of toluene and excess PET, and heated the dispersion to 130 °C for 2 hours, followed by two purification cycles using EtOH (see Methods). However, the olefinic signal for OLA remained in $^1$H NMR spectra of the product, indicating that full displacement of OLA was unsuccessful (Figure S28b).
Noting the surprising persistence of some surface-bound OLA in thiol-exchanged AZTS NCs paired with their clearly improved colloidal stability relative to NCs with OLA-only passivation, we propose that multiple OLA binding motifs with differing strengths co-exist in the as-synthesized particles. Evidence of such two-site binding behaviour has been reported in other NC systems, including PbS and CdSe.\textsuperscript{30, 94} We consider that one motif can participate in an L-for-L ligand exchange through which thiols largely displace the OLA that is dynamically bound. Our primary evidence for L-for-L exchange (as opposed to mechanisms involving proton-transfer/charged species\textsuperscript{35, 89}) is the absence of signatures of ammonium in all relevant \textsuperscript{1}NMR measurements. (Figure S26 and S29) Even though thiol binding may not be irreversible, consistent with the residual dynamism that we observed in the DOSY measurements, this replacement could still improve colloidal stability because the L-type binding of thiols to silver has been shown to be stronger than that of OLA in Ag\textsubscript{2}Se NCs samples.\textsuperscript{92}

By contrast, the binding motif that leads to the tightly bound OLA is less clear. However, we speculate briefly because our observations have some similarities to recent studies of surface chemistry of initially amine-passivated InP NCs.\textsuperscript{35} Specifically, exposure of InP NCs to other ligands (\textit{i.e.} carboxylic acids or thiols) was similarly shown to remove only ~half of surface-bound amines. Supported by calculations, it was thus proposed that the remaining amines were associated with energetically favourable/tightly-bound sites associated with under-coordinated indium atoms at facet-edges and apices. Though the correspondence between our observations on AZTS NCs and the behaviour of InP is not exact, because L-for-L exchanges were not observed in InP and targeted experiments instead detected OLAm\textsuperscript{+}-X\textsuperscript{-} species following presumed proton transfer from the incoming ligands, including the formation of thiolates.\textsuperscript{35} This particular channel appears less relevant for AZTS NCs, because we do not detect the formation of such charged molecular species when PET or DDT are added. However, the broader concept that more-strongly bound sites for L-type binding could arise from local chemical environments is likely transferrable to our multi-metallic NCs, where the gamut of chemical binding/co-ordination environments is still-larger. As a result, we speculate that the sub-population of tightly-bound (un-protonated) OLA molecules could be associated with L-type co-ordination to \textit{e.g.} under-co-ordinated Ag, surface sites associated with Sn\textsuperscript{4+} or Zn\textsuperscript{2+}, or atoms perturbed by interactions with X-type impurities. Future experiments and modelling could explore the effect of shifting the acid/base equilibrium at the NC surface, for instance using more-acidic thiols. This could deepen our understanding of the surface chemistry of AZTS NCs, which we have shown is of paramount importance to remedying their poor native colloidal stability through informed post-synthetic ligand exchange.

\textit{Thiols also increase the photoluminescence of AZTS NCs}

Having evaluated the effect of representative X- and L-type ligands on the colloidal stability of AZTS NCs, we sought to determine their impact on the optical properties. AZTS NCs synthesized using our quadruple-injection procedure exhibited a photoluminescence quantum yield (PLQY) of 3.4±1%, this being an improvement relative to the prior report on unshelled NCs.\textsuperscript{11} However, these absolute values remained modest compared to established core-only NC made from other materials, so further improvement was desirable.
We first characterized AZTS NCs treated post-synthetically with DDT, given the favourable colloidal stability that we had uncovered. We observed that the addition of DDT (26:1 DDT:OLA) to as-synthesized (OLA-passivated) NCs ultimately enables a 50% relative enhancement of the emission intensity measured in situ (Figure 5a), corroborated by an increase in the PLQY from 3.4±1% to 4.4±1%. Interestingly, this passivation process is dynamic over time: we identified a progressive brightening that asymptotes after ~1 hour upon DDT addition. The brightness enhancement depends on the amount of DDT added, and is greatest with 30:1 DDT:OLA equivalents (Figure 5a). Addition of a larger excess of DDT (>100:1 DDT:OLA) often induced a broad shoulder on the red side of the emission (700-1000nm) (Figure S30), which we speculatively attribute to the induced formation of Ag₂S NCs. We find that as-synthesized AZTS NCs analogously brighten following the addition of comparable equivalents of PET (Figure S31). In light of the improved colloidal stability and brightness achieved via post-synthetic exchange, we also explored the direct addition of DDT during the synthesis. However, the addition of 2:1 DDT:Ag to the reaction mixture promoted the formation of a white precipitate (Figure S30). This has been previously linked to lamellar silver thiolate coordination polymers that lower the reactivity of the silver precursor, and we found that these reactions yielded a product with broad emission (Figure S32).

To gain insight into the mechanism by which DDT improves the brightness of AZTS NCs, we then measured their photoluminescence dynamics. Prior to the addition of DDT, AZTS NCs (d: 3.2 nm, λpeak,PL: 710nm) exhibit decay dynamics with an average lifetime of 150 ± 10 ns (determined using a Riemann sum), but with pronounced non-monoexponential character. Similar dynamics are commonly observed from core-only NCs, and phenomenologically attributed to the effects of carrier trapping to poorly-emissive surface-oriented states. With the addition of DDT, the average photoluminescence lifetime increases modestly from 150 ± 10 ns to 170 ± 10 ns (Figure 5c), an effect that again grows in over ~1 hour (Figure S33). Notably, this improvement is
most noticeable in the decreased magnitude of the early-time decay (t<100ns), while the late-time dynamics (100-1500 ns) are not significantly affected. This is consistent with DDT ligands passivating/hindering the formation of surface traps.

To further explore the connection between the surface chemistry and photophysics, we performed post-synthetic additions of OA to a purified dispersion of OLA-passivated AZTS, using small concentrations that did not promote evident aggregation (vide supra, where e.g. 50:1 OA:OLA caused aggregation in <30 minutes). We observed that the post-synthetic addition of e.g. 10 equivalents of OA per OLA caused an immediate, significant loss of the steady-state photoluminescence when added post-synthetically (Figure 5b). Comparable PL quenching was seen when small amounts of OA were added during synthesis (Figure S34). We found that this quenching was not restored by the subsequent addition of OLA or DDT, even when either of these L-type ligands were present in high excess (Figure S35). We also assessed the effects of OA addition on the transient photoluminescence dynamics in this system. We noticed a progressive decrease (from 151 to 69 ns) in the average lifetime as a function of the amount of OA added, and that this effect is again most prominent as an enhancement of the early-time decay (t<100ns) (Figure 5d). This is consistent with the formation of quenching sites at the surface of the NCs within the ensemble. Thus, these results support our proposed model for ligand interactions at the surface, because this behaviour would be expected if OA addition indirectly caused under-passivated sites by inducing the desorption of L-type OLA via the formation OLA+–OA− adducts.

Taken together, our measurements show that thiols are an effective post-synthetic additive that improves the colloidal and optoelectronic properties of AZTS NCs. Consistent with previous findings in binary and ternary silver-containing NCs\textsuperscript{99-103}, we find that thiols (e.g. DDT, PET) displace the native OLA ligands in AZTS NCs, and are subsequently more-strongly bound. Further, we find that these advantages are realized even in the very small NCs achievable via our quadruple-injection approach. These experiments also begin to paint a picture of the surface of AZTS NCs, where we observed a correlation between treatments that colloidaly stabilize/destabilize the particles and those that suppress/enhance rapid (<50 ns) PL quenching that we associate with carrier trapping at the surface. In practical terms, the improved colloidal stability and brightness stimulated efforts to employ these particles in an optoelectronic application.
AZTS Nanocrystals Sensitize Red-to-Blue Triplet-Fusion Upconversion:

Lastly, we explored the ability of AZTS NCs to sensitize triplet-fusion upconversion. Our improved, small AZTS NCs are attractive for upconversion photochemistry,\textsuperscript{13,46} given their optical gap, the long (>100 ns) average lifetime of their photoexcitations, and their less-toxic material composition. Following leading reports,\textsuperscript{50-51,104} we designed a hybrid system where AZTS NCs absorb light and sensitize the spin-triplet state on exciton-extracting ligands. These ‘transmitter’ ligands are then expected to transfer triplets to free-floating acceptor/emitters via a Dexter-type mechanism.\textsuperscript{105} Specifically, we functionalized OLA/DDT-passivated AZTS NCs (~2.7 nm) with 9-anthracenecarboxylates (9-ACA)\textsuperscript{-} and added a standard triplet acceptor to the solution, diphenylantracene (DPA, See Methods). Notably, the short-wavelength ‘blue’ emission from DPA (λ ~ 425 nm, \(h\nu\sim 3.0\text{eV}\)) has sufficient photon energy to initiate chemical reactions, for example by activation of a radical initiator.\textsuperscript{13,106}

Upon exciting deaerated solutions of this composite system with red light (\(\lambda_{\text{ex}}\): 637 nm), we observed blue emission from DPA showing the characteristic Huang-Rhys progression and an overall peak at \(\lambda=425\text{ nm}\) that we associate with the 0-1 vibrational side-band (Scheme 2, Figure S36). This is strong evidence of upconversion via triplet sensitization and fusion, because blue emission is not identified in incomplete assemblies missing either the AZTS NCs or the organic chromophores. Then, Figure 6c displays the irradiance-dependence of the upconverted emission intensity from our AZTS-sensitized system, showing clear quadratic and linear regimes. This is further evidence of photoluminescence via triplet-fusion upconversion, showing a characteristic quadratic-to-linear transition with increasing excitation power as bimolecular fusion becomes the predominant recombination pathway for triplets.\textsuperscript{107} Thus, we conclude that ultra-small AZTS NCs can sensitize red-to-blue triplet fusion upconversion, adding to the short list of solution-based upconversion facilitated by less-toxic NC sensitizers.\textsuperscript{55,108-110}

\textbf{Scheme 2.} Cartoon of the proposed upconversion mechanism. Red light (\(\lambda_{\text{ex}}\): 637 nm) is absorbed by AZTS NCs, and the energy from these photoexcitations is transferred to the spin-triplet state on surface-anchored 9-ACA\textsuperscript{-} ligands. These triplets, in turn, transfer to free-floating DPA molecules. Triplet-state energies are from literature, and the 0-0 fluorescence peak is used to estimate the energy of the DPA \(S_1\). (Figure S36). Energies for AZTS states are estimated from the emission peak, or the centroid of a gaussian fit to the long-wavelength shoulder of the excitonic absorption.
Then, the threshold intensity ($I_{th}$) marking the quadratic-to-linear transition is a metric of upconversion performance, because systems that achieve max-efficiency performance at lower intensities are advantageous in many applications.\textsuperscript{3, 13, 50-51, 111} We extract $I_{th}$=3.1 W/cm\textsuperscript{2} from the inflection point in our excitation-density–dependent measurements (Figure 6c), which is comparable to reported systems with less-toxic NC sensitizers.\textsuperscript{55, 108-110} However, only one of these systems has generated photochemically-active deep-blue light (0-0 shoulder of DPA at $\lambda$: 415 nm) from red excitation ($\lambda$: 637 nm)$^{13}$—thus achieving a beneficially larger anti-Stokes shift ($\Delta E$=1.04 eV) relative to yellow/green excitation ($\lambda$<590nm)—and our system breaks new ground with a threshold intensity more than 10x lower. Thus, our upconversion platform built on ultra-small AZTS NCs stands as a strong candidate among the rising tide of less-toxic NC-sensitized triplet-fusion systems.

![Figure 6. Triplet-fusion upconversion using AZTS NCs. a) Experiment setup viewed through a 500 nm short-pass filter to show the upconverted blue light ($\lambda_{em.}$: 425 nm) (photo taken with an Iphone 11.) b) Steady-state absorption and emission spectra. The emission from AZTS NC and the upconverted emission from DPA molecules were collected simultaneously, and the latter has been magnified 4-fold to enhance visibility. The absorption spectra of the relevant materials were measured separately in solution. c) Excitation-intensity–dependence of the upconverted emission, showing the characteristic quadratic-to-linear transition for triplet fusion.](image)

In parallel with the upconverted emission, we observe quenching of AZTS NC photoluminescence upon the addition of 9-ACA in both steady-state (Figure S37) and transient (Figure S38) spectroscopic measurements. This is consistent with triplet energy transfer to surface-anchored ligands, owing to the energetic landscape of energy transfer of our hybrid NC/molecular system. However, given the aforementioned vulnerability of these particles to carboxylic acids, we note that the concentration of 9-ACA used is comparable to the residual concentration of OLA after purification on these thiol-exchange AZTS NCs, thus ~ten-fold fewer than the OA equivalents that induce the pronounced photoluminescence quenching we report here (Figure 5b, d). Additionally, we did not observe aggregation when ACA is added at this concentration, and the shape of the AZTS emission spectrum remained unaffected, providing evidence that the effects of etching or ripening are minimal (Figure 6b). Thus, even though carboxylic acids can be detrimental for the optical properties of AZTS NCs, we show that effective TUC remains possible through a carboxylated triplet acceptor. Still, further improvements to this emerging system may be achievable via the design and implementation of triplet-acceptor molecules with other coordinating groups, such as amines or thiols.
Conclusions

We designed, implemented, and investigated an improved synthetic route to AZTS NCs, an underexplored, less-toxic material system attracting recent research interest. Our study was mechanistically motivated, seeking to suppress the reduction of Ag and the formation of α-Ag₂S networks, and temporally separate the formation of binary (α-Ag₂S), ternary (Ag₈SnS₆), and quaternary (Ag₂ZnSnS₄) species. These intentions were inspired by our previous findings in the formation mechanism of quaternary Cu₂ZnSnS₄ NCs, and the reported effect of sulfur stoichiometry on the morphologies of Ag₂S templates. Overall, this adapted synthetic approach yielded nanomaterials that access a new size-range, exhibit enhanced colloidal stability, and possess superior photophysical properties that enabled a demonstration of triplet-fusion upconversion with AZTS NCs serving as the triplet sensitizer.

First, investigating the established reaction, we showed that a commonly employed solvent/additive (OLA) has the ability to reduce the silver precursor, particularly at elevated temperatures (>80 °C). This reduction can form metallic Ag NPs prior to sulfur injection (and the expected nucleation of metal-sulfide particles), ultimately yielding larger AZTS NCs with broader size distributions at reaction completion. Accordingly, we find that we obtain greater control in reactions run at low temperatures (~80 °C). Then, studying an OLA-based, one-pot synthesis of AZTS NCs at 80 °C, we identify that acanthite (α-Ag₂S) NCs are key intermediate species. We then explored their formation, discovering that reactions with stoichiometric sulfur access small (<5 nm), pseudo-spherical α-Ag₂S NCs that are optimal templates for conversion to AZTS. By contrast, the excess sulfur that is naturally present in one-pot AZTS reactions provokes the formation of large α-Ag₂S networks that frustrate overall size- and morphological control. We concluded that AZTS reactions could target the suppression of α-Ag₂S network intermediate by initially working under sulfur-poor conditions.

These findings motivated our development of a stepwise, one-pot procedure to modulate the formation of AZTS NCs with the aim to achieve smaller particles—not accessible through a single hot-injection—with improved control of size, morphology, and phase purity. In our quadruple injection procedure, the initial sulfur stoichiometry is regulated to access optimal α-Ag₂S templates. These particles are next cleanly converted in situ to canfieldite (Ag₈SnS₆, ATS) NCs via the injection of SnCl₄, and then the final, phase-pure AZTS product through the addition of Zn(OAc)₂. We map the evolution of these intermediates through steady-state powder X-ray diffraction and Raman measurements. Overall, we show that reactions that separate cation addition steps in time through a quadruple injection vs. single injection can yield AZTS NCs that are smaller (e.g. 2–4 nm, with emission 650-740 nm) and have improved size-dispersion (e.g. 2.1±0.3 nm) relative to previous reports, in reactions run at significantly lower temperatures (80 °C).

We then identified that the native ligand passivation of AZTS NCs from this procedure involved charge-neutral OLA, but was dynamic in nature. Thus, we used 1 and 2D ¹H NMR techniques to unravel their surface chemistry, seeking to design procedures to improve colloidal stability. We found that thiol ligands can replace loosely-bound OLA ligands, granting improved colloidal stability such that the NCs can endure multiple purification cycles without noticeable aggregation. Interestingly, even aggressive thiol treatments did not completely displace native OLA, indicating
a heterogeneous surface where some (undisplaceable) amine ligands are presumably more-tightly bound. Conversely, we found that ligand exchanges with carboxylic acids decrease the colloidal stability of AZTS NCs, while generating ammonium-based ion pair adducts in solution. We proposed that this reflects the induced loss of solubilizing OLA from weakly-bound sites on the NC surface. We then assessed the impact of these post-synthetic ligand modifications on photophysical properties of AZTS NCs. We found that the addition of thiols permits a modest increase in the emission brightness, while carboxylic acids induce pronounced quenching. Measurements of the photoluminescence dynamics show that these results were consistent with the passivation/exacerbation of surface traps. Overall, our results illustrate that a post-synthetic thiol treatment is an effective strategy to increase both the colloidal stability and the optical properties of AZTS NCs. However, while the photophysical properties were improved, the overall PLQY remained modest. As a result, we recommend further study to obtain a detailed understanding of the surface chemistry of AZTS NCs and inform advanced surface-passivation procedures.

Finally, we used our improved, less-toxic quaternary AZTS NCs in a demonstration of ‘red-to-blue’ triplet-fusion upconversion. Following functionalization with triplet-extracting 9-ACA ligands and the addition of molecular DPA annihilator/emitters in solution, we find that our hybrid system can effectively convert red light (λ_{ex} = 637 nm) to blue (λ_{UC,PL}~425 nm) photons. This NC-based system highlights how the informed synthetic design using a stepwise route to control the size and phase of less-toxic materials as well as the careful manipulation of their surface chemistry can advance the use of underexplored nanomaterials in demanding photophysical applications.
Methods

Chemicals: Silver (I) acetate [Ag(OAc)] was purchased from Alfa Aesar. Zinc (II) acetate [Zn(OAc)]₂·2 H₂O, tin (IV) chloride [SnCl₄, anhydrous], hexamethydisilathiane [TMS-S], oleylamine (OLA, technical grade 70%, and >98% primary amines), oleic acid (OA, technical grade 90%), octylamine (OCTY, 99%), 1-octadecene (ODE, technical grade, 90%), 1-dodecanethiol (DDT), undec-10-enoiac acid (UDA), 2-phenylethanethiol (PET), deuterated toluene (tol·d₈, 99%), deuterated benzene (c₆d₆, 99%), hexane (≥ 99%), toluene (99%), acetonitrile, and ethanol (95%) were purchased from Sigma Aldrich. All chemicals were used as received without further purification.

Transmission electron microscopy (TEM): Standard-resolution images were acquired using a Hitachi HT7700 microscope at 100 kV. 400-mesh copper grids (Pacific grid) were immersed in a dilute dispersion of NCs in toluene for 1 second and left to dry under air. The average size was determined over an average of 300-500 particles using the Fiji imaging-processing distribution of the ImageJ2 software.

Powder X-ray diffraction (PXRD): The samples were prepared by drop-casting a concentrated dispersion of NCs in 50/50 hexanes/toluene onto an amorphous silicon substrate, which was then allowed to dry under air. The spectra were obtained using a Bruker D8 Advance diffractometer with monochromatized Cu Kα radiation with a nickel filter (1 mm slit). The X-ray source power was set to 40 kV and 40 mA. The spectra were collected in 2θ with a step increment of 0.015° and scan speed of 0.1 s step⁻¹. The reflections were calibrated with a LaB₆ standard, and the data was processed with the Xpert Highscore software.

Raman spectroscopy: The data was collected using a Bruker Senterra Raman microscope. A 532 nm diode laser at 2 mW power was used with a 50x objective and a 3–5 cm⁻¹ resolution. Each spectrum was collected over a period of 30 seconds.

NMR: Nuclear magnetic resonance was performed on either a 400 MHz Varian MercuryPlus NMR spectrometer or a 500 MHz Agilent DD2 NMR spectrometer. 1D ¹H NMR measurements were performed on the 400 MHz instrument, while 2D DOSY, NOESY, and ROESY experiments were executed on the 500 MHz spectrometer. NOESY spectra were acquired at 300 ms mixing time, while ROESY measurements were taken at 100 ms mixing time. The titrations using UDA, OCTY, DDT, and PET were performed directly in the NMR tubes. We waited 5 minutes after ligand addition before taking the first measurement. All spectra were recorded at a 25 s delay time and 8 scans in either tol·d₈ or c₆d₆.

Steady-state absorption spectroscopy: Optical absorption spectra were taken on a Perkin Elmer Lambda 1050 UV/Vis spectrophotometer.

Steady-State Emission Spectroscopy: Spectra taken with a home-built set-up at 450 nm excitation using a pen-diode (ThorLabs CPS450) at 2.5 mW. Upconversion experiments were conducted using an externally driven λ=637 nm diode (ThorLabs, HL63133DG) at 60 mW focused to a ~228 μm radius spot, as measured using a knife-edge. The emission set-up involved an off-axis parabolic collimating mirror to direct the emission from the sample to an reflective fibre-coupler (ThorLabs PC12FC-P01), which was then sent to an OceanOptics Flame spectrometer.
Photoluminescence Quantum Yields: The relative photoluminescence quantum yields were measured according to the methods described in Würth et al. using a rhodamine 101 fluorescence standard dissolved in 95% ethanol. Absorbance values were measured using the Cary 5000 UV-Vis-NIR spectrophotometer and steady-state emission was measured using the same set up used for steady-state emission spectroscopy, but using 532 nm excitation with a pen-diode (Thorlabs CPS532).

Time-Resolved Spectroscopy: Emission lifetime measurements were acquired using a 470 nm pulsed laser diode (PicoQuant, LDH-D-C-470). The data was obtained employing a single photon avalanche diode (Micro Photon Devices, SPD-050-CTD) and PicoQuant HydraHarp 400 event timer with 32 ps bin widths. A repetition rate of 500 kHz was used to allow long-lived signals to decay.

Ag NP synthesis: Ag(OAc) (0.150 mmol) was placed in a 3-neck round-bottom flask with OLA (3 mL), degassed three times through vacuum-nitrogen cycles, and heated to 100 °C for 1 minute under nitrogen atmosphere. The solution was then cooled to room temperature, transferred to a 50 mL Falcon tube, and purified twice. Each purification step involved adding a 50:50 EtOH:MeOH antisolvent mixture and centrifuging the solution at 6000 rpm (4430 rcf) for 40 seconds to precipitate the nanoparticles. The supernatant was discarded, and the particles re-dispersed in toluene for the next wash, or further experiments. The OLA used for all experiments was technical grade (70%) unless stated otherwise. However this solvent was degassed beforehand at 120 °C for 4 hours under vacuum to remove suspected carbamate impurities.

Ag₂S synthesis: A 15 mL 3-neck round-bottom flask is charged with Ag(OAc) (0.150 mmol) and OLA (5 mL). The solution is degassed through three cycles of vacuum-nitrogen and kept under a nitrogen atmosphere at room temperature. In the meantime, the TMS-S precursor solution was prepared inside a glovebox. A vial was loaded with toluene (1 mL) and TMS-S, 0.061, or 0.150 mmol for the sulfur-poor and sulfur-rich conditions, respectively. This solution was mixed and placed in a 3 mL plastic syringe. Then, the temperature of the silver precursor solution was quickly ramped (15 °C/min) to 80 °C and the TMS-S solution was injected. The heating mantle was quickly removed and the reaction flask was cooled to 35 °C over ~2 minutes by blowing cold air. The solution was transferred to a 50 mL Falcon tube and purified by centrifugation at 4430 rcf for 40 seconds with IPA (12 mL) and MeOH (4 mL). The supernatant was discarded, and the pellet was redispersed in toluene (1 mL). A second purification step was performed by adding IPA only (~2 mL), and centrifuging at 4430 rcf for 40 seconds. The final product was redispersed in toluene (2 mL) and stored under air for further characterization.

AZTS NC synthesis: A 15 mL 3-neck round-bottom flask was loaded with Ag(OAc) (25 mg, 0.150 mmol) and sealed with rubber septa. At the same time, one 20 mL scintillation vial was charged with Zn(OAc)₂·2 H₂O (14 mg, 0.075 mmol), degassed (4 hours at 120 °C) OLA (1 mL) while stirring, and then placed in a sand bath at ~80 °C. Another 20 mL scintillation vial was loaded with degassed OLA (1 mL) and a stir bar and brought inside a N₂ glovebox to prepare the Sn precursor solution. A micropipette was used to add SnCl₄ (9 μL, 0.075 mmol) to this vial. It is important to tilt the vial (~45°) and deliver the SnCl₄ onto a dry spot at the bottom of the vial to prevent traces of water in the OLA from hydrolyzing inside of the pipette tip and forming an inconvenient gel. The vial was then quickly capped and taken out of the glovebox. The Sn precursor solution was placed in the same sand bath as the zinc precursor to promote dissolution (~10 minutes). While the
SnCl₄ dissolved, two TMS-S solutions were prepared in different 20 mL scintillation vials inside the glove box. The first solution [1] contained toluene (1 mL) and TMS-S (13 μL/0.061 mmol), while the second [2] was comprised of toluene (1 mL) and TMS-S (49 μL/0.232 mmol). Each solution was loaded into a labelled 3 mL plastic syringe and taken out of the glovebox. This completed the precursor preparation.

For the reaction, degassed OLA (3 mL) was added to the 3-neck round-bottom flask containing the Ag(OAc). This solution was degassed through three cycles of vacuum-nitrogen at room temperature and rapidly heated to 80 °C (12 °C/min) under nitrogen and stirring. As the silver solution reaches 65 °C, two 1 mL plastic syringes are loaded: one with the tin solution (Sn-OLA) and the other one with the zinc precursor (Zn-OLA), both fully dissolved and pale yellow in colour. An additional 14/20 rubber septum is pierced with all four syringes as seen in Figure S7. Once the silver solution reaches 75 °C, the heating mantle is removed as well as the existing septum on the flask under a positive nitrogen flow. This septum is quickly replaced by the one holding the four syringes with the precursor solutions. The quadruple injection happens once the reaction reaches 80 °C in the order: 1) TMS-S [1], 2) Sn-OLA, 3) TMS-S [2], and 4) Zn-OLA, with one second between injections. In reactions where we sought to track the synthesis, the septa was removed aliquots were taken as described below. In reactions targeting a single size, the flask was cooled (over ~2 minutes) by blowing cold air at the time chosen to arrest the reaction.

AZTS NCs are purified through standard EtOH workup. Essentially, the crude is transferred to a 50 mL Falcon tube and 7.5 mL of EtOH are added. This tube is centrifuged at 4430 rcf for 3 minutes. The supernatant is discarded and the NCs are re-dispersed in toluene. *The AZTS control reaction where the Sn and Zn precursors were injected together was performed in a similar way through the following injection steps: 1) TMS-S [1], 2) Sn-OLA + Zn-OLA (prepared separately but mixed and injected together), and 3) TMS-S [2] **The ATS synthesis was performed in the same way without the injection of the Zn-OLA precursor.

Aliquot experiment: After the last injection (Zn-OLA), a timer is started and 300 μL aliquots are taken using a micropipette. The aliquots are placed in room-temperature vials, quenched by the addition of 600 μL room-temperature EtOH, and centrifuged for 40 seconds at 4430 rcf. The supernatant is discarded and the NCs are re-dispersed in 300 μL toluene for further experiments. A second purification step with the minimal amount of EtOH is possible however, we found that the slightest EtOH excess can induce NC aggregation. In practice, we recommend adding a small amount of OLA between purification steps to retain their colloidal stability (See the NMR purification procedure below for details).

Purification for ¹H NMR experiments on AZTS NCs: The reaction is left to cool at ambient temperature until it reaches 35 °C (~5 minutes) after the final injection [4] and it is transferred to a 50 mL Falcon tube to be purified using EtOH. The first crash uses 7.5 mL of EtOH and the solution is centrifuged at 4430 rcf for 3 minutes. The amounts of antisolvent used are crucial for an optimal purification, as we observed that excess EtOH results in the aggregation of the NCs and jellified pellet. However, for mildly over-crashed samples, the NCs can be re-dispersed by the addition of a small amount of OLA (20-200 μL). After the first purification step, the supernatant is discarded and the NCs are re-dispersed in toluene (500 μL) and degassed OLA (25 μL). The tube is vortexed for 2 min and EtOH is added dropwise with a glass Pasteur pipette (25 drops) until
the dispersion becomes turbid. The solution is centrifuged at 4430 rcf for 20 seconds, the supernatant discarded, and the NCs re-dispersed in toluene (500 μL) and degassed OLA (15 μL). After the dispersion is vortexed for 2 min, 25 drops of ethanol are added once again until the solution becomes turbid, and the tube is centrifuged at 4430 rcf for 10 seconds. The pellet is dried under a nitrogen flow to remove solvent traces and immediately re-dispersed in tol-d8 or c6d6 for 1H NMR experiments.

1H NMR titrations: A stock solutions of UDA was prepared at 20 mg/mL in tol-d8 while PET was prepared in c6d6. The titrations were conducted through the sequential addition of 8, 24, 32, 64, 128, 256, and 512 μL of the stock solution into the NMR tube. For example, 8 μL are added for the first titration, followed by the addition of 24 μL (32 μL total), then 32 μL (64 μL total), and so forth. The tubes were shaken for 3 minutes between each measurement.

Upconversion measurements: A full prep is re-dispersed in 2 mL of toluene after purification. Then 200 μL of this solution is mixed with 10 μL of DDT and stirred for 5 minutes. The dispersion is gently purified using EtOH (see above, intentionally retaining some feint colour in the supernatant), centrifuged at 4430 rcf for 2 minutes, and re-dispersed in 200 μL of toluene. A 40 μL aliquot from this dispersion is diluted with 300 μL of toluene inside a quartz cuvette. Then 50 μL of a (1 mg/mL) solution of 9-ACA in toluene:acetonitrile (10:2) was added as along with 100 μL of a (10 mg/mL) solution of DPA in toluene. The cuvette was sealed with a rubber septum, wrapped in parafilm, and sparged with argon for 3 minutes before taking the emission measurements.
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Author Contributions

This research was initiated and performed by F.Y.V. under the supervision of M.W.B.W. M.H acquired time-resolved spectroscopic data and aided in the acquisition of steady-state spectroscopic data for upconversion measurements. P.B.G. assisted in performing and refining synthetic procedures. C.J.I. obtained and analyzed the power-dependent upconversion measurement. S.R. assisted with the acquisition and analysis of steady-state spectroscopy and PLQY data. D.C.B. provided support for 1 and 2D NMR experiments and their interpretation. The manuscript was written by F.Y.V. and M.W.B.W., with contributions of all authors, who have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Supporting information available: Additional information and experimental data.

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